



# Engineering Optical Nanoantennas based on Plasmonics and Mie Resonances

Hinamoto, Tatsuki

---

(Degree)

博士 (工学)

(Date of Degree)

2020-09-25

(Date of Publication)

2021-09-01

(Resource Type)

doctoral thesis

(Report Number)

甲第7878号

(URL)

<https://hdl.handle.net/20.500.14094/D1007878>

※ 当コンテンツは神戸大学の学術成果です。無断複製・不正使用等を禁じます。著作権法で認められている範囲内で、適切にご利用ください。



A DISSERTATION FOR THE DEGREE OF  
DOCTOR OF PHILOSOPHY

博士論文

Engineering Optical Nanoantennas based on  
Plasmonics and Mie Resonances

プラズモニクス及び Mie 共鳴に基づく  
光ナノアンテナに関する研究

July 2020

2020 年 7 月

KOBE UNIVERSITY

神戸大学大学院工学研究科

TATSUKI HINAMOTO

雛本 樹生

# Abstract

Optical nanoantennas provide efficient manipulation of light at the nanoscale at the optical frequencies. Due to its versatility, the optical nanoantennas are expected to be important building blocks in wide range of applications including optoelectronic and bio-photonic devices, sensors, and so on. The intense research efforts have developed many types of optical nanoantennas, different design, materials, and functionalities; however, it is needed to tailor nanostructures for each application mainly due to their resonant nature.

In this thesis, we develop optical nanoantennas that are designed for several applications. In Chapter 1, general information of optical antennas is provided. Following introduction of optical antennas, we provide theoretical backgrounds of governing physics, surface plasmon resonances and Mie resonances. Important functionalities and recent progress are also summarized.

Part I, consisting of Chapter 2 – Chapter 4, are devoted for the development of plasmonic nanoantennas for upconversion nanocomposites which convert near-infrared photons into visible ones. In order to overcome the inherent limitation of rare-earth doped upconversion nanomaterials, which is low conversion efficiencies due to small absorption cross sections and low quantum efficiencies of intra-4f transition, three metal nanostructures with tailored plasmonic properties are proposed. All metal nanostructures are developed based on a nanocap which partially surrounds the upconversion nanoparticle and have unique plasmonic properties.

In Chapter 2, we develop a method to control a coverage of a metal nanocap to extend the tunable range of its resonance wavelength into near-infrared spectrum for enhancement of the excitation efficiency of upconversion. In Chapter 3, we introduce anisotropy to the nanocap by elongating the structure in one direction and show that a resonance of the nanocap can be split

into two resonances. By controlling each of newly emerged resonances separately, it becomes possible to achieve simultaneous enhancement of emission and excitation processes. In Chapter 4, the metal nanocap is combined with additional metal nanoparticle to confine localized field within the gap layer where upconversion materials exists. In this system, additional degree of freedom to control the resonance arises due to the plasmon hybridization. For the above three approaches, we precisely examine the correlation between plasmonic properties and upconversion intensities and find the structure which enhance upconversion by a factor over 100.

In Part II, which is composed of Chapter 5 – Chapter 8, we focus on dielectric nanoantennas which possesses multiple modes of Mie resonances. In contrast to plasmonic nanoantennas, dielectric ones naturally have magnetic-type resonances, enabling various useful phenomena such as interferences between several resonances and control of effective permeability.

Recently developed colloidal solution of silicon nanosphere is one of ideal Mie resonators. After providing fundamental information of this material, *e.g.*, fabrication method and optical properties, in Chapter 5, its application for directional nanoantennas is demonstrated in the following chapters. In Chapter 6, we perform advanced optical measurement to evaluate the directional scattering of a single silicon nanosphere using the Fourier-plane spectroscopy. In Chapter 7, we couple the nanosphere with emitters nearby and study how the emission can be directed by a single Mie resonant silicon nanosphere. We describe that the existence of magnetic dipole in addition to electric dipole resonance enables directionality control with a subwavelength single component. Go beyond development of single optical component, in Chapter 8 we propose a concept of metafluids by treating the colloidal solution as an effective medium. Because the optically resonant nanoantennas works such like atoms which exhibit magnetic responses in liquid, unnaturally low or high refractive-index materials can be realized.

Overall, this thesis proposes novel optical antenna designs for absorption and emission enhancement, directionality control of emitters, and building blocks for artificial materials by making full use of plasmonic or Mie resonance properties. The results indicate the potential of optical nanoantennas for light control at the nanoscale by tailoring their optical properties in a myriad of ways. Implementation of these functional antennas could have a practical impact in sensing, photovoltaics, lighting, bio-photonics, and integrated optoelectronic devices.

## Acknowledgements

First, I would like to thank Prof. Minoru Fujii for being my advisor over the past 6 years. His vision supported by his experience in academia and industry has helped me a lot to conduct research, write papers or proposals, interpret new research topics, and so on. There is no doubt that the decision to join the Fujii laboratory was the best choice for me.

I would also thank Ph.D. committee members, Prof. Minoru Fujii, Prof. Takashi Kita, and Prof. Masatoshi Kitamura from Graduate School of Engineering, and Prof. Osamu Matoba from Graduate School of System Informatics, for their valuable comments and discussion. A special thanks is given to Dr. Hiroshi Sugimoto for his support both at work and in my private life. His development of the colloidal silicon nanosphere made my Ph. D. work delightful.

I thank Prof. Mark Brongersma for all his support on research at Stanford University. It was great experience for me to work under a pioneer in the nanophotonics and plasmonics fields. Because he treated me as not a visitor but one of his students, I could learn a lot and enjoy the life at Stanford. I also appreciate you connecting me with great collaborators.

I am also thankful to my world-class collaborators Dr. Søren Raza and Artyom Assadillayev at the Technical University of Denmark; Yan Joe Lee, Junkyo Suh, Qitong Li, and Dr. Irina Zubritskaya at the Stanford University. The impact of the research projects was greatly expanded by their specialized skills on the theoretical calculation, EELS measurement, the treatment of two-dimensional semiconductors, and the device fabrication.

It is my pleasure to acknowledge the contributions from all professors and colleagues in the Mesoscopic Materials Research Laboratory, Prof. Shinji Hayashi, Dr. Kenji Imakita, Dr. Kanna Aoki, Dr. Shinya Kano. In particular, I thank senior students Mr. Kaoru Yamamoto and Mr. Hiroyuki Takashina for their training and assistance in undergraduate works.

Finally, I am deeply indebted to my family, Hsieh family in the United States, and several close friends throughout these years. They mentally supported me and made it possible to complete this journey.

# Contents

|                                                                                                              |    |
|--------------------------------------------------------------------------------------------------------------|----|
| Abstract.....                                                                                                | i  |
| Acknowledgements.....                                                                                        | iv |
| Contents .....                                                                                               | vi |
| Chapter 1 General Introduction .....                                                                         | 1  |
| 1.1. Fundamentals of Optical nanoantennas .....                                                              | 1  |
| 1.1.1. Optical nanoantennas .....                                                                            | 1  |
| 1.1.2. General limitations and challenges .....                                                              | 3  |
| 1.1.3. Typical optical antenna structures .....                                                              | 5  |
| 1.2. Plasmonic optical antennas .....                                                                        | 7  |
| 1.2.1. Theory of localized surface plasmon resonances .....                                                  | 7  |
| 1.2.2. Examples of previously reported plasmonic nanoantennas .....                                          | 13 |
| 1.2.3. Plasmon hybridization.....                                                                            | 16 |
| 1.3. Mie resonant optical antennas.....                                                                      | 19 |
| 1.3.1. Mie resonances of dielectric nanostructures .....                                                     | 19 |
| 1.3.2. Kerker condition .....                                                                                | 22 |
| 1.4. Controlling light emission with optical nanoantennas .....                                              | 25 |
| 1.4.1. Emission enhancement.....                                                                             | 25 |
| 1.4.2. Excitation rate enhancement .....                                                                     | 26 |
| 1.4.3. Purcell enhancement .....                                                                             | 27 |
| 1.4.4. Directionality control .....                                                                          | 29 |
| 1.5. Chapter Overview .....                                                                                  | 32 |
| Part I.....                                                                                                  | 34 |
| Chapter 2 Controlling Surface Plasmon Resonances of Metal Nanocaps for Upconversion enhancement .....        | 34 |
| 2.1. Introduction.....                                                                                       | 35 |
| 2.2. Computational details .....                                                                             | 37 |
| 2.3. Experimental section.....                                                                               | 40 |
| 2.4. Results and discussion .....                                                                            | 42 |
| 2.5. Conclusion .....                                                                                        | 51 |
| Chapter 3 Introduction of Anisotropy to Metal Nanocaps and Its Application for Upconversion Enhancement..... | 53 |
| 3.1. Introduction.....                                                                                       | 53 |
| 3.2. Computational analysis .....                                                                            | 55 |

|                      |                                                                                                            |     |
|----------------------|------------------------------------------------------------------------------------------------------------|-----|
| 3.3.                 | Experimental method .....                                                                                  | 60  |
| 3.4.                 | Experimental results and discussion .....                                                                  | 61  |
| 3.5.                 | Conclusion .....                                                                                           | 67  |
| Chapter 4            | Engineering Resonances of Metal-Core/Dielectric-Shell/Metal-Cap Composites by Plasmon Hybridization.....   | 68  |
| 4.1.                 | Introduction.....                                                                                          | 69  |
| 4.2.                 | Numerical simulation.....                                                                                  | 71  |
| 4.3.                 | Experimental method.....                                                                                   | 75  |
| 4.4.                 | Results and discussion .....                                                                               | 76  |
| 4.5.                 | Conclusion .....                                                                                           | 83  |
| Part II              | .....                                                                                                      | 84  |
| Chapter 5            | Structural and optical properties of a colloidal solution of silicon nanospheres .....                     | 84  |
| 5.1.                 | Introduction.....                                                                                          | 84  |
| 5.2.                 | Fabrication, optical measurement, and simulation methods .....                                             | 85  |
| 5.3.                 | Structural and optical characterization.....                                                               | 89  |
| 5.4.                 | Conclusion .....                                                                                           | 92  |
| Chapter 6            | Angular Scattering Measurement of a Single Mie resonant Nanoantenna Using Fourier-plane spectroscopy ..... | 94  |
| 6.1.                 | Introduction.....                                                                                          | 94  |
| 6.2.                 | Measurement setup .....                                                                                    | 96  |
| 6.3.                 | Results and discussion .....                                                                               | 98  |
| 6.4.                 | Conclusion .....                                                                                           | 106 |
| Chapter 7            | Controlling Emission Directionality of monolayer WS <sub>2</sub> with Spherical Mie Resonator .            | 108 |
| 7.1.                 | Introduction.....                                                                                          | 108 |
| 7.2.                 | Results and discussion .....                                                                               | 111 |
| 7.3.                 | Conclusion .....                                                                                           | 122 |
| 7.4.                 | Method.....                                                                                                | 122 |
| Chapter 8            | A Colloidal Solution of Silicon Nanospheres toward All-Dielectric Metafluids.....                          | 125 |
| 8.1.                 | Introduction.....                                                                                          | 125 |
| 8.2.                 | Theory.....                                                                                                | 128 |
| 8.3.                 | Experimental results.....                                                                                  | 129 |
| 8.4.                 | Perspective: optical metafluids as effective media .....                                                   | 135 |
| 8.5.                 | Summary .....                                                                                              | 138 |
| Chapter 9            | Summary and outlook .....                                                                                  | 140 |
| References           | .....                                                                                                      | 142 |
| List of Achievements | .....                                                                                                      | 158 |

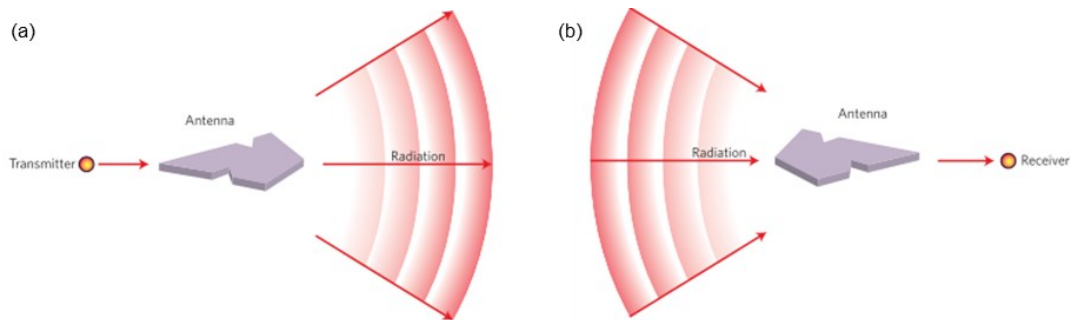
# Chapter 1

## General Introduction

### 1.1. Fundamentals of Optical nanoantennas

#### 1.1.1. Optical nanoantennas

Antennas are key components for telecommunication in the microwave and radiowave regime because of the ability to create electromagnetic fields with engineered radiation patterns and/or efficiently convert propagating electromagnetic fields into localized ones, and vice versa (Figure 1-1).[1], [2] Optical antennas are analogues of the classical radio-frequency (RF) antennas in optical regime, that is visible and near-infrared frequencies. In contrast to that the RF antennas are well-established technology and have been indispensable assets to our everyday life, the optical antennas are still under development.

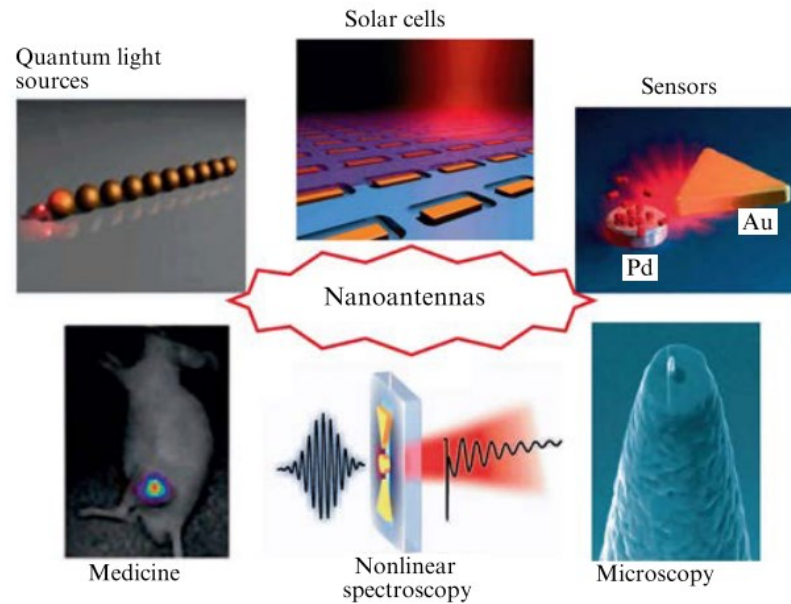


*Figure 1-1. Basic concept of antennas. The antenna has two important roles: (a) transmitter and (b) receiver. In many cases, optical nanoantennas work as both a transmitter and a receiver.[1]*

Instead of antennas, bulk optical elements such as mirror, lenses, fibers and diffractive gratings, have been utilized to manipulate electromagnetic fields in the optical regime. The field

of optics has been successfully developed in the long history; however, such classical optics relying on bulk properties of materials has intrinsic limitation, *diffraction-limited*. [3] Not only the performance, *e.g.*, focused spot size for lens, but also their dimension is restricted because of the breaks down of the geometrical optics.

One of the advantages of the optical antennas over bulky optical elements is their potential to confine light into a space much smaller than a diffraction-limited spot with sub-wavelength nanostructures. It has been thus expected for optical antennas to be alternative optical elements, for example, on integrated photonic circuits. The feature also enables to enhance light-matter interaction at the nanoscale. Because the energy of photons at optical frequencies (*i.e.* ultraviolet, visible and near-infrared) are high enough to interact with electronic transitions of matter, optical antennas provide efficient way to control and/or enhance photoluminescence (PL) and absorption of various materials including dye, molecules, and quantum emitters. For these advantages, there are wide range of the potential applications of optical antennas spanning various research fields: photonics, energy, sensing, medical, biology and so on. Some examples of the application are listed in Figure 1-2.



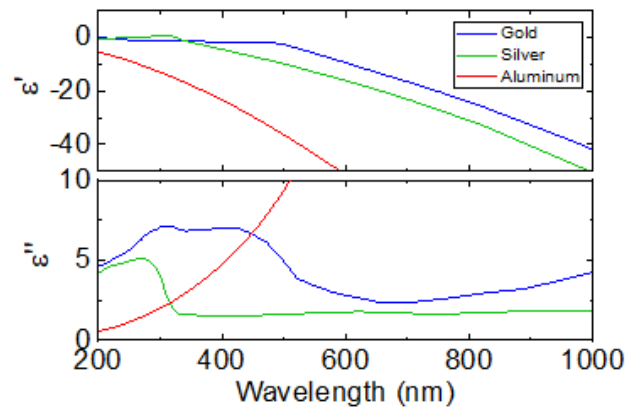
*Figure 1-2 Examples of the potential application of optical antennas in modern science.[2]*

### 1.1.2. General limitations and challenges

The basic concept of the optical antenna is similar to the RF antenna; however, the differences of the working frequencies impose difficulties on the optical antenna, hampering its widespread usage. One of the major challenges for the optical antenna are small size requirements. It is known that the characteristic dimensions of an antenna are of the order of the operation wavelength, thus for optical antennas this requires fabrication techniques which is capable of accuracies down to a few nanometers.[4] Although nano-precision fabrication technology has been rapidly developing and available these days, for example electron-beam lithography and focused ion beam lithography, the usage is still limited to research purposes due to the lack of scalability and difficulties to fabricate three dimensional structures.

Another limitation for optical antennas is material choices in the high-frequency regime. In the classical RF antenna theory, the function of an antenna is based on the oscillation of free

carriers in conductors.[4], [5] As metals behave as perfect conductors in RF regime, it is natural and easy solution to utilize metals as a material to fabricate antennas. Therefore, the classical antenna theory assume that antenna wires are perfect conductor and tends to omit Ohmic losses. In fact, the radiation efficiency of RF antennas is typically larger than 99%. However, in the higher frequency regime such as infrared and visible, the metals no longer behave as perfect conductors. This is because the oscillation of conduction electrons with a finite mass cannot follow the high-frequency excitation field and accompany certain phase delay against the driving force, leading strong Ohmic losses. This behavior can be seen in dielectric functions of metals (Figure 1-3) which have large imaginary parts in the optical frequencies. Therefore, for optical antennas it is needed to consider the material losses (*i.e.*, absorption) and/or utilize low-loss materials instead of metals.



*Figure 1-3 Dielectric functions of typical metals: gold (blue), silver (green), and aluminum (red). The top and bottom show real and imaginary parts, respectively. The data are taken from reports by Johnson and Christy (gold, silver)[6] and Palik (aluminum)[7].*

Dealing with these limitations, various types of optical antenna has been studied so far. Although any resonators whose resonances are at optical frequencies may be classified as optical antennas, just like that RF antennas are based on resonant oscillation of charges in metals, this

thesis focuses on optical nanoantennas (*i.e.*, nanoresonators). In the following section, examples of nanoantennas are provided.

### 1.1.3. Typical optical antenna structures

The optical antenna has more than 90 years history.[1], [2], [4], [8]–[11] The first proposal was made by Edward Synge in 1928. He suggested to utilize a colloid of gold nanoparticle to confine light and surpass the diffraction-limited resolution in optical imaging.[12] After a while, the field grew as near-field optics, and various optical antenna structures have been suggested as near-field optical probes.[13] The first proposal of the concept of optical antennas was a little later and reported by John Wessel in 1985, and he suggested that a gold nanoparticle can work as an antenna.[14] Because the concept of optical antenna was connected to near-field optical probes afterwards,[15] the field of optical antenna has grown up as an extensively studied research field. Although the field of optical antennas has emerged for a near-field probes in the beginning, nowadays it is widely studied for various applications.

As seen in the history, metal nanostructures have been extensively studied as optical antennas. Although details will be described later, localized surface plasmon resonances are excited in the optically small metals and make optical antennas particularly efficient at the resonance frequencies. Benefitting from the well-established RF antenna theory, various metal (plasmonic) nanostructure has been developed using the design principles of RF antennas.

Figure 1-4 shows various optical antenna structures. The simplest structure is a monopole antenna and realized by nanosphere and nanorod structure (Figure 1-4a). A dimer structure, horizontally aligned coupled nanorods, shown in Figure 1-4b,c is an analog of a linear dipole gap

antenna or a RF Hertzian dipole antenna and have a high radiation efficiency.[16] Shown in Figure 1-4d is a bow-tie antenna which represents a biconical antenna and have broadband response.[17] It is also important to note that the bow-tie antenna have strong field enhancement in the gap and is thus often used for PL and Raman enhancement. A Yagi-Uda antenna is one of the most successful RF antenna design for its directionality. The same strategy still works for optical antennas (Figure 1-4e).[18], [19] Besides them, many RF antenna designs (*e.g.*, Figure 1-4f,g) have been miniaturized and demonstrated the function as optical antennas.

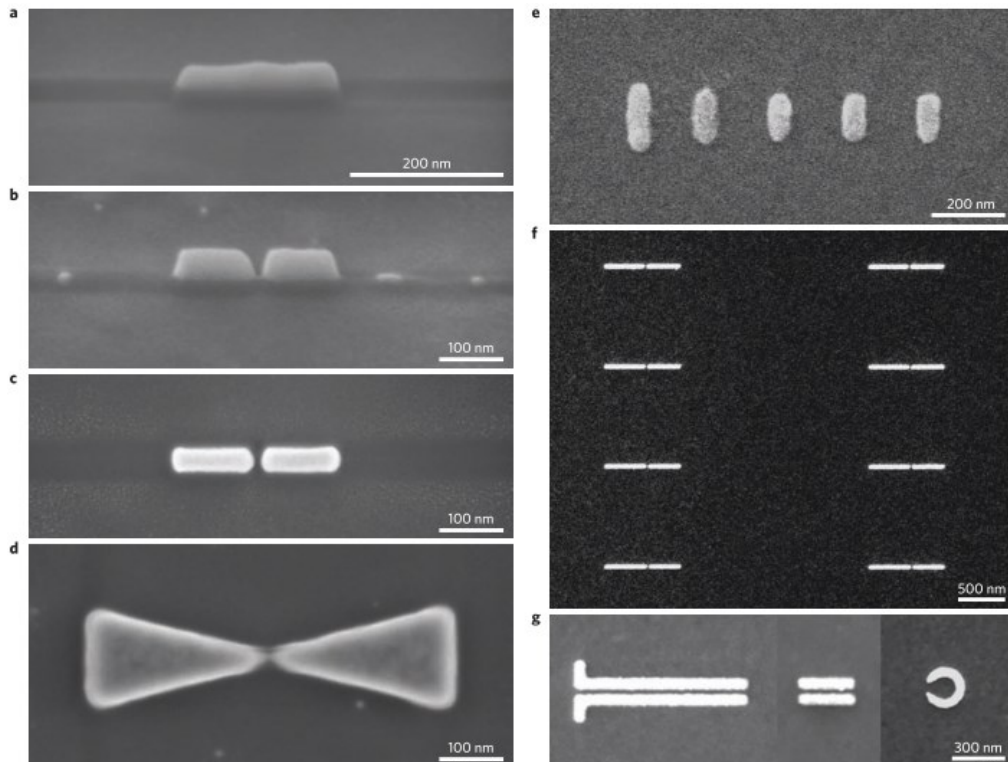


Figure 1-4 SEM images of examples of optical antenna structures.[1] (a) nanorod, (b,c) dimer, (d) bow-tie, (e) Yagi-Uda, (f) gap, and (g) plasmonic waveguide and split-ring antenna.

Although these structures have been developed as an extension of RF antennas in the early stage, the recent optical antenna is designed and optimized for specific applications. In association with development of plasmonics, the structure has been deviating from typical

antenna design and is getting more complex. Inspired by metamaterials, the use of Mie resonators, nanostructures made of high-index dielectrics, is also recent trend due to its potential for realization of low-loss or even loss-less optical antennas. These optical antennas have been developed with specific design principles, and thus it is easier to understand them with their operation principles. The fundamentals of plasmonic and dielectric optical antennas are introduced in the following section.

## 1.2. Plasmonic optical antennas

Surface plasmon resonances enable metallic optical nanoantennas to be efficient antennas. Because most of metallic optical nanoantennas are developed based on plasmonics, it is essential to introduce what the surface plasmon resonance is to explain the basics of them. In this section, fundamentals of plasmonics is provided.

### 1.2.1. Theory of localized surface plasmon resonances

Plasmonics is the field which studies interaction of electromagnetic field with free electrons in metals at the metal-dielectric interfaces or in small metallic nanostructures.[20] The term “plasmon”, sometimes referred to as the *volume plasmon*, is the collective oscillation of free electrons in metals. At the surface of the metals, a collective displacement of the electrons leads to surface charges and electromagnetic waves which can couple with propagating light when special techniques for phase-matching are employed (Figure 1-5). Because the surface wave can propagate at the interface (typical propagation lengths are 10 – 100  $\mu\text{m}$  in visible), the excitation is called *propagating* surface plasmon polariton (SPP). The derivation and detailed description of

the SPP are beyond the focus of this thesis and provided in many textbooks.[20]–[23] In contrast to the SPP which requires phase-matching techniques (*e.g.*, prism, grating, groove, *etc.*) for excitation with light, plasmons in subwavelength metal nanostructures can resonantly couple with propagating waves without any phase-matching treatments because of the certain penetration of light (*i.e.*, skin depth) and their curved surface. This non-propagating excitation is called *localized* surface plasmon resonances (SPRs), which make metallic nanostructures optical nanoantennas.

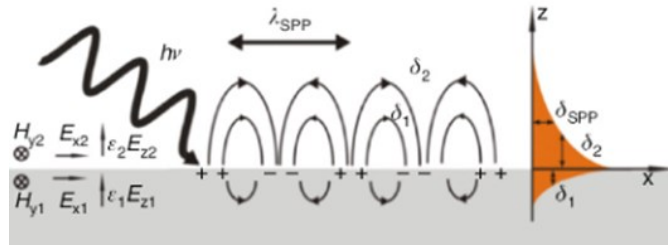


Figure 1-5 Illustration of surface plasmon polariton (SPP) modes at the continuous metal-dielectric interfaces.[24]

The theoretical derivation of the SPR can be obtained for simple geometries. Let's consider a spherical metal particle whose diameter is much smaller than the wavelength of light.[20], [25] Under this so-called *quasi-static approximation*, the phase of the oscillating electromagnetic field is constant over the particle at an instance of time as shown in Figure 1-6.

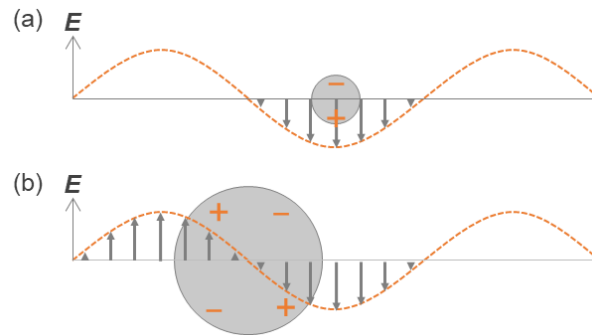


Figure 1-6 Schematic illustration of the quasi-static approximation. When a particle is sufficiently small (a) compared to the wavelength of light, the spatial distribution of electric field is uniform over the volume, while it is not uniform for a large particle (b).

The calculation model consists of a homogeneous sphere with the dielectric function  $\varepsilon(\omega)$  at the origin as shown in Figure 1-7. The sphere has radius  $a$  and is located in a uniform static field ( $\mathbf{E} = E_0 \hat{\mathbf{z}}$ ) and the medium with dielectric constant  $\varepsilon_m$ . Under static approach, the potential  $\Phi$  satisfies the Laplace equation  $\nabla^2 \Phi = 0$ , from which the electric field  $\mathbf{E} = -\nabla \Phi$  can be calculated. The general solution of this problem can be given by

$$\Phi(r, \theta) = \sum_{l=0}^{\infty} [A_l r^l + B_l r^{-(l+1)}] P_l(\cos \theta), \quad (1-1)$$

where  $P_l(\cos \theta)$  are the Legendre Polynomials of order  $l$ , and  $\theta$  is the angle between vector  $\mathbf{r}$  (position  $P$ ) and the z-axis as shown in Figure 1-7.[26] For the scattering problem of a sphere, the problem is solved so that the boundary conditions of the potentials inside ( $\Phi_{in}$ ) and outside ( $\Phi_{out}$ ) the sphere are satisfied at the surface. Given the requirements for the potentials which need to be finite value at the origin, we can write them as

$$\Phi_{in}(r, \theta) = \sum_{l=0}^{\infty} A_l r^l P_l(\cos \theta) \quad (1-2)$$

$$\Phi_{out}(r, \theta) = \sum_{l=0}^{\infty} [B_l r^l + C_l r^{-(l+1)}] P_l(\cos \theta). \quad (1-3)$$

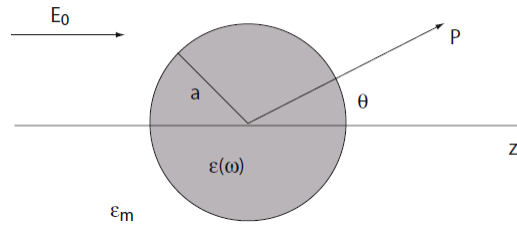


Figure 1-7 Calculation model. A homogeneous sphere in an electrostatic field.[20]

The boundary condition at  $r \rightarrow \infty$  requires  $\Phi_{out} \rightarrow -E_0 z = -E_0 r \cos \theta$ , determining  $B_1 = -E_0$  and  $B_l = 0$  for  $l \neq 1$ . At the sphere surface, the boundary conditions can be

obtained from continuity of the tangential components of the electric field and the normal components of the displacement field:

$$-\frac{1}{a} \frac{\partial \Phi_{in}}{\partial \theta} \Big|_{r=a} = -\frac{1}{a} \frac{\partial \Phi_{out}}{\partial \theta} \Big|_{r=a}, \quad (1-4)$$

$$-\varepsilon_0 \varepsilon \frac{\partial \Phi_{in}}{\partial r} \Big|_{r=a} = -\varepsilon_0 \varepsilon_m \frac{\partial \Phi_{out}}{\partial r} \Big|_{r=a}. \quad (1-5)$$

By applying these conditions, the potentials can be calculated as

$$\Phi_{in}(r, \theta) = -\frac{3\varepsilon_m}{\varepsilon + 2\varepsilon_m} E_0 r \cos \theta \quad (1-6)$$

$$\Phi_{out}(r, \theta) = -E_0 r \cos \theta + \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} E_0 a^3 \frac{\cos \theta}{r^2}. \quad (1-7)$$

Note that evaluation is required only for  $A_1$  and  $C_1$  because  $A_l = C_l = 0$  for  $l \neq 1$ . By looking at equation (1-7), we notice that the  $\Phi_{out}$  can be interpreted as the superposition of the incident field and the scattered field due to a dipole at the origin. This means that a sphere in the static field can be regarded as a dipole at the center. Based on this interpretation, we can replace the second component of equation (1-7) using the dipole moment  $\mathbf{p}$ :

$$\Phi_{out} = -E_0 r \cos \theta + \frac{\mathbf{p} \cdot \mathbf{r}}{4\pi\varepsilon_0\varepsilon_m r^3} \quad (1-8)$$

$$\mathbf{p} = 4\pi\varepsilon_0\varepsilon_m a^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} E_0. \quad (1-9)$$

By introducing the polarizability  $\alpha$  ( $\mathbf{p} = \varepsilon_0\varepsilon_m\alpha\mathbf{E}_0$ ), we can get

$$\alpha = 4\pi a^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}. \quad (1-10)$$

As can be seen in equation (1-10), the polarizability diverges and becomes large value when  $Re[\varepsilon(\omega)] = -2\varepsilon_m$ . This condition is called the Fröhlich condition and corresponds to the dipole

surface plasmon resonance of a metal sphere when the applied field oscillates in time. Because of this resonant behavior, metal nanostructures can work as optical antennas in the optical frequencies.

For more intuitive visualization, we then evaluate the distribution of the electric field  $\mathbf{E} = -\nabla\Phi$  from the potentials (equation (1-6) and (1-7)):

$$\mathbf{E}_{\text{in}} = \frac{3\varepsilon_m}{\varepsilon + 2\varepsilon_m} \mathbf{E}_0 \quad (1-11)$$

$$\mathbf{E}_{\text{out}} = \mathbf{E}_0 + \frac{3\mathbf{n}(\mathbf{n} \cdot \mathbf{p}) - \mathbf{p}}{4\pi\varepsilon_0\varepsilon_m} \frac{1}{r^3} \quad (1-12)$$

, where  $\mathbf{n}$  is the unit vector in the direction of the point P of interest. We can see that the both internal and external fields are enhanced at the resonant condition of  $\alpha$ . This field enhancement is one of the most important nature of surface plasmon resonance as it enhances light-matter interaction in the small volume. Intuitively, it can be expected that an emitter located in the enhanced region feels stronger electric field than that in the free space, resulting in enhanced light emission due to surface plasmon resonance.

At the resonant condition, the scattering and absorption processes are also resonantly enhanced. Before showing the result, here we introduce important physical quantities to evaluate optical responses (*i.e.*, scattering or absorption) of nanoantennas. As the scattered ( $W_{\text{sca}}$ ) or absorbed ( $W_{\text{abs}}$ ) electromagnetic energy depend on the intensity of illuminated light, it is convenient to normalize them by the illumination light intensity ( $I_i$ ) as[27]

$$C_{\text{sca/abs}} = \frac{W_{\text{sca/abs}}}{I_i}. \quad (1-13)$$

Here,  $C_{sca}$  and  $C_{abs}$  are scattering and absorption cross sections, respectively. As expected from the term “cross section”, the quantities have unit of  $[m^2]$  because the power in [Watts] is divided by the intensity in  $[Watts/m^2]$ . Note that in two-dimensional problems, such as infinitely long wire, the cross sections have unit of  $[m]$ . The scattering and absorption cross section corresponds to the illumination area where scattered or absorbed light flux has been injected from. The total of  $C_{sca}$  and  $C_{abs}$  is also important quantity called extinction cross section ( $C_{ext}$ ), which describes how strongly the nanoantenna can interact with light.

Here we omit the derivation, but the scattering and absorption cross sections for the metal sphere under the quasi-static approximation can be calculated by evaluating Poynting vector over an imaginary sphere surrounding the sphere. From reference [20], they can be written as:

$$C_{sca} = \frac{k^4}{6\pi} |\alpha|^2 = \frac{8\pi}{3} k^4 a^6 \left| \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right|^2 \quad (1-14)$$

$$C_{abs} = k \text{Im}[\alpha] = 4\pi k a^3 \text{Im} \left[ \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right]. \quad (1-15)$$

Figure 1-8 shows the scattering and absorption cross section spectra of a gold sphere (80 nm in radius) in the quasi-static approximation calculated using the equations above. At the 508 nm, the surface plasmon resonance is excited, and the spectra have peaks as indicated by a gray arrow. One may notice in the figure that the absorption is much larger than the scattering. For small particles  $a \ll \lambda$ , the absorption dominates the response; however the scattering can overwhelm the absorption for large particle due to the rapid scaling of  $C_{sca} \propto a^6$ , while  $C_{abs} \propto a^3$ .

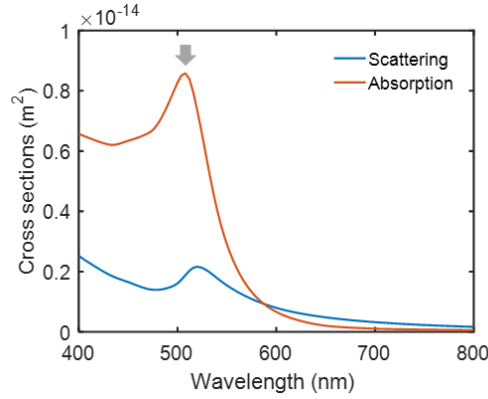


Figure 1-8 Scattering (blue) and absorption (orange) spectra of a gold nanosphere ( $a = 40$  nm) calculated by equations (1-14) and (1-15) under the quasi-static approximation, with the empirical dielectric function taken from [6].

In this section, the surface plasmon resonance of a small sphere have been theoretically explained under the quasi-static approximation. The theory well explain the field enhancement and the characteristics of scattering and absorption spectra due to the dipole resonance; however, for larger particles, more complex approaches such as Mie theory is required because the quasi-static approximation is not valid anymore (see Figure 1-6b).

### 1.2.2. Examples of previously reported plasmonic nanoantennas

It is known that plasmonic responses of metal nanostructures (*i.e.*, polarizability  $\alpha$ ) strongly depends on the shape of them. It is worthy to note that, in general, it is difficult to obtain analytical solution of optical responses of metal nanostructures. Although the plasmonic response of a small sphere has been derived in the previous section, such an analytical approach can be applied only for some simple structures such as a sphere, spheroid, core-shell particle, particle on mirror structure, dimer. If it is needed to include the retardation effect beyond the quasi-static approximation, a spheroid including a sphere is the only structure for which the rigorous solution

can be obtained so far. For more complex structures, electromagnetic simulation techniques are needed to know their optical responses.

Here we introduce typical plasmonic antenna structures which have been reported previously. As described above, the development of optical antennas started from a proposal to utilize a nanosphere as near-field tips of scanning probe microscopy (Figure 1-9a,b)[2], [12] The sphere is the simplest geometry and can be synthesized easily. Although the surface plasmon resonance is relatively insensitive to the scaling of nanostructure, as the resonance condition is determined by the dielectric functions under the dipole approximation (equation (1-10)), it is known that it is very sensitive to the morphology (Figure 1-9c). A nanorod is one geometry which have a widely tunable resonance. By changing the diameter-to-length aspect ratio, the longitudinal surface plasmon resonance can be tuned from ~600 nm to near-infrared region.[28]

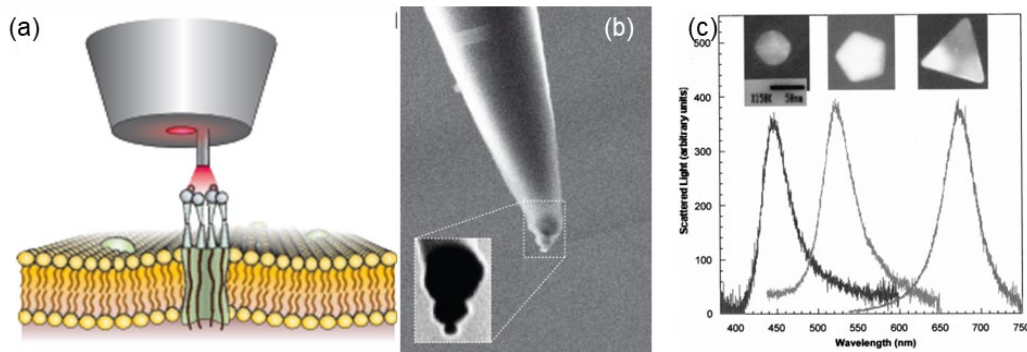


Figure 1-9. (a) Schematic illustration of biological imaging with near-field tip made of an optical antenna.[29] (b) SEM image of a near-field probe made of a gold trimer antenna supported by a dielectric tip.[2] (c) Scattering spectra of silver nanoparticles with different geometries.[30]

Extra degrees of freedom in structural design can be added by coupling the metal nanostructures with another. Dimer geometry consisting of two nanospheres or nanodisks is often studied structure.[16], [31]–[36] Due to the strong field confinement within the gap, it is a useful platform to enhance fluorescence, non-linear optical effects, chemical reactions, and so on (Figure

1-10a,b). The so-called *gap plasmon* can also be realized by placing plasmonic nanoparticles on mirror (NPoM) because the nanoparticle couple with its image formed by the mirror. The NPoM has great advantage on the controllability of the gap length, down to picometer scale, and has been extensively studied by J. Baumberg and M. Mikkelsen groups to demonstrate various applications (Figure 1-10c).[37], [38], [47]–[56], [39], [57]–[60], [40]–[46] These simple structures are versatile for not only fluorescence but also wide range of phenomena including Raman signals, non-linear optical effects, refractive index sensing, *etc.*

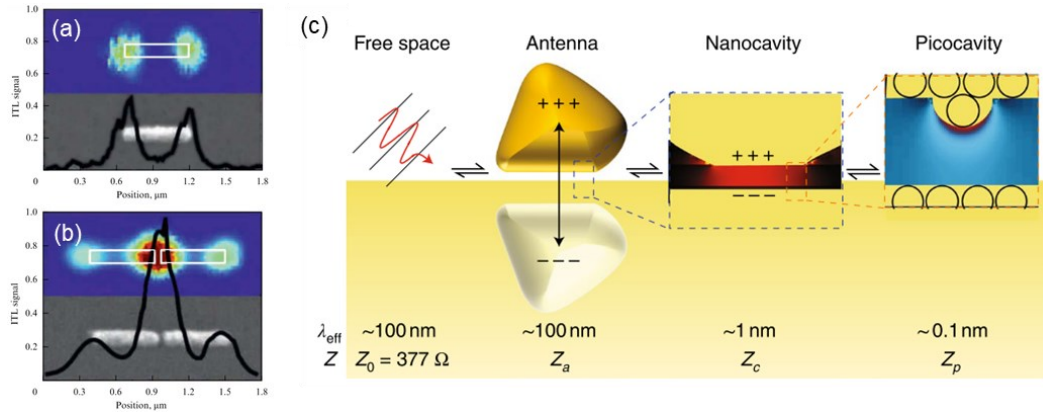
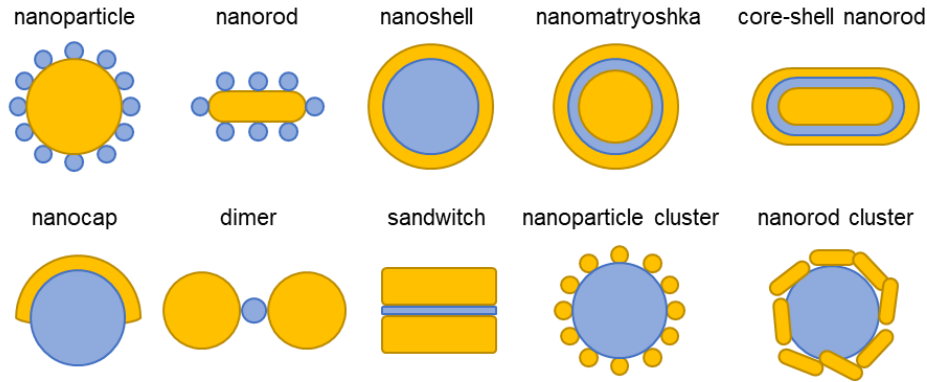


Figure 1-10. Coupled plasmonic nanoantennas. (a,b) Two-photon luminescence signal near (a) single and (b) dimer nanoantennas.[31] (c) Illustrations of various nanoparticle on mirror (NPoM) antennas.[40]

Recently, stand-alone plasmonic nanocomposites, into which a metal nanostructure and an emitting material are integrated, has been attracting attention in different fields because it can be a functional building block in optoelectronics and biophotonics applications. A large variety of metal nanostructures have been employed for the formation of stand-alone plasmonic nanocomposites and the enhancement of photoluminescence. As schematically summarized in Figure 1-11, they are nanoparticles[61]–[64], nanorods[65]–[69], nanoshells[70], [71], nanomatyoshkas[72], core-shell nanorods[73], [74], nanocaps[75]–[77], nanoparticle dimers[36],

[78], metal-insulator-metal sandwiches[79], nanoparticle clusters[80], [81], and nanorod clusters[82].



*Figure 1-11 Schematics of stand-alone plasmonic nanocomposites where metal nanoantennas and emitting materials are integrated. The yellow and blue region indicate metal and emitting materials, respectively.*

Variety of geometries have been proposed so far; however, each geometry has pros and cons. For example, the simple geometries such as the nanoparticle or nanorod can be fabricated easily, but the limited degree of freedom makes it difficult to spread hot-spots of the electric field over the large volume where emitters exist. In case of closed system such as nanoshell or matryoshka, the extraction efficiency of light emission tends to be low. Therefore, it is needed to optimize antenna structures for each application or properties of target emitters.

### 1.2.3. Plasmon hybridization

Advancement in fabrication techniques, including the chemical synthesis and lithographic processes, have led to development of various plasmonic nanostructures. In order to know the plasmon response of complex structures, such as spectral responses, charge and field distribution, and origin of the resonant mode, numerical simulation is required. In 2003, E. Prodan *et. al.* presented a simple and intuitive picture to explain the plasmon response of complex

nanostructures.[83] In the picture, the plasmon response can be understood as the interaction or *hybridization* of plasmons in elementary geometries, in analogue of molecular orbital theory.

As an example, the plasmon hybridization model for a metal nanoshell is illustrated in Figure 1-12. In case of the nanoshell, the plasmon response can be understood as the interaction between plasmons supported by a sphere and a hollow cavity. The sphere and cavity plasmons induce surface charges at the outer and inner interface, respectively, and interact with each other via the thin metal shell. The interaction results in the splitting of the resonances into two resonances which have different charge distributions. The higher energy mode ( $|\omega_+\rangle$ ) corresponds to the antibonding plasmon (antisymmetric coupling), while the lower energy mode ( $|\omega_-\rangle$ ) corresponds to bonding plasmon (symmetric coupling). The picture provides important intuition that the resonance energies (*i.e.*, wavelength) can be tuned by the shell thickness because it determines the coupling strength. For example, the thinner shell would promote stronger interaction, resulting in red-shifting of the bonding mode and blue-shifting of the antibonding mode.

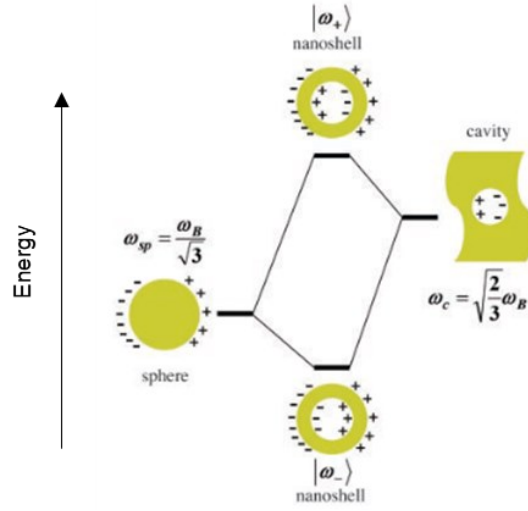


Figure 1-12 An energy-level diagram describing the plasmon hybridization model. The plasmon response of metal nanoshell can be understood by the hybridization of the sphere and cavity plasmon.[83]

The model was first proposed to explain the plasmon response of metal nanostructures; however, it is a general picture to describe the “strong” coupling of two electromagnetic cavities and can be applied to arbitrary geometries not only particle plasmons in metals (examples are shown in Figure 1-13). Utilizing this powerful approach, we will develop a new plasmonic antenna in Chapter 4.

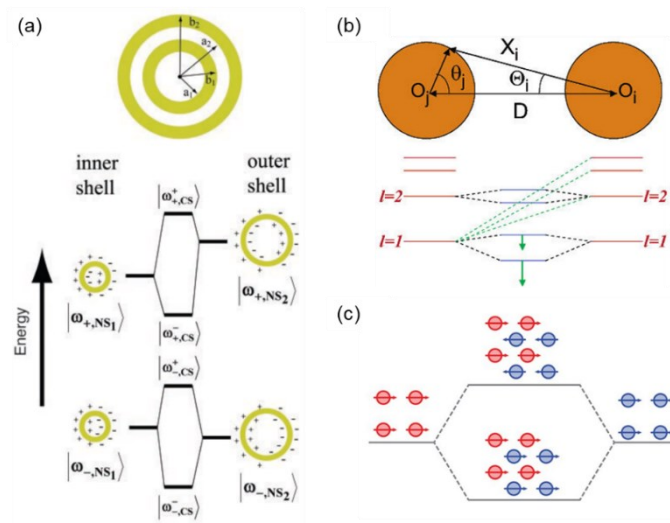


Figure 1-13 Plasmon hybridization models for a nanomatryoshka[83], particle dimer[84], and hybridized lattice resonance[85].

### 1.3. Mie resonant optical antennas

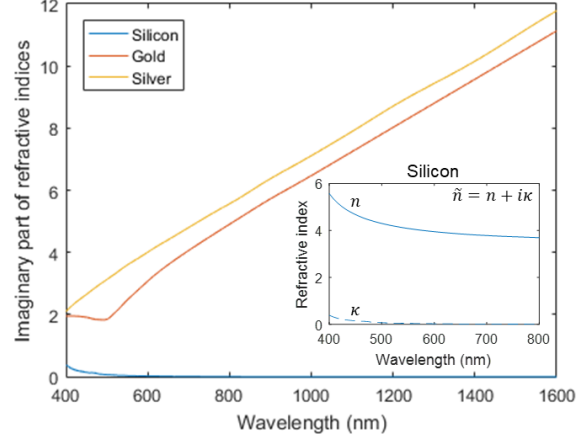
Since the first proposal of the optical antenna, metallic (plasmonic) antennas have been studied enthusiastically; however, only some applications have been realized in practice due to their drawbacks including high energy dissipation of metals at optical frequencies and their incompatibility with complementary metal oxide semiconductor (CMOS) processes. Recently, dielectric nanoantennas made of high-refractive-index dielectrics have been emerged in nanophotonics and metamaterials and are opening up new opportunities as low-loss (possibly lossless) optical antennas.

#### 1.3.1. Mie resonances of dielectric nanostructures

Dielectric nanoantennas are nanostructures made of high-refractive-index dielectrics including semiconductors. They resonate at optical frequencies due to light penetration in and concentration inside the nanostructures. This type of resonance is often referred to as Mie resonance and recently attracting massive research attentions due to its low-loss nature and interference effects between multipoles.[86]–[89].

The losses of plasmonic and dielectric materials can be quantitatively compared via their imaginary parts of refractive indices ( $\tilde{n} = n + i\kappa$ ) which represent losses of materials.[26] In Figure 1-14,  $\kappa$  of typical dielectric (silicon) and plasmonic (gold and silver) materials used for optical antennas are compared in visible and near-infrared wavelengths. As can be seen, silicon shows 10 to 100 times lower losses compared to gold and silver in optical frequencies. Although silicon still has small losses in the visible especially at wavelengths shorter than  $\sim 500$  nm, semiconductors are completely lossless materials below the bandgap energies (silicon:  $\sim 1.12$  eV

at 300 K). Therefore, dielectric nanoantennas have a potential to be low-loss or even lossless optical antennas.



*Figure 1-14. Optical losses of dielectric versus plasmonic materials. Imaginary parts of refractive indices of silicon (blue), gold (orange), and silver (yellow) are plotted. The inset is the real (solid) and imaginary (dashed) parts of the refractive index of silicon in visible. The data of silicon is taken from ref. [7], while that of gold and silver are from ref. [6].*

The Mie resonance from which dielectric nanoantennas are empowered occurs when the effective light wavelength in the structure becomes comparable to their geometrical cross sections. The mechanism of the Mie resonance can be explained via Mie theory[90] which is the exact solution of Maxwell's equations for a scattering problem by a small particle. Note that the quasi-static approximation is not appropriate to describe the Mie resonance because even the lowest order dipole resonance relies on the retardation of light within the particle. From the Mie theory, the scattering cross section of a small particle under planewave illumination with wavelength  $\lambda$  can be written as

$$C_{sca} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n+1)(|a_n|^2 + |b_n|^2) \quad (1-16)$$

, where  $k = 2\pi/\lambda$ , and  $a_n$  and  $b_n$  denote  $n$ -th order Mie coefficients.[27] The  $a_n$  and  $b_n$  expresses the amplitude of electric and magnetic multipoles, respectively (e.g.,  $a_1$ : electric dipole,  $a_2$ : electric quadrupole,  $b_1$ : magnetic dipole,  $b_2$ : magnetic quadrupole, etc.).

The calculated scattering efficiency of a dielectric nanosphere with radius  $R$  and refractive index  $n$ , is shown in Figure 1-15a as a function of the size parameter ( $2R/(\lambda/n)$ ) and  $n$ . [89] It can be seen that the first peak appears around  $2R/(\lambda/n) \sim 1$ , and multiple peaks follow it in the larger size parameter range. The peaks become stronger as  $n$  gets higher, indicating important criteria that high refractive index ( $\sim 2$ ) is required to excite prominent Mie resonances.

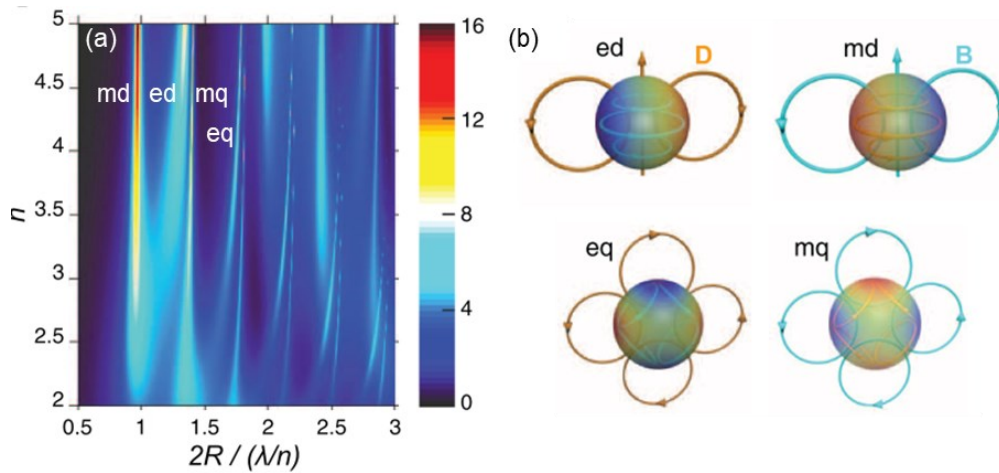


Figure 1-15 (a) Scattering efficiency of a lossless dielectric nanosphere. The horizontal and vertical axes are the size parameter and refractive index, respectively. (b) Field structures of Electric and magnetic dipole (ed, md) and quadrupole (eq, mq) resonances.[89]

It is convenient to see the field structures for better understanding of the modes (Figure 1-15b). In case of the Mie resonance, the lowest order resonance corresponds to magnetic dipole (md) mode, while only electric modes dominate optical responses of plasmonic nanospheres. This mode originates from the circular displacement current of electric field inside the particle and

occurs due to the field penetration and phase retardation. The second one corresponds to electric dipole (ed) mode, which has similar characteristics with the dipole plasmon resonance.

### 1.3.2. Kerker condition

The possession of the magnetic response as a natural mode in simple structures is a key characteristic of the Mie resonator and making it a particularly fascinating structure. One of the most important phenomena which is enabled by the optical magnetism is unidirectional scattering. In 1983, Kerker *et. al.* suggested that a magneto-dielectric sphere may show unique scattering behavior at the condition where the values of electric permittivity  $\epsilon$  and magnetic permeability  $\mu$  become equal ( $\epsilon = \mu$ ). [91] At the condition, so-called *first Kerker condition*, scattering in backward direction is completely suppressed, and only forward scattering remains. Although such behavior had not been achieved in optical frequencies, because material in nature do not have the magnetic response in the frequency range, it has been suggested and demonstrated that the unidirectional light scattering is possible using the electric and magnetic Mie resonances. [92], [93]

The mechanism of the Kerker-type unidirectional scattering occurs due to the interference between the electric and magnetic dipoles in the far-field. Figure 1-16 illustrates the field lines of the modes. For the electric dipole, the phase of electric field is symmetric in the illumination axis (the direction of  $k$ ), whereas that is asymmetric for the magnetic dipole mode. Due to this scattering parity difference, the scattering is cancelled in backward and enhanced in forward direction (*i.e.*, zero-backward scattering) when the amplitudes of electric and magnetic dipoles are equivalent ( $a_1 = b_1$ ).

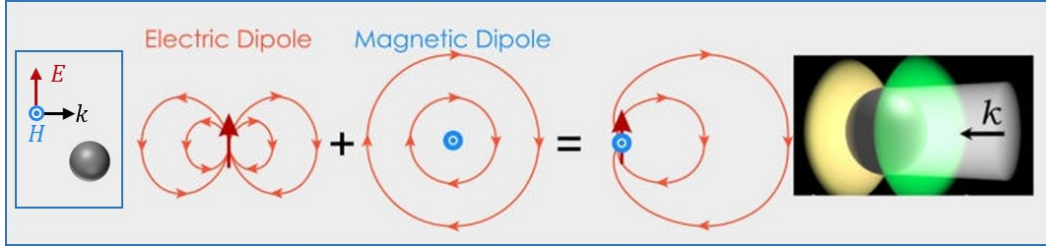


Figure 1-16 Explanation of unidirectional scattering at Kerker condition. The electric field lines show that the destructive and constructive interference in backward and forward, respectively, results in the unidirectional scattering. The figure on the right illustrates that the color of the Kerker particle is different depends on the observation direction.[94]

The spectral scattering response of directionality of the dielectric particle is shown in Figure 1-17. Figure 1-17a-c is the calculated scattering spectra of a sphere with  $n = 4$ . In order to visualize each contribution of multipoles, the Mie coefficients of electric  $a_1$  and magnetic  $b_1$  dipoles are decomposed and in Figure 1-17b. Due to different spectral position, shape, and width, the  $a_1$  and  $b_1$  intersect each other at several points. Given the relative phase of the resonances against incident field, that is, both of electric and magnetic dipoles are in-phase, the zero-backward scattering, the first Kerker condition in other words, is achieved in the long-wavelength (i.e., smaller size parameter) side of the magnetic dipole peak as shown by the dashed line.

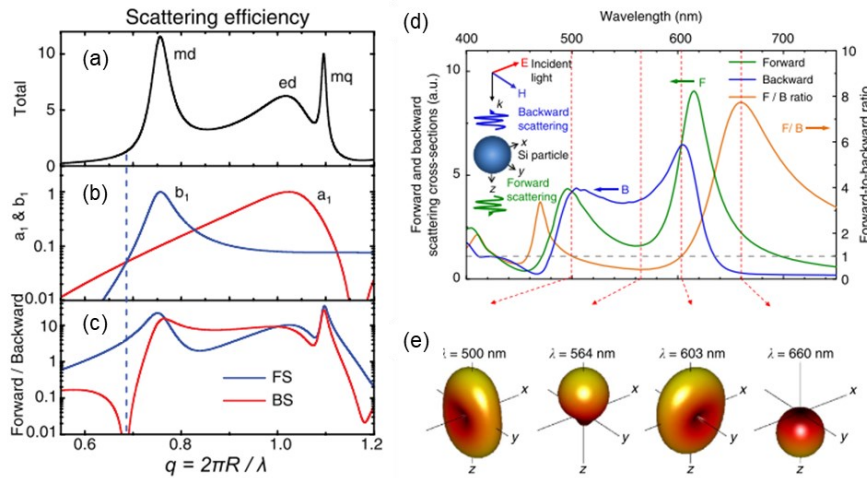


Figure 1-17 (a) Scattering efficiency of a dielectric sphere with  $n = 4$ . (b) Mie coefficients of electric  $a_1$  and magnetic  $b_1$  dipoles and (c) Forward/Backward scattering spectra of the sphere.[89] (d)

*Forward and backward scattering and forward-to-backward ratio spectra of a silicon nanosphere with radius of 75 nm. (e) Far-field scattering patterns at the characteristic wavelengths.[93]*

The more realistic calculation is shown in Figure 1-17d,e, which are scattering spectra of a silicon nanosphere of 75 nm in radius. It is worthy to note that the backward scattering intensity does not fall into zero in typical experimental setups using a microscope, which is considered in the calculation, because of certain detection solid angles of objectives. The forward and backward scattering spectra show clear peaks corresponds to electric and magnetic dipoles. The spectrum of forward-to-backward (F/B) ratio show the response of directionality, exhibiting peak at the first Kerker condition at 660 nm. The far-field radiation patterns at the electric and magnetic dipole resonances and the point of highest and lowest F/B ratios are shown in Figure 1-17e. We can see the radiation in backward (-z) direction is suppressed at 660 nm. In contrast to that, the radiation pattern at 564 nm shows almost-zero-forward scattering. At this condition, the relative phase of the magnetic dipole is out-of-phase, resulting in suppression of forward scattering, which is referred to as the second Kerker condition. Due to these different radiation patterns depending on the wavelength, the dielectric antennas are capable of frequency-selective light routing (see the right panel of Figure 1-16).

The largest motivation to develop such directional nanoantennas is to utilize them as a scattering element of planar metasurfaces. The metasurfaces are composed of many small scatterers which modulate phase or amplitude of reflected or transmitted light; however, their efficiency cannot exceed 50% if each element scatters light in both forward and backward direction likewise the dipole radiation pattern. It has been demonstrated that the near-unity transmission metasurface can be realized by an array of directional silicon nanoantennas.[95]

## 1.4. Controlling light emission with optical nanoantennas

The control of light emission from various emitters near optical nanoantennas is one of the most important function for them. Here we describe some important functions of antennas coupled with emitters.

### 1.4.1. Emission enhancement

The emission enhancement is of great importance of optical antennas. In general the enhancement can be achieved in three processes. As can be seen in the schematic illustration in Figure 1-18, an emitter can be considered as a transmitter. When an emitter is placed near an antenna, the radiation can couple with the modes of the antenna and re-radiated into the far-field. Through this process, the radiation efficiency (*i.e.*, quantum efficiency) of the emitter is modified, thus the number of photons emitted can be increased or decreased. By reciprocity, the photons came from the far-field can couple with the modes of the antenna, resulting in efficient excitation of the emitter (absorption enhancement). The other mechanism is directionality. When the radiated light is detected by a receiver, only some portion of the light within a certain solid angle can be collected because of finite detector dimension. Thus, the number of photons the detector receives can be increased by directing the radiation in the direction of the detector.

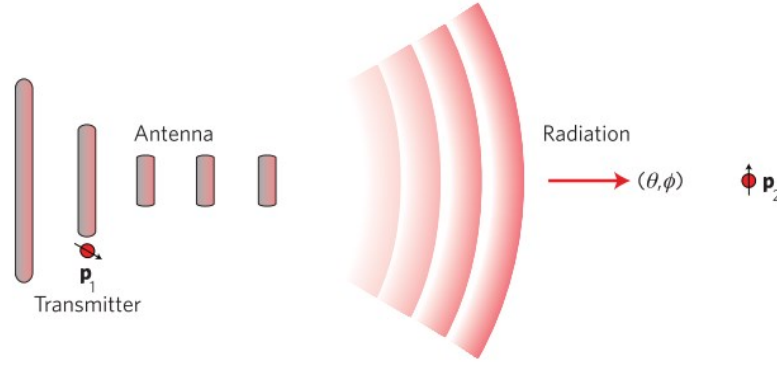


Figure 1-18 Illustration of modified radiation of a emitter (transmitter) when it is coupled to an optical antenna.[1]

Therefore, we can express the emission enhancement factor (EF) by the following equation.[52]

$$EF = \frac{I}{I_0} = \frac{\eta}{\eta_0} \frac{\gamma_{ex}}{\gamma_{ex}^0} \frac{QE}{QE_0} \quad (1-17)$$

, where  $\eta$  is the collection efficiency which is related to the directionality,  $\gamma_{ex}$  is the excitation rate, and  $QE$  is the quantum efficiency of the emitter near the optical antenna. For all terms, the sub or superscript 0 denote the values without the antenna. In the following section, these contributions are explained in detail.

#### 1.4.2. Excitation rate enhancement

As discussed above, the metal nanoparticle induces field enhancement at the surface when the surface plasmon resonance is excited. Similar field localization occurs near and inside dielectric nanoparticle at the Mie resonance. If an emitter is placed in the enhanced field, the emitter feels stronger electric field than in the free space. Intuitively speaking, more photons can interact with the emitter near the resonator.

Formally, excitation rate enhancement can be described with the Fermi's golden rule.

Transition rate  $\gamma$  from the initial state  $|i\rangle$  to final state  $|f\rangle$  can be written as

$$\gamma_{if} = \frac{2\pi}{\hbar} |\langle f | \mathbf{E} \cdot \mathbf{p} | i \rangle|^2 \rho_f \quad (1-18)$$

where  $\mathbf{E}$  is the local electric field,  $\mathbf{p}$  is the transition dipole moment, and  $\rho_f$  is the density of the final state.[96] In this equation, an optical nanoantenna can increase  $\mathbf{E}$ , increasing the transition rate from the initial to final state. Given the emitter we utilize in the following chapters, it is worthy to note that the emitted light intensity  $I$  is proportional to  $|\mathbf{E}|^{2n}$  for an  $n$ -photon process. Therefore, the excitation rate enhancement can be written as  $\gamma_{ex}/\gamma_{ex}^0 = |E/E_0|^{2n}$ .

### 1.4.3. Purcell enhancement

As can be seen in (1-18), the transition rate depends on the density of the final state  $\rho_f$ . When a cavity (or antenna) exists near the emitter, modes of the cavity can be added to  $\rho_f$  as some of the final states. If the cavity mode is radiative, the energy stored in the cavity can be radiated as photons, indicating the possibility of emission rate enhancements. Because the modification of the spontaneous emission rate was theoretically predicted by Purcell, this effect is referred to as *Purcell effect*. [97], [98]

A Purcell factor, which is the ratio between the modified ( $\Gamma_{cav}$ ) and free-space ( $\Gamma_0$ ) spontaneous emission rates of a dipole in a closed cavity whose fundamental mode is resonant at the transition wavelength  $\lambda$  is given as

$$F_p = \frac{\Gamma_{cav}}{\Gamma_0} = \frac{3Q\lambda^3}{4\pi^2 V_0} \quad (1-19)$$

, where  $Q$  is the quality factor of the cavity mode, and  $V_0$  is its volume.[23], [98] Note that equation (1-19) assumes the dipole which is placed at the center (anti-node) of the cavity and hence the mode volume independent on the dipole position. In the case of open resonator, the identification of the mode volume becomes complicated problem, and thus numerical simulation is usually required.[99]

From equation (1-19), we notice that a cavity with high  $Q$  and small  $V_0$  gives large  $F_p$ . In Figure 1-19a, the quality factor and the effective cavity volume of optical cavities are compared. In spite of the relatively low quality factor, the mode volume of the plasmonic cavity is significantly small (e.g., on the order of  $10^{-6} V_\lambda$  can be obtained in gap mode [47]). Therefore, metal nanoantennas are, in general, advantageous to achieve high Purcell factors. In Figure 1-19b, the Purcell factor and the effective mode volumes are compared. It can be seen that the gap geometry results in the high Purcell factor.

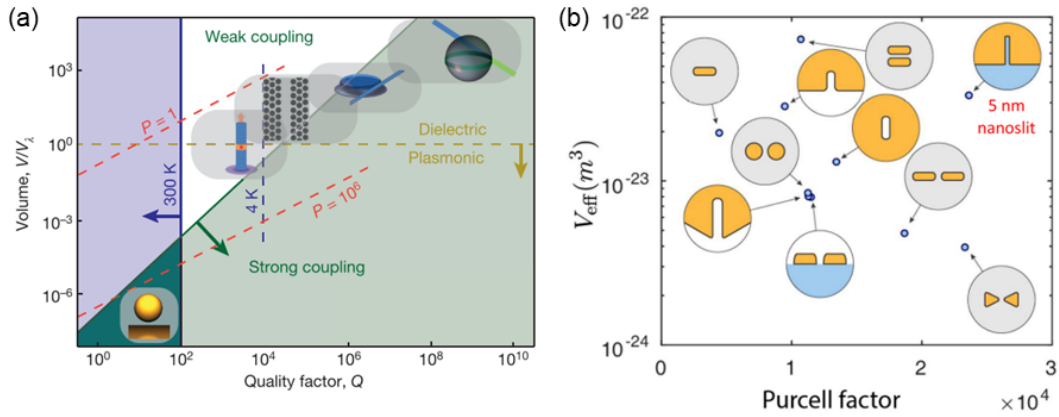


Figure 1-19 (a) Comparison of optical cavities (the quality factor versus effective cavity volume): from right, whispering gallery sphere, microdisk, photonic crystal, micropillors, and plasmonic nanoparticle on mirror cavities.[47] The effective cavity volume is scaled by  $V_\lambda = (\lambda/n)^3$  (b) Comparison of plasmonic cavities, the Purcell factor versus the effective mode volume).[100]

Although the Mie resonant cavity is not compared above, the Mie resonant mode tends to spread out the entire volume, limiting the light localization to the sizes on the order of  $\lambda/4$ . [86] The mode volume is thus larger than plasmonics; nonetheless, some smart approach still makes it possible to attain high Purcell factors, for example, by utilizing extraordinarily high-Q mode of the bound state in the continuum. [86], [101]–[103]

Here we formulate the quantum efficiency enhancement by a nanoantenna in the more convenient form. The quantum efficiency of a dipole emitter near a nanoantenna is expressed as

$$QE = \frac{\gamma_r \times W_r}{\gamma_{tot} \times W_r + W_{nr}} \quad (1-20)$$

where  $W_r$  and  $W_{nr}$  are intrinsic radiative and non-radiative decay rates of an emitter, respectively, and  $\gamma_{tot}$  and  $\gamma_{rad}$  are the enhancement factors of total and radiative decay rates by the nanoantenna, respectively. Thus, the enhancement of the quantum efficiency can be written as

$$\frac{QE}{QE_0} = \frac{\gamma_r \times (W_r + W_{nr})}{\gamma_{tot} \times W_r + W_{nr}} = \frac{\gamma_r \times (W_r/W_{nr} + 1)}{\gamma_{tot} \times W_r/W_{nr} + 1} \quad (1-21)$$

, where  $QE_0 = W_r/(W_r + W_{nr})$ .

#### 1.4.4. Directionality control

The collection efficiency is determined by the relationship between the solid angle of detection and the radiation pattern of emission. Because the detection solid angle is fixed to certain value in general experiment, the directionality of the emission determines the emission enhancement due to collection efficiency.

The major approach to achieve directional emission by an optical antenna is to utilize RF Yagi-Uda antenna design, which is consist of a one-dimensional array of antenna elements (Figure 1-20a).[19] In 2010, Curto *et. al.* demonstrated that radiation pattern of a quantum dot can be modified to unidirectional by the coupling with the metallic Yagi-Uda antenna (Figure 1-20b).[18] After the report, controlling directionality of light emission with plasmonic nanoantennas is extensively studied.[2], [4], [104]

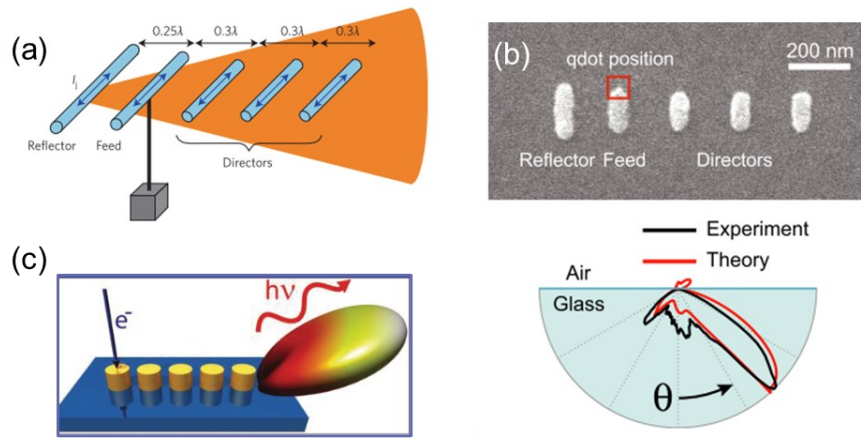


Figure 1-20 Examples of directional nanoantennas based on Yagi-Uda design.[18], [19], [104]

Go beyond metallic antennas based on RF antenna design, Rolley *et. al.* reported that a “single” dielectric nanosphere can work as a directional nanoantenna for an emitter placed near the surface in 2012.[105] This excellent approach suggests that the footprint of the directional antenna can be shrunk down to sub-wavelength scale. Another advantage is that the dielectric antenna is low loss. They mentioned that the directionality occurs due to the coherent excitation of electric and magnetic dipole Mie resonances. The theoretically explained that by assuming contributions from only the dipoles. It is important to note that the exact solution for the directionality including multipoles has not been reported so far. As shown in Figure 1-21, the directionality can be further improved utilizing an array of the dielectric sphere likewise the Yagi-

Uda antenna. In case of the Mie-type Yagi-Uda antenna, there is higher degree of freedom for engineering thanks to the magnetic resonances. The hybrid approach to utilize plasmonic element as a feeder and dielectric ones is also reported. [106]

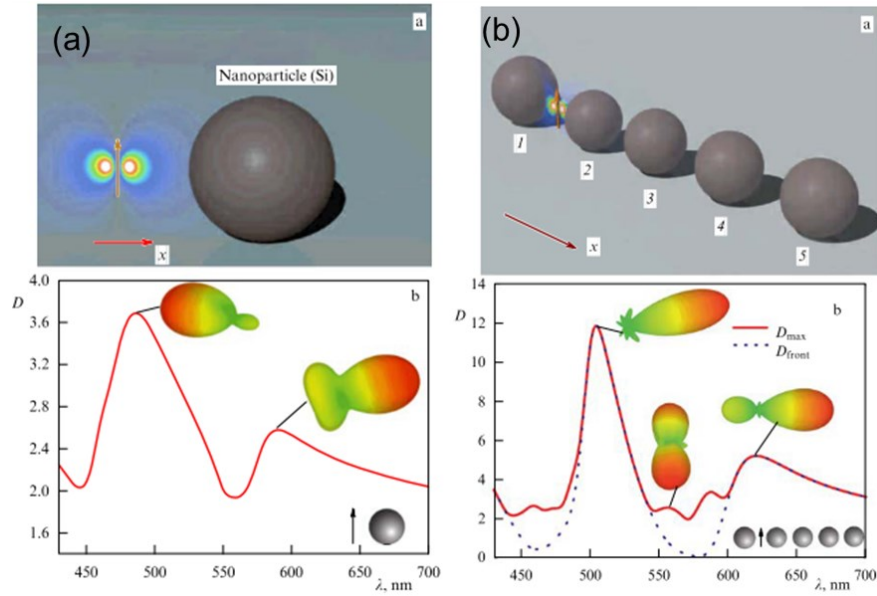


Figure 1-21 Directional emission by (a) a dielectric nanosphere and (b) array of the sphere.[107]

The experimental demonstration of directionality control with the dielectric nanoantenna was reported by Cihan *et al.* in 2018.[108] They positioned a silicon nanowire with 100-200 nm in diameter on a monolayer MoS<sub>2</sub> and demonstrated directionality enhancement more than 25-fold by comparing top-to-bottom ratios between with and without the nanowire.

Up to now, no experimental demonstration has been reported for the directional emission with a spherical Mie resonator. This is important because the nanosphere can be sub-wavelength in three-dimension, while nanowire requires infinitely long for light in one direction. Additionally, the directionality of the sphere has not been analyzed with the exact solution of Maxwell's equation such as Mie theory. We will deal with these issues in Chapter 7.

## 1.5. Chapter Overview

In this thesis, we develop several types of optical nanoantennas based on surface plasmon resonances and Mie resonances. General introduction was described above in Chapter 1.

As introduced in section 1.2.2, stand-alone plasmonic nanocomposites where metal nanoantennas and emitting materials are incorporated are promising platform to improve or alternate various conventional emitters. In Part I, consisting of Chapter 2 – Chapter 4, we develop metal nanoantenna structures for such nanocomposites, targeting for photon upconversion which convert near-infrared photons into visible ones. In order to overcome the inherent limitation of rare-earth doped upconversion nanomaterials, which is low conversion efficiencies due to small absorption cross sections and low quantum efficiencies of intra-4f transition, three metal nanostructures with tailored plasmonic properties are proposed. All metal nanostructures are developed based on a nanocap, which partially surrounds the upconversion nanoparticle, so as to be able to deal with the upconversion which exhibit large stokes shift between the excitation and emission wavelengths.

In Chapter 2, we develop a method to control a coverage of a metal nanocap to extend the tunable range of its resonance wavelength into near-infrared spectrum for enhancement of the excitation efficiency of upconversion. In Chapter 3, we introduce anisotropy to the nanocap by elongating the structure in one direction and show that a resonance of the nanocap can be split into two resonances. By controlling each of newly emerged resonances separately, it becomes possible to achieve simultaneous enhancement of emission and excitation processes. In Chapter 4, the metal nanocap is combined with additional metal nanoparticle to confine localized field within the gap layer where upconversion materials exists. In this system, additional degree of freedom to control the resonance arises due to the plasmon hybridization. For the above three approaches, we precisely examine the correlation between plasmonic properties and upconversion intensities and find the structure which enhance upconversion by a factor over 100.

In Part II, consisting of Chapter 5 – Chapter 8, we focus on dielectric nanoantennas empowered by the Mie resonances. Utilizing the multiple resonances, we propose several applications of the dielectric nanoantenna.

In Chapter 5, we first provide general information on recently developed colloidally synthesized silicon nanosphere, which is utilized in the following chapters. In Chapter 6, we develop a measurement setup which is capable of precise directionality measurement of single nanoantennas. In Chapter 7, we focus on unidirectional optical nanoantennas. As described in section 1.4.4, directional emission has not been realized with a dielectric sphere. We place a silicon nanosphere on an ideal emitter, a two-dimensional semiconductor, and show how the emission can be directed by a single Mie resonator. Theoretical analysis is also given and shows that the existence of magnetic dipole in addition to electric dipole resonance enables directionality control with a subwavelength single component. In Chapter 8, we propose one of the most unique application of the colloidally synthesized nanoantennas: optical metafluids. Thanks to the unnaturally occurring magnetic response at optical frequencies, we show that macroscopic optical parameters (*e.g.*, effective refractive index) can be controlled by treating the solution as an effective medium.

We summarize the results in this thesis in Chapter 9 and present future outlook.

## Part I

### Chapter 2

## Controlling Surface Plasmon Resonances of Metal Nanocaps for Upconversion enhancement

*Adapted from Tatsuki Hinamoto, et. al., JPCC, 121. 8077-8083 (2017)*

The metal nanocap, which is a metal shell partially covering a dielectric core, is promising plasmonic nanoantennas to enhance photoluminescence by combining luminescent nanomaterials as the core. The nanocap exhibit multiple surface plasmon resonances called electric and magnetic dipole modes. Both modes are highly tunable and accompany strongly enhanced electric field which spreads into the dielectric core, indicating the potential for photoluminescence enhancement of rare-earth ion doped upconversion nanoparticles. So far, the resonance wavelengths of the nanocap has been controlled primarily by the ratio of the shell thickness and core diameter, so-called core/shell ratio; however, it requires to enlarge the structural size to bring the lowest order resonance into near-infrared wavelengths (e.g., the excitation wavelength of the upconversion is 980 nm for  $\text{Er}^{3+}$ ).

In Chapter 2, we develop a method of nanocap coverage control to tune the resonance from visible to near-infrared spectra with negligible impact on the nanocomposite's entire dimension. In this method, the nanocap is formed by the two-step evaporation of metal over nanospheres from different angles. The method has been proposed theoretically, but experimental demonstration has not been reported.

We fabricate nanocomposite composed of an Er and Yb doped  $\text{Y}_2\text{O}_3$  ( $\text{Y}_2\text{O}_3:\text{Yb,Er}$ ) nanoparticle and a Au nanocap with the method and study the plasmonic properties by numerical simulations and optical measurements. We show that the magnetic dipole resonance can be shifted from around 700 nm to over 900 nm by changing the nanocap coverage. We also demonstrate that the controllability of the resonance enables to maximize the upconversion intensity of the nanoparticle inside. The largest enhancement factors of 64 and 101-folds for the green ( $\sim 560$  nm) and red ( $\sim 660$  nm) emissions, respectively, are achieved by comparing the upconversion intensity of the composite to that of the nanoparticle without the nanocap.

## 2.1. Introduction

Rare-earth doped upconversion materials, which convert near infrared photons into visible or ultraviolet photons, have a potential for applications as security ink[109], a 3D display[110], [111], a wavelength conversion layer of a solar cell[112], and a fluorescent probe for bio-imaging[113]–[115] and drug delivery[116]. However, the intensity of upconversion luminescence is often not high enough for practical applications due to the small excitation cross section and the low radiative transition rate of the parity forbidden intra-4f shell transitions of rare-earth ions. Substantial efforts, including the development of new host media and optimization of assisting dopants, have been devoted to improve the upconversion efficiency.[117], [118] Another promising approach for the improvement of upconversion efficiency is utilizing surface plasmon resonance of metal nanostructures.[71], [96], [113], [117], [119]–[124] A variety of composite nanoparticles (NPs) consisting of upconversion materials and metal nanostructures have been developed[71], [75], [115], [125]–[127] and the enhancement of the upconversion has

been demonstrated. The composite NPs reported so far are upconversion NPs with a Ag NP core (4-fold enhancement) [115], those decorated with Au NPs (4-fold enhancement) [125], Ag NPs (9 and 14.4 –fold enhancement) <sup>14</sup>, and Au nanorods (28-fold enhancement) [82], and those with a Ag nanocap (48-fold enhancement) [75].

The enhancement factor of upconversion by surface plasmon resonance is the multiplication of that of the incident electric field ( $L(\omega_{\text{exc}})$ ) and that of the quantum efficiency ( $Z(\omega_{\text{flu}})$ ),  $Y = |L(\omega_{\text{exc}})|^{2n} Z(\omega_{\text{flu}})$ , where  $n$  is the number of photons involved in the excitation of the luminescence and is usually from 1.5 to 3 depending on the upconversion processes.[128], [129] In order to achieve maximum upconversion enhancement in composite NPs, controlling the surface plasmon resonance wavelengths to  $\omega_{\text{exc}}$  and  $\omega_{\text{flu}}$  is crucial. Furthermore, spatial overlap between the hot spots of surface plasmon resonances and an upconversion material should be maximized to effectively utilize the enhanced electric fields.

As a metal nanostructure to achieve these criteria, we chose a metal nanocap (or semi-shell) for the formation of composite NPs. In a metal nanocap, in addition to an electric dipole (ED) mode equivalent to a metal full-shell, a magnetic dipole (MD) mode that emits light in the direction of the nanocap axis due to oscillating current loop exists. Both the electric and magnetic dipole modes have strongly enhanced electric fields near a nanocap rim at the resonance wavelengths and thus can contribute to upconversion enhancement if an upconversion material is around the rim. Another advantage of a metal nanocap is that the surface plasmon resonance wavelengths can be controlled in a wide range by the size, thickness and coverage.[130]–[139]

In a previous work, we prepared an upconversion composite NP with a metal nanocap and studied the optical properties for different nanocap thicknesses.[75] In this work, we develop

a method to control the surface plasmon resonance wavelengths of a metal nanocap to maximize the upconversion enhancement. Among several structural parameters determining the resonance wavelengths, the coverage is practically the most important one because the wavelengths can be controlled without strongly affecting the size of a NP. We extend the method developed by Yu *et al.*[140] for the formation of micro-meter scale nanocaps to sub-100 nm scale to make it usable for upconversion enhancement of NPs. In this work, we first study the optical response of a composite NP composed of an upconversion NP and a metal nanocap with different coverages by numerical simulation to determine the structural parameters for the composite NPs formation. We then synthesize a composite NP composed of an Yb and Er codoped  $\text{Y}_2\text{O}_3$  ( $\text{Y}_2\text{O}_3\text{:Yb,Er}$ ) NP and a Au nanocap and analyze the structure by transmission electron microscope (TEM). Finally, we study the scattering and upconversion properties of a large number of single composite NPs to understand the relation between the surface plasmon resonance wavelength and the upconversion enhancement factor.

## 2.2. Computational details

Numerical simulation of the optical properties of a  $\text{Y}_2\text{O}_3\text{:Yb,Er}$  NP with a Au nanocap is performed by the MNPBEM toolbox[141], which is based on the boundary element method. Calculation model is shown in Figure 2-1. The radius ( $r$ ) of a  $\text{Y}_2\text{O}_3$  NP, which is a core of a composite NP, is 47.5 nm. We distinguish the shape of a nanocap by the opening angle ( $\phi$ ). The nanocap outline is defined by a sphere with a radius  $R = r + t$ , where  $t$  is the thickness of metal at the top of a nanocap (30 nm). The center of the sphere is placed  $t/2$  above from the center of a  $\text{Y}_2\text{O}_3$  NP. The edge of the model structure is rounded with ellipse.[142] The refractive indices of

air (surrounding medium) and  $\text{Y}_2\text{O}_3$  are set to 1.00 and 1.91, respectively. The refractive index of Au is obtained from Johnson-Christy.[6] The scattering cross section is obtained by integrating the pointing vector at the far-field. The scattering spectra of a composite NP under the illumination by randomly oriented light are obtained by averaging the spectra for six different conditions of incident wave.

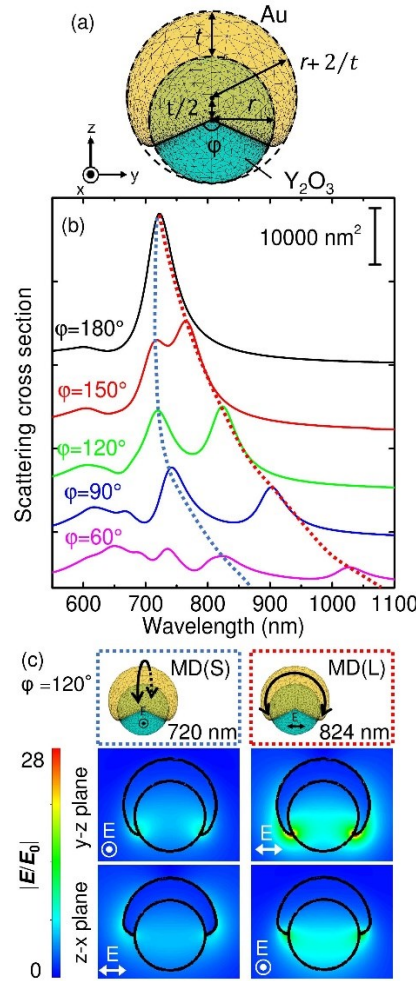


Figure 2-1. (a) A model structure of a  $\text{Y}_2\text{O}_3$ :Yb,Er NP with a Au nanocap. (b) Calculated scattering cross sections as a function of wavelength with different  $\phi$  for a  $\text{Y}_2\text{O}_3$ :Yb,Er NP with a Au nanocap. (c) Electric field distribution ( $|E/E_0|$ ) of short wavelength (MD(S): 720 nm) and long wavelength (MD(L): 824 nm) magnetic dipole modes in y-z and z-x cross sections.  $\phi = 120^\circ$ .

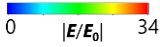
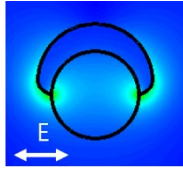
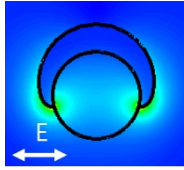
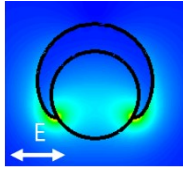
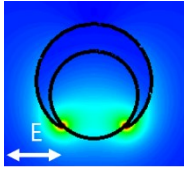
A nanocap made by a two-step angled vapor deposition method has two-fold rotational axis symmetry and due to the anisotropy, the degeneracy of the magnetic dipole mode is lifted. Figure 2-1b shows calculated scattering spectra of a  $\text{Y}_2\text{O}_3:\text{Yb,Er}$  NP with a Au nanocap for randomly polarized plane waves illuminated from all directions. When  $\varphi$  is  $180^\circ$ , a peak appears at 700 nm, which is assigned to a magnetic dipole mode. This peak is excited when the incident electric field is perpendicular to the nanocap axis. A weak peak at 600 nm is assigned to the electric dipole mode excited by the electric field parallel to the nanocap axis. Magnetic quadrupole modes are overlapped on the electric dipole mode and cannot be distinguished clearly.

For  $\varphi < 180^\circ$ , an asymmetry around the nanocap axis splits the magnetic dipole mode into a shorter wavelength magnetic dipole (MD(S)) mode and a longer wavelength magnetic dipole (MD(L)) mode. The scattering spectra for  $\varphi = 180, 150, 120, 90$ , and  $60^\circ$  are shown in Figure 2-1b. The longer wavelength mode shifts from 722 nm to 1030 nm, while the shorter wavelength one to 810 nm, when  $\varphi$  decreases from  $180^\circ$  to  $60^\circ$ . Figure 2-1b suggests that the resonance wavelength of a Au nanocap can be brought to the most efficient excitation wavelength of a  $\text{Y}_2\text{O}_3:\text{Yb,Er}$  (975 nm).

In Figure 2-1c, the z-x and y-z cross sections of the electric field distributions of the short and long wavelength magnetic dipole modes at the resonance wavelengths (720 nm and 824 nm, respectively) are shown for  $\varphi = 120^\circ$ . Apparently, the field enhancement is larger in the long wavelength mode. The largest field enhancement reaches 28.4-fold at the rim of a nanocap. The electric field distributions of the long wavelength mode at the resonance wavelengths for different opening angles are summarized in Table 2-1. The values of the maximum field enhancements at the resonance wavelengths and at 975 nm are also shown. The maximum field enhancement at

975 nm as well as that at the resonance wavelength increase with increasing the coverage. Therefore, we can expect higher upconversion enhancement for composite NPs with larger coverage.

*Table 2-1. Electric field distribution of long wavelength magnetic dipole mode (MD(L)) at the resonance wavelengths for different opening angles ( $\phi$ ). The maximum electric field enhancement factors ( $|E/E_0|_{\max}$ ) at the resonance wavelengths and at 975 nm are also shown.*

| $\phi$                                                                                                                          | 180°                                                                               | 150°                                                                               | 120°                                                                                | 90°                                                                                  |
|---------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
| $\lambda_{\text{resonance}}$                                                                                                    | 722 nm                                                                             | 768 nm                                                                             | 824 nm                                                                              | 904 nm                                                                               |
| Electric field distribution in y-z plane<br> |  |  |  |  |
| $ E/E_0 _{\max}$ at $\lambda_{\text{resonance}}$                                                                                | 21                                                                                 | 25                                                                                 | 28                                                                                  | 31                                                                                   |
| $ E/E_0 _{\max}$ at 975 nm                                                                                                      | 4.8                                                                                | 4.9                                                                                | 5.9                                                                                 | 11.8                                                                                 |

### 2.3. Experimental section

**Synthesis of upconversion NPs.**  $\text{Y}_2\text{O}_3:\text{Yb},\text{Er}$  NPs are synthesized by a homogeneous precipitation method.[143] 13.2 g of  $(\text{NH}_3)_2\text{CO}$ , 187 mg of  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , 2.3 mg of  $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , and 2.3 mg of  $\text{Yb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Wako Chemicals) are dissolved in 50 mL of distilled water. After stirring, the solution is heated to 100°C and kept for 1 h. The solution is filtered with a membrane filter, and the powder remains on the filter is annealed at 850°C for 2 h.

**Au nanocap formation.** We fabricate a Au nanocap on an  $\text{Y}_2\text{O}_3\text{:Yb,Er}$  NP by a two-step angular metal evaporation method[140] as schematically shown in Figure 2-2a.  $\text{Y}_2\text{O}_3\text{:Yb,Er}$  NPs are placed on a fused quartz substrate ( $10 \times 15 \text{ mm}^2$ ) by drop-coating the ethanol solution (4 mg/L) following a UV-ozone treatment for 30 minutes at  $100^\circ\text{C}$ . After depositing Ti adhesion layer (0.25 nm), Au (15 nm) is deposited on the substrate with the angle  $\theta$  from the normal to the substrate, followed by a second deposition with the angle  $-\theta$  (15 nm). In an ideal case, the opening angle becomes  $\phi_{\text{ideal}} = 180^\circ - 2\theta$ , although the shape of a fabricated NP deviates from the ideal ones due to migration of evaporated Au on a NP, non-parallel Au beam from a point-like source, etc. With this method, one can control the opening angle in a wide range very easily. However, the shape of a nanocap is distributed as will be shown later. In this work, we measure the optical properties of large number of individual composite NPs and analyze the data by taking into account the distributions. After the nanocap formation, the composite NPs are transferred to polydimethylsiloxane (PDMS, SYLGARD-184, Dow Corning) resin.[130]

**Structural and optical characterization.** The structure of composite NPs is evaluated by transmission electron microscope (TEM), high angle annular dark-field scanning TEM (HAADF-STEM), and STEM energy-dispersive spectroscopy (STEM-EDS) by using JEM-2100F (JEOL) operating at 200 kV. For the TEM observations, composite NPs are dispersed in ethanol by ultrasonication and the solution is dropped on a carbon-coated copper grid.

Scattering spectra of a single composite NP are measured by inverted microscope as shown in Figure 2-2b. White light from a halogen lamp is focused onto the sample through a dark-field objective ( $\text{NA} = 0.9$ ,  $\times 100$ ), and the scattered light is collected through the same objective. Scattered light in the region of  $2 \text{ }\mu\text{m}$  in diameter is selected by a pin-hole, focused onto the

entrance slit of a spectrometer (iHR320, HORIBA Jobin Yvon) and detected by a liquid N<sub>2</sub> cooled charge coupled device (CCD) and InGaAs diode array for visible and near infrared (NIR) wavelength range, respectively. For the scattering spectrum measurement, second order diffraction is removed by using a 750 nm long-pass filter. Upconversion spectra are obtained by the same setup by using a 975 nm semiconductor laser for excitation. The excitation power was 12.9 kW/cm<sup>2</sup> at the sample point.

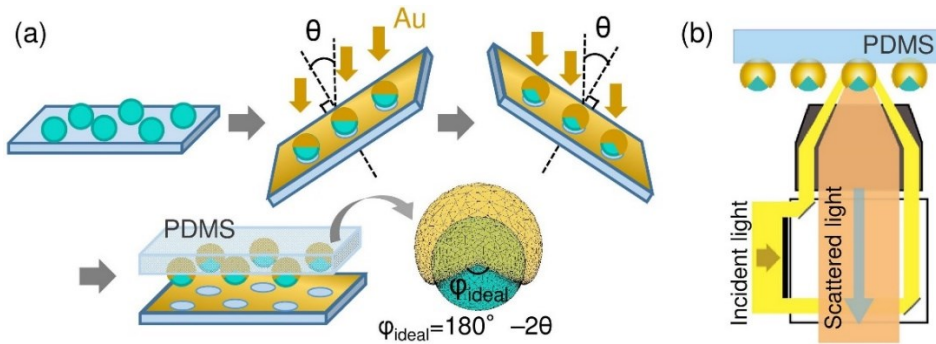


Figure 2-2. (a) Fabrication procedure of a Y<sub>2</sub>O<sub>3</sub>:Yb,Er NP with a Au nanocap. Au is deposited twice with the deposition angle of  $\theta$  and  $-\theta$ . In an ideal case, the opening angle ( $\phi_{ideal}$ ) becomes  $\phi_{ideal} = 180^\circ - 2\theta$ . (b) Scattering measurement geometry of single composite NPs. A composite NP is illuminated from the opposite side of a nanocap.

## 2.4. Results and discussion

**Structural analyses of composite NPs.** Figure 2-3a shows TEM images of Y<sub>2</sub>O<sub>3</sub>:Yb,Er NPs. The average diameter obtained from the TEM image is 95 nm with the standard deviation of 16.9 nm. Figure 2-3b shows typical scattering and upconversion spectra excited at 975 nm of a single Y<sub>2</sub>O<sub>3</sub>:Yb,Er NP placed on a fused quartz substrate. The scattering intensity increases monotonously to shorter wavelength due to the Mie scattering.[27] The NP exhibits green (560

nm) and red (660 nm) upconversion due to the transitions from the  $4S_{3/2}$  and  $4F_{9/2}$  states, respectively, to the  $4I_{15/2}$  ground state of  $Er^{3+}$  ions.

Figure 2-3c shows TEM images of composite NPs prepared with  $\theta = 0, 15, 30$ , and  $37.5^\circ$ . The dark region is a Au nanocap and the light one is a  $Y_2O_3:Yb,Er$  NP. Although the shape of Au nanocaps is different from NP to NP, we can see that the coverage of a nanocap is controlled by  $\theta$ ; the opening angle decreases with increasing  $\theta$  as expected. However, the opening angle deviates from the  $\phi_{ideal} = 180^\circ - 2\theta$  relation above  $\theta = 30^\circ$ , and the difference of the opening angle between  $\theta = 30^\circ$  and  $37.5^\circ$  is small. In the case of a  $Y_2O_3:Yb,Er$  NP 95 nm in diameter,  $\theta = 37.5^\circ$  is almost the largest deposition angle for the formation of a nanocap. Above this angle, a Au film on a NP and that on a substrate partially adhere, which makes transfer of composite NPs to PDMS resin very difficult and decreases the yield. Further increase of  $\theta$  is possible in a larger NP. For example,  $\theta = 45^\circ$  is possible for a  $Y_2O_3:Yb,Er$  NP 139 nm in diameter. As will be shown later, with larger  $\theta$  in larger NPs, the surface plasmon resonance wavelengths can be controlled in a wider range. However, in this work, we focus on sub-100 nm NPs to demonstrate that the present process is applicable to small NPs and show the data of larger NPs only for the demonstration of the resonance wavelength tunability.

Figure 2-3d shows a high-angle annular dark-field (HAADF) scanning TEM image of a composite NP fabricated with  $\theta = 37.5^\circ$ . The formation of a nanocap can clearly be seen. The HAADF image allows us to estimate the thickness of a Au nanocap at the top and it is in this case 43 nm. In Figure 2-3e, the energy-dispersive X-ray spectroscopy (EDS) mapping of the same composite NP is shown. The image also confirms the formation of a composite NP with a Au nanocap.

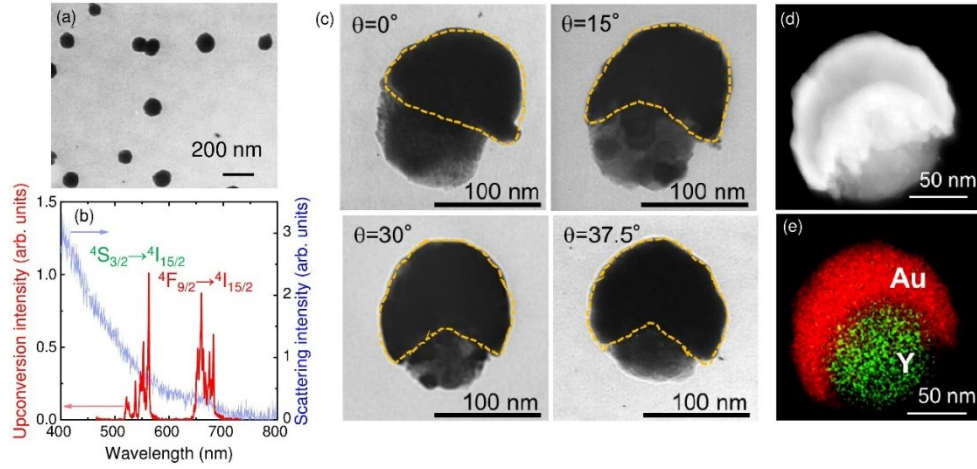


Figure 2-3. (a) TEM image of  $\text{Y}_2\text{O}_3:\text{Yb,Er}$  NPs. (b) Scattering (blue) and upconversion spectra of  $\text{Y}_2\text{O}_3:\text{Yb,Er}$  NPs excited at 975 nm (red). (c) TEM images of a  $\text{Y}_2\text{O}_3:\text{Yb,Er}$  NP with a Au nanocap prepared with different deposition angle  $\theta$ . (d) HAADF STEM image and (e) EDS mapping image of a  $\text{Y}_2\text{O}_3:\text{Yb,Er}$  NP with a Au nanocap ( $\theta = 37.5^\circ$ ).

**Scattering and upconversion properties of single composite NPs.** Figure 2-4a shows normalized scattering spectra of single composite NPs with the  $\theta$  from  $0^\circ$  to  $45^\circ$ . Since there are distributions in the spectral shape and peak wavelength as will be shown later, we pick up a typical spectrum for each  $\theta$  to discuss the evolution of the spectral shape with  $\theta$ . The average diameter of  $\text{Y}_2\text{O}_3:\text{Yb,Er}$  NPs is 95 nm for the composite NPs with the  $\theta$  from  $0^\circ$  to  $37.5^\circ$  and it is 139 nm for  $\theta = 45^\circ$ . In  $\theta = 0^\circ$ , the scattering spectrum consists of two peaks. The spectral shape is similar to that obtained by the numerical simulation in Figure 2-1b. The long wavelength peak can thus be assigned to the magnetic dipole mode, while the weak short wavelength one to the electric dipole mode. The electric dipole mode is very weak and hardly observed when  $\theta > 0^\circ$ . The magnetic dipole mode shifts to longer wavelength with increasing  $\theta$ , being consistent with the numerical simulation. On the other hand, splitting of the mode predicted by the simulation is not observed.

This may be due to smaller splitting of the mode arising from smaller structural anisotropy in fabricated nanocaps than that of the model structure

In Figure 2-4b, the wavelengths of the scattering peaks are plotted for 60 single composite NPs with different  $\theta$ . The data of NPs with different  $\theta$  are plotted by different colors. In composite NPs with  $\theta = 0^\circ$ , if both the electric and magnetic dipole modes are observed, the wavelengths of both modes are plotted by circles. If only one scattering peak is observed, the wavelength is plotted by squares. Although the data are largely scattered, we can see that the scattering peak shifts to longer wavelength with increasing  $\theta$  for  $\theta \leq 30^\circ$  and then saturates. This is consistent with the TEM observations that the opening angle  $\varphi$  reaches minimum at  $\theta = 30^\circ$ . In Figure 2-4c, the scattering peak wavelength is shown by the box chart[144] as a function of  $\theta$ . In composite NPs with  $\theta = 0^\circ$ , the wavelength of the magnetic dipole mode is considered. In the graph, resonance wavelength obtained from the numerical simulation in Figure 2-1b is also shown by converting the opening angle  $\varphi$  in the simulation to  $\theta$  by assuming  $\theta = (180^\circ - \varphi) / 2$ . We can see overall agreement between experiments and calculations.

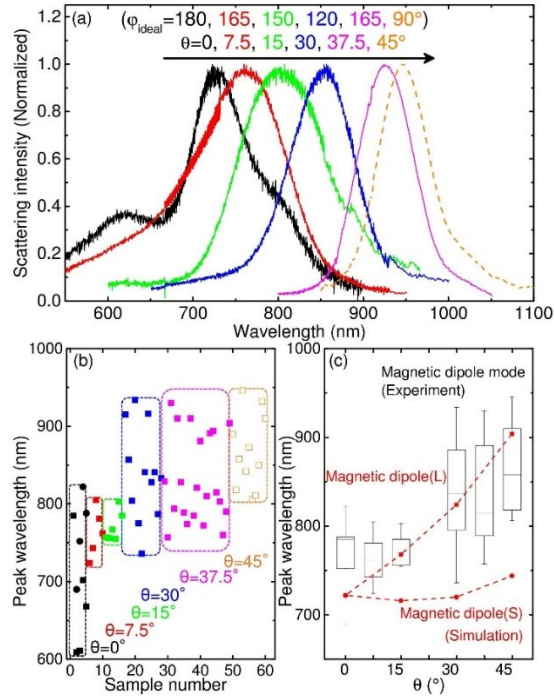


Figure 2-4. (a) Scattering spectra of single composite NPs.  $\theta$  is changed from 0 to 45°. Average diameter of NPs is 95 nm for  $0 \leq \theta \leq 37.5^\circ$  (solid curve) and 139 nm for  $\theta = 45^\circ$  (broken curve). (b) Peak wavelengths of 60 single composite NPs. The data of composite NPs with different  $\theta$  is plotted by different colors. Composite NPs with one (square) and two (circle) peaks are distinguished by the shape of the symbols. (c) Box chart of the resonance wavelength as a function of  $\theta$ . Resonance wavelength obtained from numerical simulation is also shown under the assumption that  $\theta = (180^\circ - \varphi) / 2$ .

We measure upconversion spectra of single composite NPs by the same setup as that for the scattering measurements. The excitation wavelength is 975 nm. Figure 2-5a shows upconversion spectra of single  $\text{Y}_2\text{O}_3:\text{Yb,Er}$  NPs without (black) and with (red) a Au nanocap ( $\theta = 30^\circ$ ). The spectral shape is not strongly affected by the nanocap formation, except for the intensity ratio of the red to green luminescence. Figure 2-5b and c shows the peak intensities of the green and red luminescence, respectively, for 49 single composite NPs prepared with different  $\theta$ . The intensities of  $\text{Y}_2\text{O}_3:\text{Yb,Er}$  NPs without a Au nanocap are shown by a gray horizontal band. In almost all composite NPs, the intensity increases by the formation of a nanocap. Furthermore,

although the data are largely scattered, we can see the  $\theta$  dependence of the intensity. The intensity is the largest when  $\theta = 30^\circ$  and  $37.5^\circ$ ; it is at maximum 63 and 101-fold enhanced for green and red emissions respectively, compared to the average intensity of single  $\text{Y}_2\text{O}_3\text{:Yb,Er}$  NPs without a Au nanocap. Figure 2-5d shows the intensity ratio of the red to green emission. Without a Au nanocap, the ratio is  $0.93 \pm 0.098$  (gray horizontal band). The ratio increases by the formation of a nanocap. What is interesting in Figure 2-5d is that the ratio distributed in much wider range in composite NPs than in NPs without a Au nanocap. For example, when  $\theta = 15^\circ$ , it is distributed from 1.7 to 4.7. The very large distribution of the ratio indicates that a small variation of a nanocap structure strongly affects the emission process of  $\text{Er}^{3+}$ .

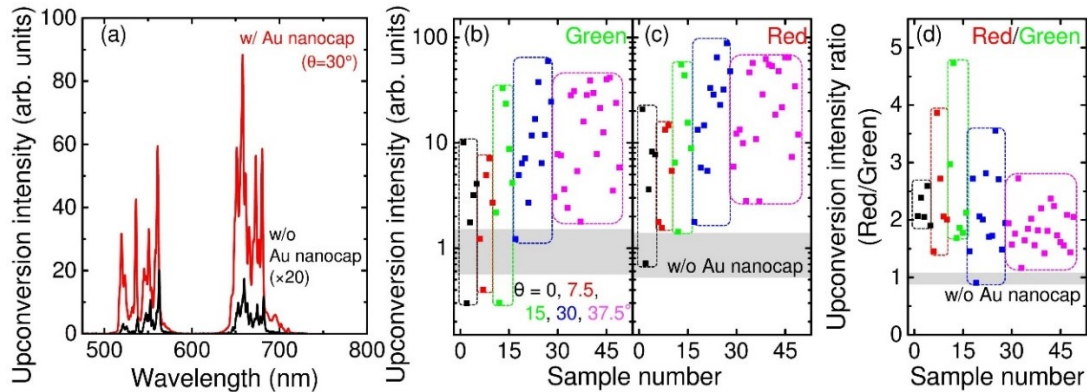


Figure 2-5. (a) Upconversion spectra of single  $\text{Y}_2\text{O}_3\text{:Yb,Er}$  NPs without (black) and with (red) a Au nanocap ( $\theta = 30^\circ$ ). The former spectrum is multiplied by 20. (b) Green and (c) red upconversion intensities and (d) the intensity ratio of the red to green emissions of 49 single composite NPs. The data of composite NPs with different  $\theta$  is plotted by different colors. The gray bands in (b), (c) and (d) are the data obtained for single  $\text{Y}_2\text{O}_3\text{:Yb,Er}$  NPs without a Au nanocap. The width of the gray bands represents the maximum and minimum of the distributions of the data.

In order to investigate the relation between the upconversion enhancement and the surface plasmon resonance wavelength of a Au nanocap, we plot the intensities of green and red emissions as a function of the peak wavelengths of the scattering spectra in Figure 2-6a and b, respectively.

Note that the ordinate is the logarithmic scale. In composite NPs with  $\theta = 0^\circ$ , the wavelength of the magnetic dipole mode is considered. In Figure 2-6a and b, we can see that the upconversion intensity depends on the resonance wavelength. It increases with increasing the wavelength and saturates around 800 nm except for a few exceptions that have very small enhancement factors despite very long resonance wavelengths. Figure 6c shows the intensity ratio of the red to green emission as a function of the resonance wavelength. The ratio is distributed in a wide range when the resonance is in a shorter wavelength range. The distribution is reduced with increasing the resonance wavelength and the value approaches to that of  $\text{Y}_2\text{O}_3:\text{Yb,Er}$  NPs without a Au nanocap.

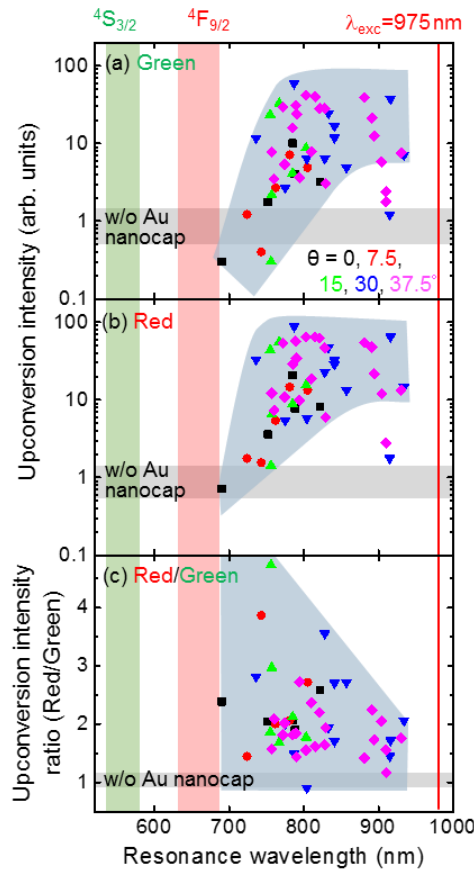


Figure 2-6. Upconversion intensities of (a) green and (b) red emissions and (c) the ratio of red to green emissions of single  $\text{Y}_2\text{O}_3:\text{Yb,Er}$  NPs with a Au nanocap as a function of the resonance

wavelength (scattering peak wavelength). Composite NPs prepared with different  $\theta$  are shown with different colors and symbols. The gray horizontal bands are the data obtained for single  $Y_2O_3:Yb,Er$  NPs without a Au nanocap. The width of the gray bands represents the maximum and minimum of the distributions of the data. The excitation wavelength of upconversion (975 nm) is shown by a red vertical line. The green and red upconversion bands are shown by green and red vertical bands, respectively.

In general, fluorescence enhancement by plasmonic nanostructures occurs via two processes.[96] If the resonance wavelength is close to the excitation wavelength ( $\omega_{exc}$ ), the effective excitation cross section is enhanced, while, if the resonance is close to the emission wavelength ( $\omega_{flu}$ ), the radiative decay rate is enhanced. In Figure 2-6a and b, the upconversion intensities increase significantly as the resonance wavelength leaves the emission wavelengths and approaches the excitation wavelength. This indicates that excitation cross-section enhancement plays a major role in the upconversion enhancement of the present composite NPs.

In the present system, the excitation process involves energy transfer from  $Yb^{3+}$  to  $Er^{3+}$ . Lu et al.[145] studied the effect of surface plasmon resonances on the absorption and energy transfer processes of  $NaYF_4:Er,Yb$  NPs and found that both the absorption and energy transfer processes are influenced in a weak excitation regime, while the energy transfer process is not strongly affected in a strong excitation regime. Our excitation power range is above the strong excitation regime of their work. Therefore, in this work, we expect that the energy transfer is not strongly affected by the surface plasmon resonances and that the enhancement of the absorption process is the main cause of the excitation cross-section enhancement.

In the numerical simulation in Table 1, the enhancement factor of the electric field at 975 nm increases monotonously till the resonance wavelength reaches 904 nm. This is in contradiction with the data in Figure 2-6, where the upconversion enhancement saturates around 800 nm. One

of the possible reasons for the enhancement saturation is the saturation of the emission states as well as the intermediate states due to the strong incident field enhancement. In a weak excitation condition, where an intermediate excited state is not saturated, the number of photons involved in the excitation process ( $n$ ) is 1.5-2.0 in green and red upconversion of  $\text{Er}^{3+}$ . In the excitation range exceeding the saturation threshold of an intermediate state,  $n$  approaches one. Further increase in the excitation power results in the saturation of the emission states and the upconversion intensity. In general,  $n$  is obtained from the slope of the excitation power dependence of the upconversion intensity. Unfortunately, it was not possible to measure the excitation power dependence of a single composite NP in a wide range and to obtain reliable value of  $n$ . Therefore, we estimated the value of  $n$  for an ensemble of  $\text{Y}_2\text{O}_3:\text{Yb},\text{Er}$  NPs without a Au nanocap. The obtained values are 1.06 and 0.88 for green and red emissions, respectively, at the present excitation condition ( $12.9 \text{ kW/cm}^2$ ). These values indicate that the intermediate states are saturated even in NPs without a Au nanocap. Therefore, in composite NPs with a Au nanocap, it is possible that the incident field is enhanced to the regime of the saturation of the emission states when the resonance wavelength is around 800 nm. In this strong excitation regime, further increase of the incident field by bringing the resonance wavelength near the excitation wavelength is not very beneficial for the upconversion enhancement. On the other hand, at reduced excitation power, continuous increase of the upconversion intensity until the resonance wavelength reaches 975 nm is expected. However, due to small upconversion intensities of single composite NPs, it was not possible to obtain systematic data in a low excitation power range.

Although the contribution of radiative decay rate enhancement is considered to be relatively small in the present composite NPs, the effects appear as strong enhancement of the

red/green intensity ratio and its large variation. The observed large variation of the ratio suggests that emission process is strongly affected by small variation of a Au nanocap structure, and resultant small change of the field distribution. In Figure 2-6c, as the resonance wavelength moves from the emission wavelength to the excitation wavelength, the variation of the red/green intensity ratio is reduced. This can be explained by the decreased contribution of the emission rate enhancement to the observed upconversion enhancement. In general, the effect of the emission rate enhancement appears as a shortening of the luminescence lifetime[96]. However, upconversion from a single composite NP is too weak to measure the decay dynamics.

## 2.5. Conclusion

Upconversion composite NPs composed of a  $\text{Y}_2\text{O}_3\text{:Yb,Er}$  NP and a Au nanocap with different coverages were developed and the structural and optical properties were studied. The formation of a composite NP and the successful control of the coverage were confirmed by TEM observations. The surface plasmon resonance wavelength obtained from scattering spectra of single composite NPs reveal that it can be controlled from around 700 nm to over 900 nm. A clear correlation was observed between the upconversion intensity and the surface plasmon resonance wavelength. The upconversion intensity increases significantly as the resonance wavelength increases from around 700 nm to 800 nm, and above 800 nm, it almost saturates. The largest upconversion enhancement factors for green and red emissions reach 64 and 101, respectively. Therefore, the opening-angle-controlled metal nanocap is a very promising material for an

upconversion enhancement. The next step will be the development of a process to produce the structure with more controllable manner.

## Chapter 3

# Introduction of Anisotropy to Metal Nanocaps and Its Application for Upconversion Enhancement

*Adapted from Tatsuki Hinamoto, et. al., JPCC, 123. 25809-25815 (2019)*

A stand-alone plasmonic nanocomposite into which a metal nanostructure and an emitting material are integrated is a promising building block for optoelectronics and biophotonics devices. One of the fundamental challenges for such nanocomposites is limited controllability of the surface plasmon resonance due to low degree of freedom in structure design. In the case of metal nanocap, the structural parameters to control the plasmonic properties are the constituent material, core/shell ratio and coverage as shown in Chapter 3.

In Chapter 3, we introduce anisotropy to the metal nanocap by elongating the structure. The elongated nanocap has more flexibility to engineer plasmonic properties than conventional one because additional structural parameter (*i.e.*, aspect ratio) arises. We show that the elongation of the nanocap results in splitting of the magnetic dipole resonance, and the resonance wavelengths can be controlled in a wide wavelength range by the aspect ratio. As an application of the elongated nanocap, we demonstrate strong enhancement of the near-infrared to visible upconversion of an  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  doped  $\beta\text{-NaYF}_4$  nanorod by tuning the resonance wavelength of an elongated Au nanocap placed on it to the excitation wavelength.

### 3.1. Introduction

Plasmonic nanostructures control electromagnetic field at the nanoscale and engineer the radiation property, *i.e.*, the radiation pattern, the quantum efficiency, and the excitation rate, of a coupled emitter such as a molecule, an ion and a quantum dot.[8], [11], [18], [39], [146]–[149] Among various kinds of plasmonic nanostructures, a stand-alone plasmonic nanocomposite, into which a metal nanostructure and an emitting material are integrated, has been attracting attention in different fields because it can be a functional building block in optoelectronics and biophotonics devices. A large variety of metal nanostructures have been employed for the formation of stand-alone plasmonic nanocomposites. They are nanoparticles[61]–[64], nanorods[65]–[69], nanoshells[70], [71], nanomatryoshkas[72], core-shell nanorods[73], [74], nanocaps[75]–[77], core-cap couples[150], nanoparticle dimers[36], [78], metal-insulator-metal sandwiches[79], nanoparticle clusters[80], [81], and nanorod clusters[82].

Prerequisite properties of metal nanostructures used in plasmonic nanocomposites are the existence of multiple resonances for the enhancement of both the excitation and emission processes of a coupled emitter, wide tunability of the resonance wavelengths, accessibility of an emitter to the hot spots, capability of the radiation pattern control, etc. A metal nanocap is one of the metal nanostructures having these properties. It possesses the magnetic dipole mode arising from circulating current along the cap surface in addition to the electric dipole mode; the resonance wavelengths can be controlled by the structural parameters.[130], [134], [135], [151], [152] Furthermore, it has a unique focusing property for the radiation of a coupled emitter.[76], [77], [150] The resonance wavelength of the magnetic dipole mode depends on the length of the current path. Therefore, introduction of anisotropy in the nanocap structure results in the splitting

of the magnetic dipole mode, which further increases the flexibility of the radiation control property.

In this thesis, we propose a metal nanocap being elongated to the direction perpendicular to the nanocap axis (elongated nanocap) as a novel platform for a plasmonic nanocomposite. First, through full-wave numerical simulation, we examine the spectral response of the elongated nanocap with various aspect ratios. We show that elongation of a nanocap to one direction lifts the degeneracy of the magnetic dipole mode and that the resonance wavelengths can be controlled in a wide wavelength range by the aspect ratio. We then develop a process for the fabrication of a nanocomposite composed of an  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  doped hexagonal-phase  $\text{NaYF}_4$  ( $\beta\text{-NaYF}_4$ ) nanorod and an elongated nanocap made of Au. We demonstrate by single particle scattering measurements in combination with transmission electron microscope (TEM) observations that the surface plasmon resonance wavelengths can be controlled in a wide wavelength range as predicted by numerical simulations. Finally, we demonstrate strong enhancement of the near-infrared to visible upconversion of an  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  doped  $\beta\text{-NaYF}_4$  nanorod by tuning the resonance wavelength of a Au nanocap placed on it to the excitation wavelength.

### 3.2. Computational analysis

We performed the computational analysis of an elongated nanocap using a boundary element method (BEM).[141], [153] The structure composed of an elongated Au nanocap and a  $\beta\text{-NaYF}_4$  nanorod was modeled with a freely available modeling software Gmsh[154]. Figure 3-1a and b shows the simulation model of a  $\beta\text{-NaYF}_4$  nanorod with an elongated nanocap. A  $\beta\text{-$

$\text{NaYF}_4$  nanorod has a hexagonal cross-section; the dimension of the nanorod is defined by the length (long axis:  $L$ ) and the diameter of the incircle (short axis:  $S$ ). A nanocap covers the upper half of the nanorod. The outer surface of the nanocap is inscribed to an ellipse: the half-lengths of the major and minor axes are  $T + S/2 - S'/8$  and  $T/4 + S'/2$ , respectively, where  $T$  and  $S'$  are the thickness of the nanocap and the diameter of the circumcircle of the nanorod's hexagonal cross section, respectively. The edge of the nanocap is rounded. The dielectric function of Au is taken from a literature[6], while a constant value of  $1.475^2$  is used for  $\beta\text{-NaYF}_4$ . All simulations were performed in vacuum.

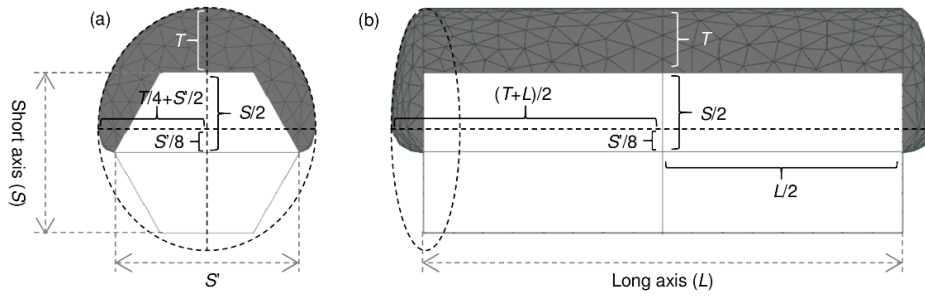


Figure 3-1. Simulation model of an elongated nanocap formed on a  $\beta\text{-NaYF}_4$  dielectric nanorod. (a) front and (b) side view of the structure. The structure is defined by structural parameters: the length of the long axis ( $L$ ) of the nanorod, the diameters of the incircle ( $S$ ) and circumcircle ( $S'$ ) of the hexagonal cross section of the nanorod, and the thickness of the nanocap ( $T$ ).

Figure 3-2a and b show the extinction spectra of elongated nanocaps with the aspect ratios ( $S/L$ ) of 1 and 4, respectively, and Figure 3-2c shows the color plot of extinction spectra as a function of wavelength and long axis length (*i.e.*, aspect ratio). The short axis length and the nanocap thickness are set to 50 nm and 20 nm, respectively, while the long axis length is changed from 50 nm to 200 nm. The spectra are obtained by averaging the spectra of 6 different

illumination geometries, that is, the direction of propagation and polarization ( $\mathbf{k}$ ,  $\mathbf{E}$ ) are ( $k_z$ ,  $E_y$ ) (1-1), ( $k_z$ ,  $E_x$ ) (1-2), ( $k_y$ ,  $E_z$ ) (2-1), ( $k_y$ ,  $E_x$ ) (2-2), ( $k_x$ ,  $E_y$ ) (3-1), and ( $k_x$ ,  $E_z$ ) (3-2). When the aspect ratio is 1 (Figure 3-2a), the extinction spectrum is dominated by almost one resonance, which can be assigned to a magnetic dipole (MD) mode (transverse mode) arising from a current loop in the nanocap.[76], [130], [134], [135], [150]–[152] The small splitting of the peak arises from the small anisotropy of the nanocap model even when the aspect ratio is 1 (see the illustration in the inset). A small peak at 554 nm is an electric dipole (ED) mode (axial mode). When the aspect ratio is 4, the splitting of the MD mode becomes large, and the long wavelength peak reaches around 1020 nm (Figure 3-2b). Figure 3-2c shows the color plot of extinction spectra as a function of wavelength and long axis length. The short axis length is fixed. We can see the increase of the splitting of the MD mode with increasing the aspect ratio. Hereafter, we denote the MD modes at short and long wavelengths as MD (S) and MD (L), respectively, because they arise from current loops along the long and short axes, respectively. The wavelength of the MD (S) mode is almost independent of the aspect ratio, while that of the MD (L) mode depends strongly on the ratio.

To gain more insight into the LSPR modes in elongated nanocaps, we show the extinction spectra in different excitation geometries in Figure 3-2d-i. The geometries are shown in the inset of each figure. The MD (L) mode is excited when the electric field of the excitation light is polarized along the long axis (Figure 3-2d and h), while the MD (S) mode is excited when the polarization is along to the short axis (1-2 and 2-2 geometries in Figure 3-2e and g). In 2-1 and 3-2 geometries (Figure 3-2f and i), the polarization is perpendicular to both the long and short axes. In these geometries, the ED mode (axial mode) is excited around 550 nm.[76], [130], [134], [135],

[150]–[152] The ED mode is almost independent of the aspect ratio and is much weaker than the MD modes. Therefore, the contribution of the ED mode is very limited in Figure 3-2a and b.

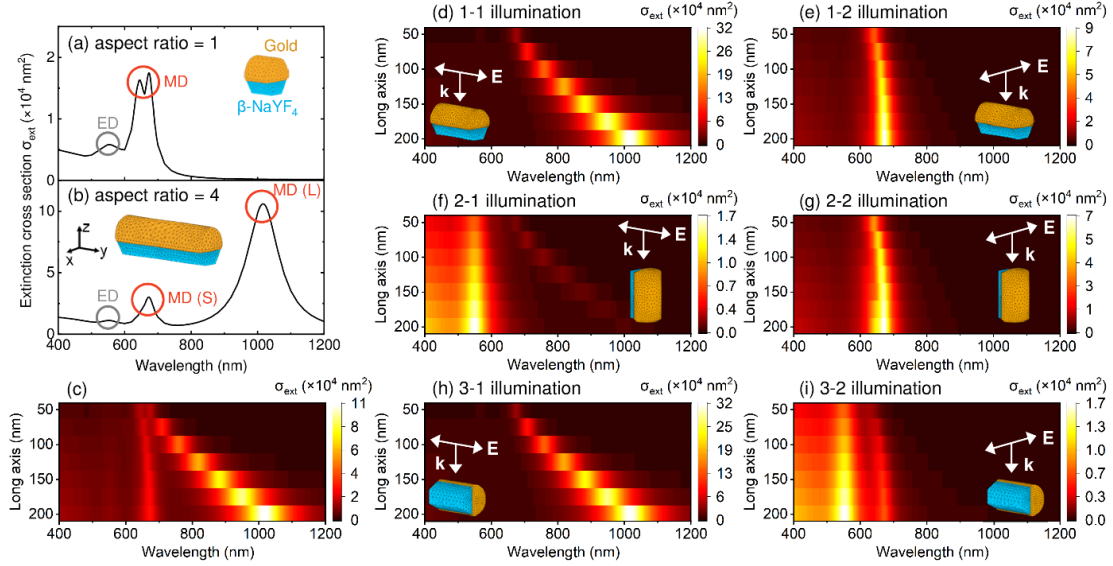


Figure 3-2. Simulated extinction spectra of elongated nanocap in free space. The short axis length is 50 nm and the nanocap thickness is 20 nm. The long axis length is changed from 50 nm to 200 nm. (a–b) Extinction spectra of nanocaps with the aspect ratios of 1 (long axis = 50 nm) (a) and 4 (long axis = 200 nm) (b). (c) Color plot of extinction spectra as a function of wavelength and long axis length (i.e., aspect ratio). In (a–c), the spectra are obtained by averaging the spectra of 6 different illumination geometries shown in the insets of (d–i). (d–i) Color plots of extinction spectra as a function of wavelength and long axis length (i.e., aspect ratio) for different illumination geometries; (d) 1-1, (e) 1-2, (f) 2-1, (g) 2-2, (h) 3-1, and (i) 3-2. Insets are schematic drawings of the illumination geometries.

Based on the information obtained from Figure 3-2, we deduce optimized structure to maximize upconversion of an  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  doped  $\beta\text{-NaYF}_4$  nanorod. In the system,  $\text{Er}^{3+}$  absorbs 980 nm photons with a help of  $\text{Yb}^{3+}$  ions and emits green (560 nm) and red (660 nm) photons via multi-step excitation processes. Therefore, large upconversion enhancement is expected if LSPR resonances of a nanocap are brought to these wavelengths. Figure 3-3a shows the extinction spectrum of a structure satisfying the condition; the lengths of short and long axes of a  $\beta\text{-NaYF}_4$

nanorod are 46 nm and 186 nm (aspect ratio  $\approx 4$ ), respectively, and the thickness of a Au nanocap is 20 nm. The MD (L) mode is tuned to the excitation wavelength and the MD (S) mode is tuned to the red emission.

In order to quantitatively evaluate the upconversion enhancement, we first calculate the electric field distribution ( $|E/E_0|$ ). Figure 3-3b and c show electric field distributions at 660 nm and 980 nm in the planes shown in the inset. In both cases, the electric fields are strongly enhanced in the whole volume of the  $\beta$ -NaYF<sub>4</sub> nanorod. The enhancement factors at the center of the nanorods are 7.8 and 5.8 for MD (S) and MD (L) modes, respectively.

We then calculate the antenna efficiency ( $\eta_a$ ), which is defined by the ratio of the enhancement factor of the radiative decay rate ( $\gamma_{radiative}$ ) to that of the total decay rate ( $\gamma_{total}$ ).[1], [149], [155] Figure 3-3d shows the antenna efficiency spectrum obtained by averaging the calculated antenna efficiencies for point dipoles along x, y and z directions placed at the center of the nanorod. Similar to the extinction spectra, the antenna efficiency spectrum is dominated by two peaks, corresponding to the MD (S) and MD (L) modes. The antenna efficiency is around 30% at the red emission wavelength. This value is much larger than the quantum efficiency of Er<sup>3+</sup> and Yb<sup>3+</sup> doped  $\beta$ -NaYF<sub>4</sub> generally reported (typically  $\sim 1\%$ )[156], [157]. Therefore, we can expect roughly 10-fold enhancement of the quantum efficiency by the Purcell effect.

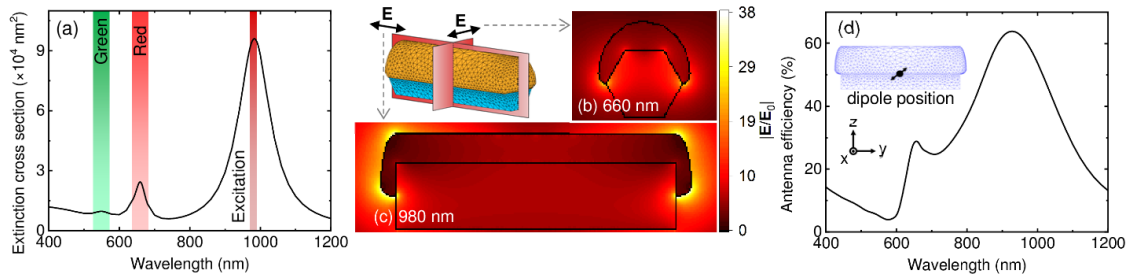


Figure 3-3. (a) Calculated extinction spectrum (averaged spectra of 6 different illumination geometries in Figure 3-2), (b,c) electric field distributions at 660 nm (b) and 980 nm (c), and (d) antenna efficiency of an  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  doped  $\beta\text{-NaYF}_4$  nanorod with a Au nanocap. The short axis length, the long axis length, and the nanocap thickness are 46 nm, 186 nm, and 20 nm, respectively. The structure is optimized to bring the MD (L) mode to the excitation wavelength (980 nm) and the MD (S) mode to the red emission wavelength (660 nm). The antenna efficiency is obtained by averaging the calculated antenna efficiencies for point dipoles along x, y and z directions placed at the center of the nanorod.

### 3.3. Experimental method

Figure 3-4 shows the fabrication procedure of an  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  doped  $\beta\text{-NaYF}_4$  ( $\beta\text{-NaYF}_4\text{:Er/Yb}$ ) nanorod with an elongated Au nanocap. First,  $\beta\text{-NaYF}_4\text{:Er/Yb}$  nanorods with the aspect ratio of 1 to 4 were synthesized by a hydrothermal method.[110], [158] Synthesized nanorods were placed on a glass slide by drop-casting the diluted suspension. Following the deposition of a titanium (Ti) adhesion layer (1 nm in thickness), Au (20 or 30 nm in thickness) was deposited on top of the nanorods by thermal evaporation with the deposition rate of 0.1 nm/s. The nanorods were isolated from the glass slide by ultrasonication in ethanol, and the solution was concentrated by centrifugation. Finally, the solution was dropped on a carbon-coated TEM mesh for TEM observations (JEM-2100F (JEOL), JED-2300T (JEOL) and H-7000 (Hitachi)). In TEM images, together with single nanorods with the structure similar to the model structure in Figure 3-1 and 2, dimers, trimers, agglomerates, nanorods with an Au nanocap on the side surface, *etc.* were observed. We recorded the positions of single isolated nanorods with the structure similar to the model structure in a TEM mesh for the optical measurements. With this procedure, one-to-one correspondence of a TEM image and optical spectra becomes possible.

The TEM mesh was then transferred to a custom-built inverted optical microscope (Nikon) for the optical spectroscopy. For the measurement of scattering spectrum, a sample was epi-illuminated by a halogen lamp through a bright and dark field objective (100 $\times$ /0.9 NA, LU Plan Fluor, Nikon) in dark-field geometry. In a scattering image, an individual nanorod, the position of which was recorded in advance by TEM observations, was selected by a pin-hole (200  $\mu$ m in diameter) placed at the confocal plane of the microscope, and the image was sent to the entrance slit of a monochromator (iHR320, Horiba Jobin Yvon) equipped with a liquid-nitrogen-cooled charge coupled device (CCD) and an InGaAs diode array (Symphony, Horiba Jobin Yvon). The 200  $\mu$ m pin-hole corresponds to 2  $\mu$ m in the image plane. Following the measurement of the scattering spectrum, the upconversion spectrum of the same nanorod was measured by the same setup. For the upconversion measurement, the sample was epi-illuminated coaxially through the same objective by 975 nm light (1.1 kW/cm<sup>2</sup>) from a semiconductor laser.

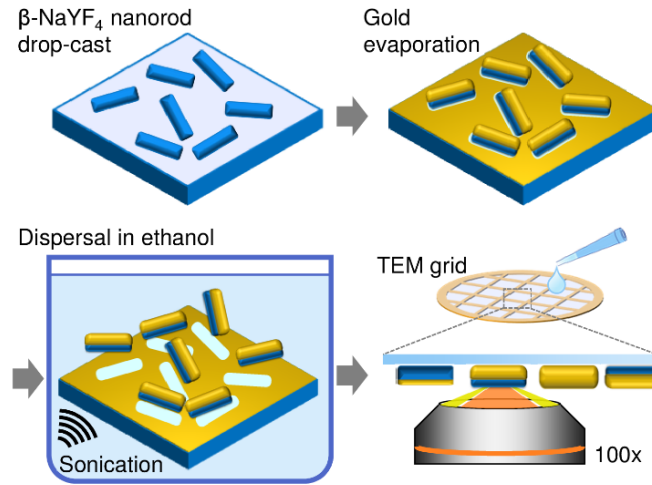


Figure 3-4. Schematic illustration of the fabrication procedure of the  $\beta$ -NaYF<sub>4</sub> nanorod with Au nanocap.

### 3.4. Experimental results and discussion

Figure 3-5a-d show TEM images of synthesized  $\beta$ -NaYF<sub>4</sub>:Er/Yb nanorods with different aspect ratios; the typical dimensions estimated from TEM images are 100 × 150 nm (aspect ratio 1.5), 100 × 200 nm (aspect ratio 2), 75 × 230 nm (aspect ratio 3), and 50 × 200 nm (aspect ratio 4), respectively. Figure 3-5e-h are the TEM image, the HAADF-STEM image, the EDS mapping image (Au and F), and the schematic illustration, respectively, of a  $\beta$ -NaYF<sub>4</sub>:Er/Yb nanorod (105 × 177 nm) on which a Au nanocap (30 nm in thickness) is formed. The dark region in the TEM image is a Au nanocap and the bright region is a  $\beta$ -NaYF<sub>4</sub> nanorod. From the HAADF image, we can see that the nanocap covers the upper part of the nanorod. The surface of the Au nanocap is very smooth. TEM images of other samples with different aspect ratios are shown in Figure 3-5i and k together with the schematic illustrations (Figure 3-5j and l, respectively).

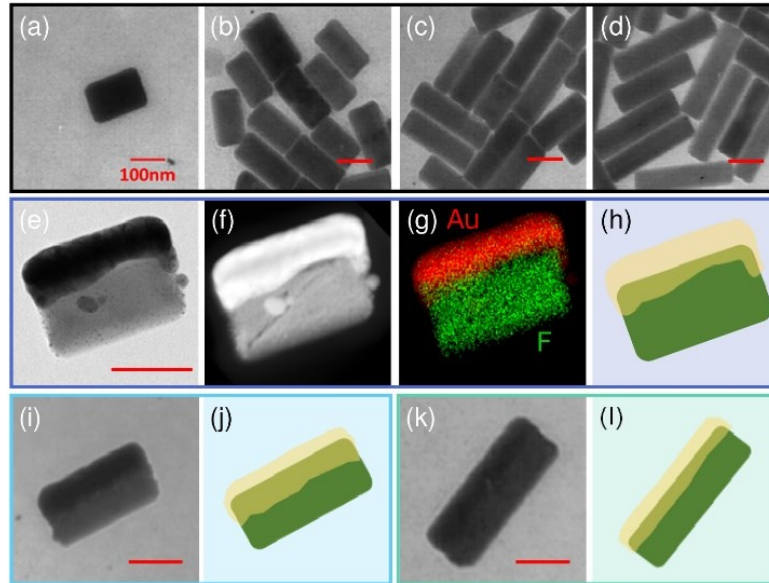


Figure 3-5. (a-d) TEM images of  $\beta$ -NaYF<sub>4</sub>:Er/Yb nanorods with different aspect ratios. The dimensions estimated from TEM images are 100 × 150 nm (aspect ratio 1.5) (a), 100 × 200 nm (aspect ratio 2) (b), 75 × 230 nm (aspect ratio 3) (c) and 50 × 200 nm (aspect ratio 4) (d). (e-g) TEM image (e), HAADF-STEM image (f), EDS mapping image (Au and F) (g), and schematic illustration (h) of a  $\beta$ -NaYF<sub>4</sub>:Er/Yb nanorod (105 × 177 nm) with a Au nanocap (30 nm in thickness). (i, j) TEM image and schematic illustration of a  $\beta$ -NaYF<sub>4</sub>:Er/Yb nanorod (100 × 220 nm)

*with a Au nanocap (20 nm in thickness). (k, l) TEM image and schematic illustration of a  $\beta$ -NaYF<sub>4</sub>:Er/Yb nanorod (95 × 300 nm) with a Au nanocap (20 nm in thickness).*

Figure 3-6a shows the scattering spectrum of the nanorod in Figure 3-5k (aspect ratio ~3). It has two peaks at 697 nm and 979 nm. The spectral feature is very similar to the calculated extinction cross section spectra in Figure 3-1 and 2, although the intensity ratio is different. As mentioned above, for the scattering measurements, a high numerical aperture objective is used. In this setup, all resonance modes including ED, MD (S) and MD (L) can be excited regardless of the orientation of nanorods. However, the intensity ratio depends on the nanorod orientation and it is not controlled in this work. Therefore, we do not discuss the spectral shape and focus only on the peak wavelengths. In some nanorods, we observed only one peak. This is either due to the overlap of two peaks because of the small separation or due to very small intensity of one of the peaks. In the former case, the peak can be separated by a polarization-resolved scattering measurement.

We measured the scattering spectra for many isolated nanorods. The peak wavelengths obtained from the spectra are plotted in Figure 3-6b-d. In these graphs, the abscissa is the wavelength, and the ordinate is the length of the long axis. The length of the short axis is 100, 75 and 50 nm for Figure 3-6b, c and d, respectively. The nanocap thickness is 30 nm in Figure 3-6b, and is 20 nm in Figure 3-6c and d. If we observe two peaks clearly in a spectrum, the short wavelength one is plotted with a blue triangle, while the long wavelength one is plotted with a black triangle. If only one peak is observed, it is plotted with a green square symbol. In the figures, scattering cross sections obtained by simulations are also shown by color gradients. We can see relatively good agreement between the wavelengths of scattering peaks and scattering cross

sections. The agreement indicates that the observed scattering peaks are MD (S) and MD (L) modes of Au nanocaps. The small difference between experiments and calculations may arise from structural imperfection of synthesized nanorods such as the variation of nanocap shape.

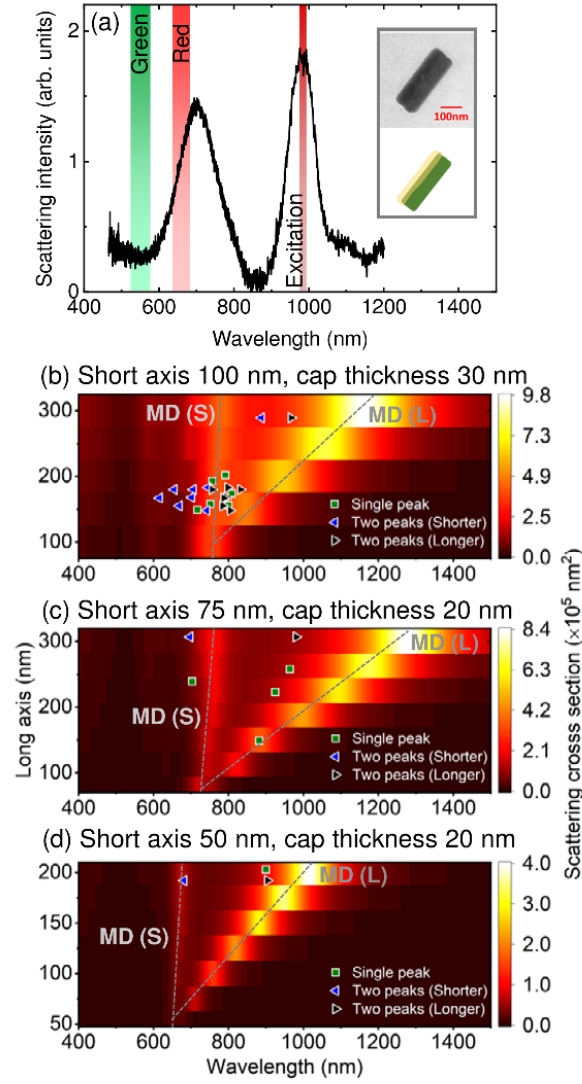


Figure 3-6. (a) Scattering spectrum of a  $\beta$ -NaYF<sub>4</sub>:Er/Yb nanorod (95 × 300 nm) with an Au nanocap (20 nm in thickness). Insets are the TEM image and the illustration. (b-d) Color maps of calculated scattering cross section as a function of wavelength (abscissa) and long axis length (ordinate). The short axis length is (b) 100 nm, (c) 75 nm and (d) 50 nm. The Au nanocap thickness is (b) 30 nm and (c, d) 20 nm. On the graphs, peaks in measured scattering spectra are shown by

symbols. In the case of spectra with two peaks, the short wavelength one is plotted with a blue triangle, while the long wavelength one is plotted with a black triangle. In the case of spectra with one peak, it is plotted with a green square symbol.

Figure 3-7a shows an upconversion spectrum of the nanorod in Figure 3-5k (aspect ratio  $\sim 3$ ) (red). An upconversion spectrum of a  $\beta$ -NaYF<sub>4</sub> nanorod without a Au nanocap is also shown as a reference (black). The nanorod without a Au nanocap is prepared by exactly the same procedure as that with a Au nanocap, *i.e.*, a Au nanocap is accidentally removed from it during the ultrasonication process. Therefore, both nanorods experienced the same thermal history. This is very important to compare the upconversion intensity and extract the effect of an Au nanocap because upconversion efficiency of a  $\beta$ -NaYF<sub>4</sub>:Er/Yb nanorod is very sensitive to the thermal history. The green ( $\sim 550$  nm) and red ( $\sim 660$  nm) emission bands correspond to the  $^4S_{3/2}$  and  $^4F_{9/2}$ , respectively, to  $^4I_{15/2}$  transition in the  $4f$  state of Er<sup>3+</sup> ions. We can see strong enhancement of the upconversion intensity by the formation of the nanocap.

In Figure 3-7b, the intensities of the green and red emissions of  $\beta$ -NaYF<sub>4</sub>:Er/Yb nanorods with Au nanocaps divided by those of a  $\beta$ -NaYF<sub>4</sub>:Er/Yb nanorod without a Au nanocap (the sample in the inset of Figure 3-7a) are plotted as a function of the wavelength of the scattering peak. In the case of a nanorod with multiple scattering peaks, the longest wavelength one is adopted. Note that, within the present work, it is not possible to quantitatively estimate the enhancement factor because the reference  $\beta$ -NaYF<sub>4</sub>:Er/Yb nanorod without an Au nanocap is chosen randomly. Therefore, the ordinate of Figure 3-7b is arbitrary units. We can see clear correlation between the resonance wavelength and the enhancement factor; it increases rapidly as the resonance wavelength approaches the excitation wavelength of upconversion (980 nm). The clear correlation indicates that the observed upconversion enhancement is predominantly due to

the coupling with the plasmonic modes of elongated Au nanocaps, although a small fraction of the observed trend (at most factor of 6) is due to nanorod length (volume) increase from left to right in Figure 3-7b.

In general, Au nanocap affects the excitation process, energy transfer process, relaxation process and emission process of upconversion of a  $\beta$ -NaYF<sub>4</sub>:Er/Yb nanorod.[20], [145], [159] The strong increase of the upconversion intensity as the resonance wavelength approaches the excitation wavelength indicates that the enhancements of the excitation field and/or the energy transfer rate are the dominant factor for the upconversion enhancement. Although it is not easy to experimentally distinguish these mechanisms, given the relatively weak excitation intensity (1.1 kW/cm<sup>2</sup>), the former would be dominant. Concerning the emission process, we estimated by numerical simulations that the antenna efficiency of a nanocap is ~30%, which is larger than the quantum yield of Er<sup>3+</sup> and Yb<sup>3+</sup> doped  $\beta$ -NaYF<sub>4</sub> generally reported (~1%).[156], [157] Therefore, the Purcell enhancement may also contribute to the upconversion enhancement. Further studies especially the decay rate measurements of single nanorods are necessary for the quantitative discussion of the Purcell enhancement.[145]

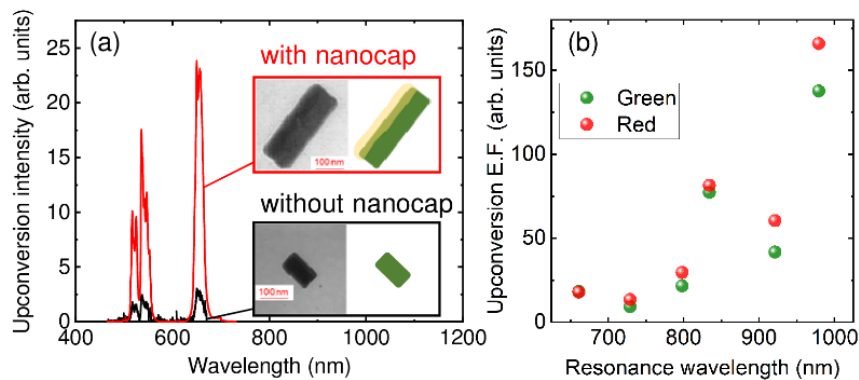


Figure 3-7. (a) Upconversion spectrum of a  $\beta$ -NaYF<sub>4</sub>:Er/Yb nanorod (95 × 300 nm) with a Au nanocap (20 nm in thickness) (red). An upconversion spectrum of a  $\beta$ -NaYF<sub>4</sub> nanorod without a Au

*nanocap is shown as a reference (black). Insets are the TEM images and the illustrations. (b) Green and red upconversion enhancement factor as a function of the resonance wavelength of the nanocap. In the case of a nanorod with multiple scattering peaks, the longest wavelength one is adopted.*

### 3.5. Conclusion

We proposed an elongated metal nanocap as a component of a stand-alone plasmonic nanocomposite. We first showed by numerical simulation that two MD modes exist in an elongated metal nanocap and the resonance wavelengths can be controlled in a wide range. We then fabricated  $\beta$ -NaYF<sub>4</sub>:Er/Yb nanorods with Au nanocaps and performed the comprehensive structural characterizations. The scattering spectra of individual nanocomposites revealed that the designed structure can be successfully produced and the resonance wavelength can be controlled in a wide range. Finally, we studied upconversion of  $\beta$ -NaYF<sub>4</sub>:Er/Yb nanorods with Au nanocaps and found that tuning the resonance wavelength of the Au nanocap to the excitation wavelength results in the significant enhancement. To the best of our knowledge, this is the first report for the fabrication of an elongated metal nanocap and the study of the plasmonic property. Because of the high degree of freedom to tune the resonance wavelengths, this structure can be used for the enhancement of a variety of optical phenomena such as Raman scattering, second/third harmonic generations, etc.

## Chapter 4

# Engineering Resonances of Metal-Core/Dielectric-Shell/Metal-Cap Composites by Plasmon Hybridization

*Adapted from Tatsuki Hinamoto, et. al., JPCC, 122, 174650-17472 (2018)*

When a plasmonic nanostructure is combined with another one, the elementary surface plasmon resonances split into two new resonances at different frequencies due to the interaction between the resonators. Such plasmonic response can be described by “plasmon hybridization picture” in analogy with molecular orbital theory. Because the splitting energy can be sensitively tuned via coupling strength of the system, the distance between resonators for example, the plasmon hybridization is an effective route to design novel plasmonic nanostructures with tailored plasmonic properties.

In Chapter 4, we design a novel plasmonic nanocomposites consisting of metal core, dielectric shell, and metal nanocap based on the plasmon hybridization picture. In this system, the hybridization of the localized surface plasmon modes of the core and the cap results in the emergence of novel bonding and antibonding modes. The latter mode has wide tunability in the resonance wavelength and strong field confinement at the position of the dielectric shell. These features indicate that the proposed nanocomposite is an excellent candidate for upconversion nanocomposites. We thus develop the nanocomposites with  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  doped upconversion shell as the dielectric shell and demonstrate upconversion enhancement in the structure. The comparison of the upconversion intensity between the metal-core/dielectric-shell structure and

the metal-core/dielectric-shell/metal-cap structure revealed that the cap formation increases the intensity several fold.

#### 4.1. Introduction

Photon upconversion, which converts low-energy photons into a high-energy photon, has applications in a variety of fields including fluorescent probes for bio-imaging[114], wavelength conversion layers in solar cells[112], [160], full-color 3D displays[161] and security inks[109].[113], [122], [162], [163] Among several upconversion systems, those utilizing long-lived intermediate states of rare-earth ions have superior properties such as high chemical stability and sharp emission bands.[162], [164] However, the upconversion fluorescence intensity is usually not high enough for practical applications due to the small excitation cross section of parity forbidden intra-4f transitions of rare-earth ions and due to the low quantum efficiency (<1%[165]).[123], [166]

One of the promising approaches to overcome these problems is engineering an electromagnetic environment around an upconversion material utilizing a localized surface plasmon resonance (LSPR) of a metal nanostructure [96], [119], [121], [123], [166]–[169]. Many groups have successfully enhanced upconversion of rare-earth doped nanomaterials by formation of nanocomposites composed of metal nanostructures and upconversion nanomaterials; for example, a metal core with an upconversion shell[62], [115], a metal nanorod decorated with upconversion nanoparticles[67], an upconversion nanoparticle with a metal nanoshell[71] or metal nanocap[75]–[77], [120], an upconversion nanoparticle decorated with metal

nanoparticles[126] or nanorods[82], etc. The highest enhancement factor reaches 101-fold for an upconversion nanoparticle with a metal nanocap[76].

In general, the upconversion enhancement factor is expressed as

$$Y = |L(\omega_{\text{exc}})|^{2n} Z(\omega_{\text{em}})$$

, where  $L(\omega_{\text{exc}})$  is an enhancement factor of an incident electric field at the excitation wavelength,  $Z(\omega_{\text{em}})$  is that of a quantum efficiency at the emission wavelength, and  $n$  is the number of photons involved in the excitation, which is typically from 1.5 to 2.0 in upconversion. [128] Therefore, a metal nanostructure should have a largely enhanced electric field at the excitation wavelength and high antenna efficiency at the emission wavelength. Simultaneously satisfying these conditions is not straightforward in simple metal nanostructures such as a metal nanoparticle and a metal nanorod, and thus development of a structure with higher freedom of design capable of controlling the resonance wavelengths and the electric field distributions is necessary to maximize the upconversion enhancement.

In this thesis, we propose a composite nanoparticle composed of a metal core, an upconversion shell and a metal cap as a candidate of an upconversion nanocomposite that has large freedom of design capable of tuning the LSPR wavelengths. Given the theoretical research of similar structures like perforated gold/silica/gold multilayer nanoshells[170] and gold core/gold semishell[171], the metal core/upconversion shell/metal nanocap (CSCap) nanocomposite is expected to possess highly tunable and multiple resonances due to the plasmonic hybridization of a metal core and a cap[83]. The structure may also confine an incident electric field in an upconversion shell between the metal core and the metal cap. In this thesis, we first perform comprehensive numerical simulation of a CSCap nanocomposite to reveal the

optical responses, i.e., the scattering spectra, the electric field distributions, the antenna efficiencies, and the radiation patterns. We then fabricate CSCap nanocomposites composed of an Au nanoparticle core, an  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  co-doped yttrium silicate shell, and an Ag cap by a process, which combines liquid phase syntheses and vapor deposition. We analyze the structure in detail by scanning transmission electron microscopy. We show that the scattering spectra of single CSCap nanocomposites agree well with those of the numerical simulation. We also show that the upconversion intensity of CSCap nanocomposites is several fold larger than that of metal-core/dielectric-shell (CS) nanocomposites even in a non-optimized structure.

## 4.2. Numerical simulation

The optical responses of a CSCap structure are calculated using the MNPBEM toolbox, which is based on the boundary element method (BEM).[141] Figure 4-1a shows a model structure consisting of an Au core, an yttrium silicate shell (as an upconversion layer) and an Ag cap. The boundary elements were refined so that they become finer near the rim of the cap by a modeling software (Gmsh[154]). Empirical dielectric functions were employed for Au and Ag,[6] and the refractive indices of air (surrounding medium) and yttrium silicate were set to 1.0 and 1.8[172], respectively.

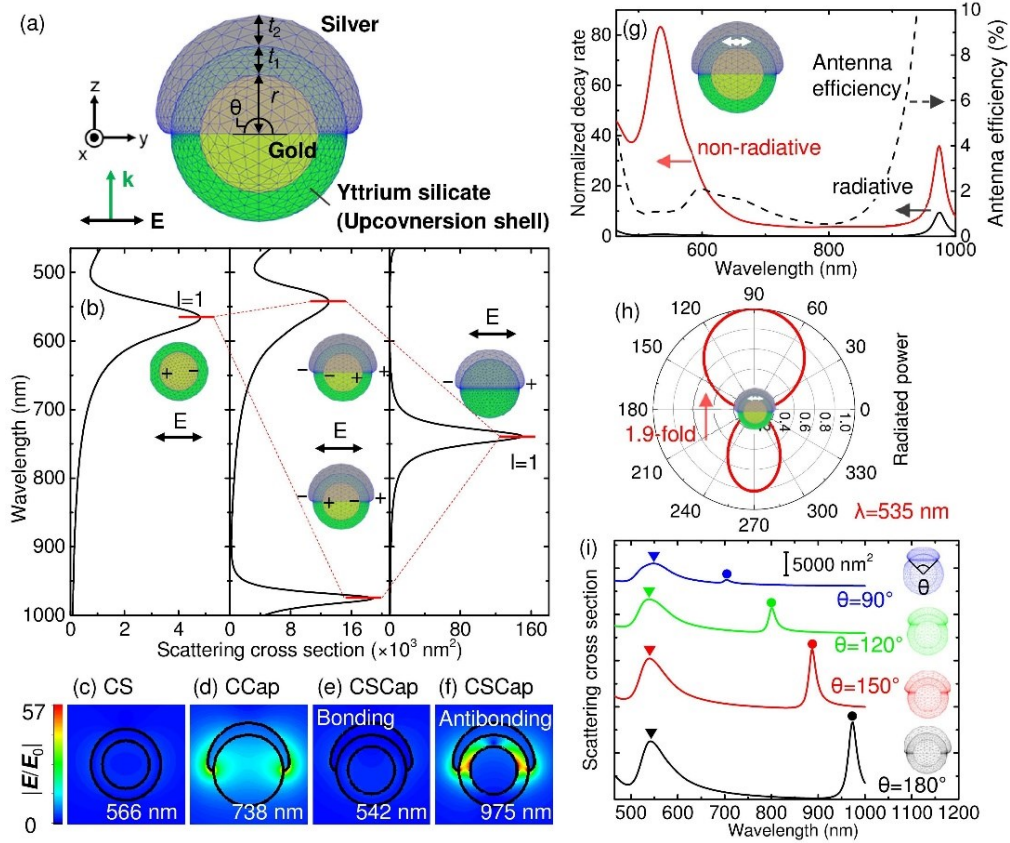


Figure 4-1. (a) Model structure for BEM simulation of a CSCap structure. (b) Scattering spectra of an Au core/yttrium silicate shell (CS) structure (left), an Au core/yttrium silicate shell/Ag cap (CSCap) structure (middle), and a yttrium silicate core/Ag cap (CCap) structure (right). The charge distributions of the resonance modes are schematically shown. (c-f) Electric field distributions at resonance wavelengths; CS at 566 nm (c), CCap at 738 nm (d), and CSCap at 542 nm (e) and 975 nm (f). (g) Normalized radiative (black) and non-radiative (red) decay rates (solid lines) and an antenna efficiency (dashed line) of a CSCap structure as a function of wavelength. (h) Polar plot of the far-field radiated power of a CSCap structure. The dipole is placed at the center of the upconversion layer along the x-axis as shown in the inset of (g). (i) Scattering spectra of CSCap structures with different cap coverages.

Figure 4-1b (middle) shows a calculated scattering spectrum of a CSCap structure illuminated by a plane wave polarized along the y-axis and propagating in the z-direction. The core radius ( $r$ ) and the thicknesses of the shell ( $t_1$ ) and the nanocap ( $t_2$ ) are set to 32, 15.5 and 16.4 nm, respectively. The coverage ( $\theta$  in Figure 4-1a) of the nanocap is set to  $180^\circ$ . As references,

scattering spectra of an Au core/yttrium silicate shell (CS) structure (left) and an yttrium silicate core/Ag cap (CCap) structure (right) are shown. The CS structure exhibits the LSPR of an Au nanosphere at 566 nm, while the CCap exhibits the LSPR at 738 nm. The latter mode is assigned to the magnetic (transverse) dipole mode driven by the current loop in the nanocap.[130], [131], [134], [135], [152] The LSPR resonance of CSCap can be explained by the hybridization of the two LSPRs [83]. The hybridization results in the splitting of the LSPRs into bonding (542 nm) and antibonding (975 nm) modes (Figure 4-1b (middle)). The wavelength of the bonding mode is close to that of the LSPR of the CS structure, while that of the antibonding mode shifts to a very long wavelength.

In Figure 4-1c-f, the electric field distributions of the three structures in Figure 4-1b at the LSPR wavelengths designated in the figures are shown. For the CS structure (Figure 4-1c), the electric field enhancement is small (at most 4.4-fold). On the other hand, it reaches 54-fold for the CCap structure (Figure 4-1d). However, the field enhancement of the CCap structure is predominantly outside of the dielectric nanoparticle and thus the contribution of the enhanced field to the upconversion enhancement of the dielectric nanoparticle is limited. In contrast to this, the field enhancement of the antibonding mode in the CSCap structure is predominantly in the region of the upconversion shell (Figure 4-1f), and the maximum enhancement factor reaches 57-fold. To quantitatively compare the electric field enhancement factor of these structures, we average the enhancement factor of the electric field ( $|E/E_0|_{ave}$ ) over the dielectric materials in the y-z plane. The average enhancement factor is 2.1, 12.5, 1.9, and 18.4 for the CS, CCap, CSCap (bonding mode), and CSCap (antibonding mode) structures, respectively.

Figure 4-1g shows the radiative and non-radiative decay rates normalized to a radiative decay rate in free-space for a point dipole oriented along the x-axis at the center of the upconversion shell. The inset shows the point where the dipole is placed. In the spectrum of the non-radiative decay rate, two peaks corresponding to the bonding and antibonding modes appear at 534 and 975 nm, respectively. In Figure 4-1g, the antenna efficiency, which is defined by the ratio of the enhancement factor of a radiative rate to that of the total decay rate, is also shown. The antenna efficiency at the upconversion emission wavelengths of  $\text{Er}^{3+}$  (~550 and 660 nm) is around 1-2%. Although this value is small, given a small quantum efficiency of upconversion nanoparticles around 100 nm in diameter (~0.1%[157]), the CSCap can improve the quantum efficiency of the upconversion.

Figure 4-1h shows an emission pattern of the bonding mode ( $\lambda=535$  nm) in the x-z plane for the point dipole placed at the same position. The pattern shows that the CSCap structure can direct the upconversion emission in the z-direction as reported for a nanocrescent antenna recently.[77] The power radiated in the direction of the nanocap is 1.9-fold larger than that in the opposite direction.

As will be shown later, the ideal nanocap structure in Figure 4-1a is hard to produce in practical materials. Especially, the cap coverage often tends to be smaller than  $180^\circ$ . Therefore, we calculated the scattering spectra of CSCap structures with different cap coverages ( $\theta$ ) (Figure 4-1i). The change of the coverage does not strongly affect the LSPR wavelength of the bonding mode (marked with ▼). On the other hand, that of the antibonding mode (marked with ●) is very sensitive to the coverage; it can be controlled from 705 to 975 nm by changing the coverage from  $90^\circ$  to  $180^\circ$ .

### 4.3. Experimental method

Figure 4-2a shows the fabrication process of a CSCap structure. First, Au colloidal nanoparticles of 64 nm in diameter were produced by a seeded growth synthesis strategy[173] (Figure 4-2a, step 1). Au nanoparticles were coated with citric acid and then a SiO<sub>2</sub> shell was formed by the Stöber method[174] (Figure 4-2a, step 2). On the surface of the SiO<sub>2</sub>-coated Au nanoparticles, an Er<sup>3+</sup> and Yb<sup>3+</sup> doped yttrium silicate shell was formed to make a CS structure by the homogeneous precipitation method[143] (Figure 4-2a, step 3). After these liquid phase processes, the CS particles were annealed at 700°C for 3 hours. Following the redispersion of the CS particles in water, they were placed on a quartz substrate by dropping the diluted suspension. The concentration of the solution was adjusted so that the average particle density became about 0.03 particles/um<sup>2</sup> for optical measurements, *i.e.*, a single particle spectroscopy. By depositing Ag (20 nm in thickness) on the substrate, an Ag nanocap was formed (Figure 4-2a, step 4). Finally, CSCap particles were transferred from the quartz substrate to a polydimethylsiloxane (PDMS, SYLBGARD-184) film as schematically shown in Figure 4-2b.[130] An advantage of this procedure is that the orientation of CSCap particles are well-defined. On the other hand, the relatively complicated procedure makes the yield of isolated CSCap particles being a subject of single particle spectroscopy small.

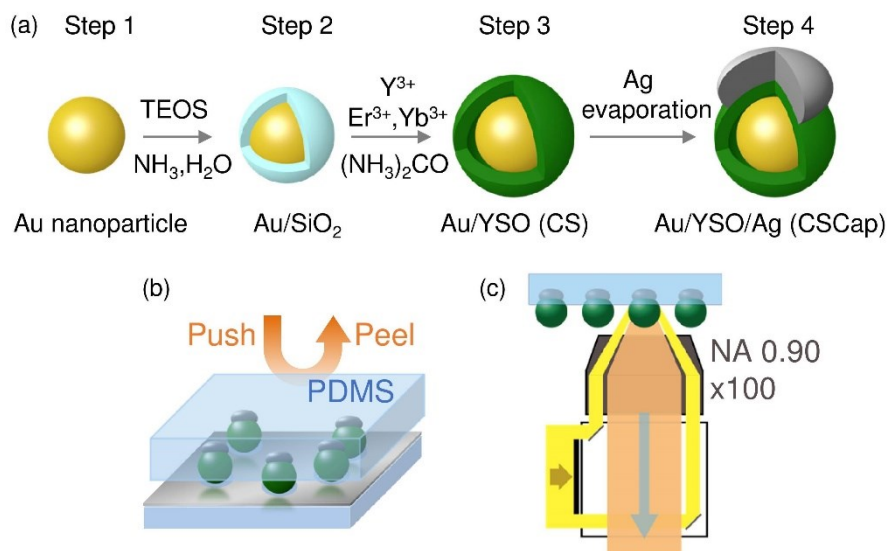


Figure 4-2. Schematic illustrations of (a) the fabrication procedure of a CSCap structure, (b) the process to transfer CSCap particles from quartz to PDMS, and (c) the geometry of the dark-field scattering spectroscopy by epi-illumination.

The structure of CSCap particles was evaluated by a transmission electron microscope (TEM), high angle annular dark-field scanning TEM (HAADF-STEM), and STEM energy-dispersive X-ray spectroscopy (STEM-EDS) (JEOL JEM-2100F (200 kV)).

The experimental setups for the measurements of the scattering and upconversion spectra of individual particles are shown. Briefly, the scattering spectra of individual CSCap particles were measured by a custom-built inverted microscope connected to a spectrometer (iHR320, Horiba Jovin Yvon) equipped with a liquid N<sub>2</sub> cooled charge coupled device (CCD) and an InGaAs diode array. For the measurement of scattering spectra, white light from a halogen lamp was illuminated through a dark-field objective (100x, NA=0.9) and the scattered light was sent to the spectrometer via the same objective (Figure 4-2c). The upconversion spectra were measured by the same setup. The excitation source was a 975 nm (90 mW) semiconductor laser.

#### 4.4. Results and discussion

In Figure 4-3a-d, TEM images of particles at the fabrications steps in Figure 4-2a are shown. Figure 4-3a shows a TEM image of Au nanoparticles. The average diameter obtained from the TEM images is  $64.1 \pm 6.5$  nm. Formation of Au nanoparticles is also confirmed by the absorption spectrum with the LSPR peak at 538 nm. Figure 4-3b shows a TEM image after the formation of a SiO<sub>2</sub> shell. The formation of the shell increases the average diameter to  $100.7 \pm 13.0$  nm. Shell formation is also confirmed by the shift of the LSPR absorption peak from 538 nm to 541 nm. Figure 4-3c shows the TEM image after the formation of an Er<sup>3+</sup> and Yb<sup>3+</sup> co-doped yttrium silicate shell and annealing at 700°C for 3 hours in air (CS particle). The diameter shrank to  $94.9 \pm 7.1$  nm due to the condensation of the SiO<sub>2</sub>/yttrium silicate shell by annealing. Figure 4-3e and f show an HAADF-STEM image and STEM-EDS profiles, respectively, of a CS particle. Figure 4-3f indicates that the core is made of Au and the shell is composed of Y, O and Si. Note that the high Si content in the core region is an artifact due to the overlap of the EDS signal of a small satellite of a Au M line on that of a Si K $\alpha$  line (1.74 keV).[175] The thickness of the yttrium silicate shell (dark gray shell in Figure 4-3c) is  $10.0 \pm 1.8$  nm. The electron diffraction pattern indicates that the shell is amorphous. Figure 4-3d shows a TEM image of a CSCap particle. An Ag nanocap (dark gray region on the top of the image) is placed on top of a CS nanoparticle. The HAADF image and the EDS mapping image of the same particle in Figure 4-3g and h, respectively, confirm successful formation of the CSCap structure. The coverage ( $\theta$ ) of nanocaps estimated from the TEM image in Figure 4-3d is around 100°. The coverage may be increased if a two-step angled deposition method is applied, although it makes the shape of a nanocap complicated.[76], [137]

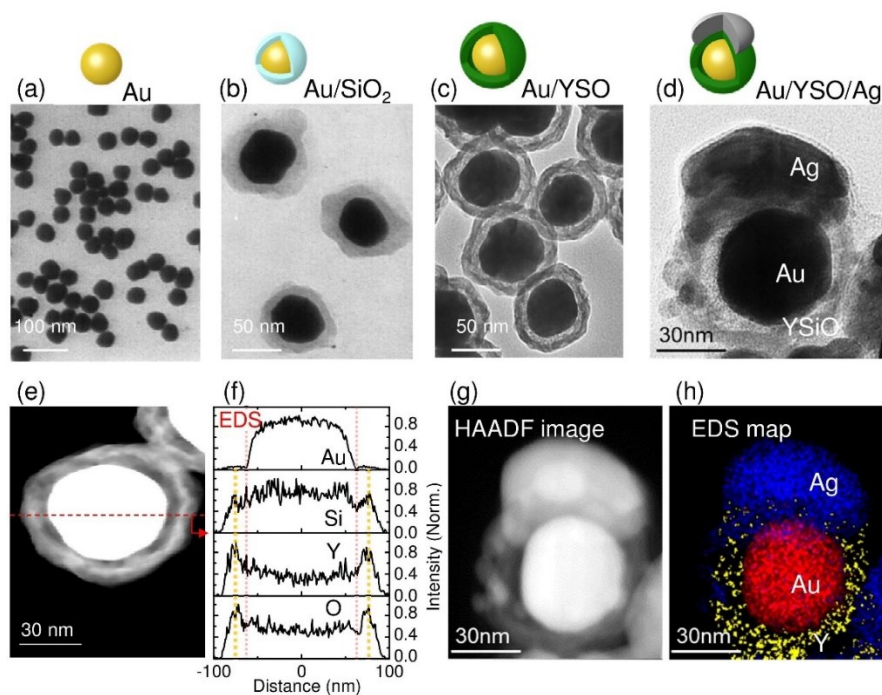


Figure 4-3. (a-d) TEM images of nanocomposites at each fabrication step. (a) Au colloidal nanoparticles. (b) SiO<sub>2</sub>-coated Au nanoparticles. (c) Au nanoparticles with SiO<sub>2</sub> shell and Er<sup>3+</sup> and Yb<sup>3+</sup> co-doped yttrium silicate shell (CS). (d) Au core/Er<sup>3+</sup> and Yb<sup>3+</sup> co-doped yttrium silicate shell/Ag shell (CSCap) composite nanoparticles. (e) HAADF-STEM image of a CS particle and (f) the STEM-EDS profile (Au, Si, Y and O) along the dashed line in (e). (g) HAADF-STEM image and (h) EDS mapping image of a CSCap nanoparticle.

Figure 4-4a shows typical scattering spectra of a single CS nanoparticle and a single CSCap nanoparticle. The CS nanoparticle has a scattering peak due to the LSPR of an Au nanoparticle around 560 nm. The peak wavelengths obtained for 50 single CS nanoparticles are shown in Figure 4-4b (black circles). The average peak wavelength is 562 nm, and the variation is very small. The peak wavelength is in good agreement with that of a numerical simulation in Figure 4-4c.

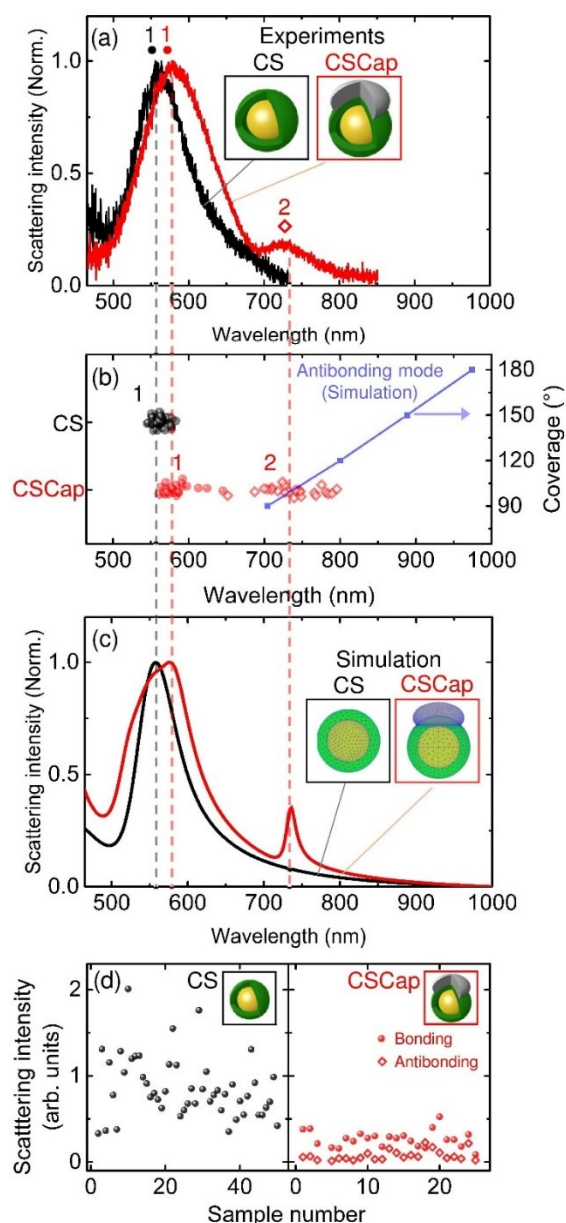


Figure 4-4. (a) Scattering spectra of a single CS nanoparticle (black) and a single CSCap nanoparticle (red). (b) Peak wavelengths of 50 single CS (black) and 24 single CSCap nanoparticles (red). Resonance wavelength of the anti-bonding mode obtained from the data in Figure 1i is also shown as a function of a nanocap coverage (blue, right y-axis). The vertical dashed lines correspond to the average resonance wavelengths. (c) Calculated scattering spectra of a CS particle and a CSCap particle with the coverage of 100°. (d) Scattering intensities of 50 single CS particles and 24 single CSCap particles.

The scattering spectrum of a CSCap nanoparticle is significantly different from that of a CS nanoparticle. The peak shifts to longer wavelength and is broadened. Furthermore, an

additional small peak appears around 737 nm. These peaks can be assigned to the bonding and anti-bonding modes of a CSCap particle discussed before. The variations of the peak wavelengths of 24 individual particles are shown in Figure 4-4b (red circles and red diamonds). As discussed above, the resonance wavelength of the anti-bonding mode depends strongly on the nanocap coverage. In Figure 4-4b, the calculated resonance wavelength of the anti-bonding mode is shown as a function of the coverage (blue line). The blue line and the red vertical line intersects around  $100^\circ$ . This value is consistent with the TEM images in Figure 4-3d. Figure 4-4c shows the calculated scattering spectrum of a CSCap particle with the Ag coverage of  $100^\circ$  for randomly polarized plane wave illumination. The calculated spectrum agrees very well with the experimental one.

In Figure 4-4d, the scattering peak intensities of single composite nanoparticles are plotted. We can see that the scattering intensity of CSCap nanoparticles are  $\sim 0.3$ -fold of that of CS nanoparticles. This seems to be in contradict with the calculated  $\sim 1.5$ -fold enhancement of the scattering intensity. The observed small scattering intensity of the CSCap nanoparticles is considered to be due to the directional scattering as discussed in Figure 4-1h. A CSCap scatters light preferentially to the direction of the cap, which is opposite to the detection direction in this work (Figure 4-2c).

Considering upconversion enhancement of  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  co-doped yttrium silicate in the shell of a CSCap nanoparticle, the optimum resonance wavelength of the anti-bonding mode is around 975 nm. However, in the CSCap structure produced in this work, the resonance wavelength is around 735 nm, and thus we do not expect the enhancement of the excitation efficiency. On the other hand, we can expect the enhancement of the quantum yield because the

scattering peaks are overlapped with the green and red emission bands of  $\text{Er}^{3+}$ . Figure 4-5a shows a typical upconversion photoluminescence (PL) spectrum of a single CS particle when it is excited at 975 nm. We can see green ( $\sim 550$  nm) and red ( $\sim 660$  nm) emission corresponding to the transitions from  $^4\text{S}_{3/2}$  and  $^4\text{F}_{9/2}$  states to the ground  $^4\text{I}_{15/2}$  state of  $\text{Er}^{3+}$ , respectively. A scattering spectrum of the same particle is shown. The LSPR overlaps with the green emission.

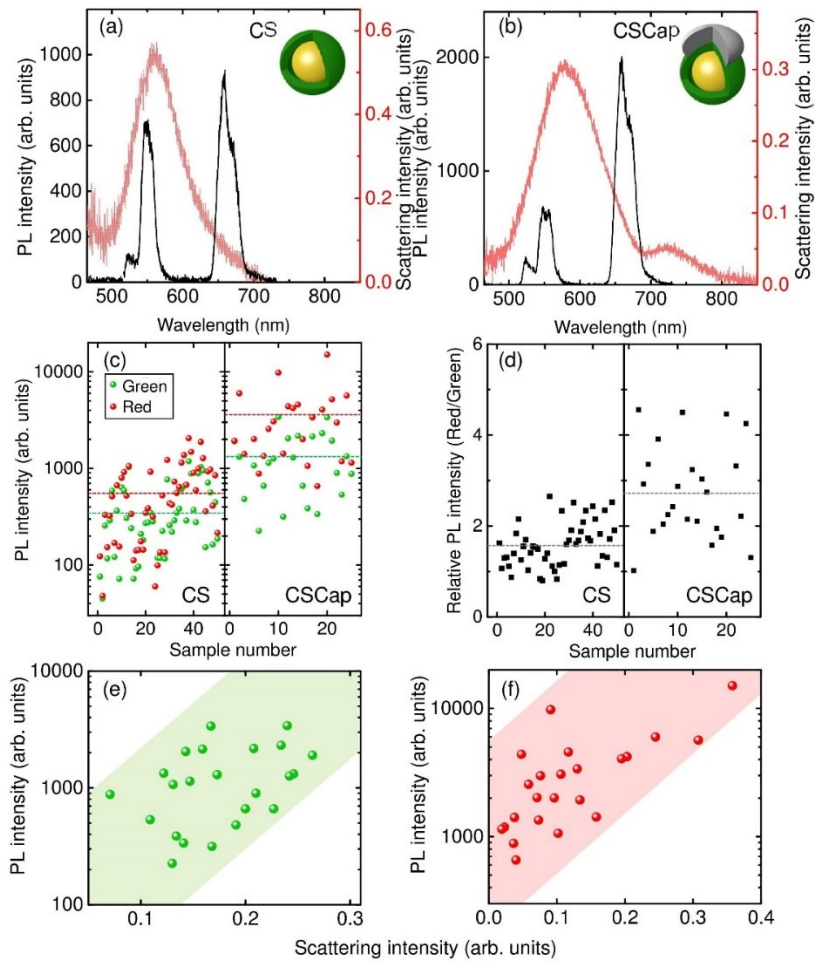


Figure 4-5. Upconversion PL and scattering spectra of (a) a CS nanoparticle and (b) a CSCap nanoparticle. Scatter plots of (c) upconversion PL peak intensities and (d) the intensity ratio of the red to green emissions obtained for 50 CS and 24 CSCap particles. Horizontal dashed lines are the average values. PL intensity of (e) green and (f) red upconversion emissions as a function of scattering intensity at the emission wavelengths of single CSCap nanoparticles.

In Figure 4-5b, an upconversion PL spectrum of a single CSCap particle is shown together with the scattering spectrum. In addition to the intensity, the intensity ratio of the red to green emission is changed from that of a CS particle. To evaluate the upconversion enhancement factor quantitatively, the emission intensity obtained for 50 CS particles and 24 CSCap particles are shown in Figure 4-5c. The horizontal dashed lines are the average intensities. Although the intensities are scattered in a wide range, those of CSCap particles are as a whole larger than those of CS particles. The average intensity increases by a factor of 3.5 and 6.0 for the green and red emissions, respectively. Since the red emission is more strongly enhanced than the green one, the red to green intensity ratio is also modified as shown in Figure 4-5d. As mentioned above, a CSCap particle emits photons preferentially to the direction of the nanocap, which is opposite to the direction of our PL detection setup. Therefore, larger enhancement factor is expected if the emission is collected from the nanocap side. In Figure 4-5e and f, the intensity of the green and red emissions, respectively, are plotted as a function of the scattering intensity at the emission wavelengths. Although the data are scattered in a wide range, we can see clear correlation between the PL intensity and the scattering intensity. This is an evidence that the observed upconversion enhancement is due to that of the antenna efficiency. The observed larger enhancement of the red emission than the green emission by the formation of a nanocap can be explained by the larger Purcell enhancement in the red region caused by the red shift of the LSPR resonance of the bonding mode and the emergence of the anti-bonding mode at the longer wavelength side (Figure 4-4a). The results are consistent with the experimental results. The effect of heating on the red/green ratio<sup>[159]</sup> is considered to be negligibly small because nanocap formation does not

strongly affect the absorption cross section at the excitation wavelength (975 nm) when the coverage is 100° (Figure 4-4c) .

## 4.5. Conclusion

We have studied a composite nanoparticle composed of a metal core, an upconversion shell and a silver nanocap as a novel upconversion composite nanoparticle. Numerical simulation revealed that hybridization of the core and cap surface plasmon modes results in the emergence of the bonding and anti-bonding modes, and that the resonance wavelength of the anti-bonding mode is controlled in a wide wavelength range by a nanocap coverage. Furthermore, in the anti-bonding mode, the electric field is effectively confined in an upconversion shell. For the fabrication of the composite nanoparticle, we developed a process that combines liquid phase synthesis and vapor deposition processes. We confirmed the formation of the composite nanoparticles by STEM and STEM-EDS. The scattering spectra of single composite nanoparticles agreed very well with the numerical simulation. The comparison of the upconversion intensity between the metal-core/dielectric-shell structure and the metal-core/dielectric-shell/metal-cap structure revealed that the cap formation increases the intensity several fold.

## Part II

### Chapter 5

#### Structural and optical properties of a colloidal solution of silicon nanospheres

##### 5.1. Introduction

Dielectric nanoantennas made of high-refractive-index dielectrics are drawing much attention in the nanophotonics field due to the electric and magnetic Mie resonances which show high scattering efficiency with low-loss.[9], [86], [182]–[188], [88], [89], [176]–[181] As was discussed above, materials which have high-refractive-index in combination with small absorption coefficient are required to realize the Mie resonances. Given this requirement, silicon or gallium phosphide nanostructures are best candidates for visible operation.[188], [189]

Since the pioneer works in 2012[190], [191], which reported strong magnetic response of a silicon nanosphere in the visible and infrared ranges, the silicon nanosphere are one of the most commonly utilized materials in this field. One of the advantages of the nanosphere is that its optical responses can be analytically calculated by the Mie theory. Several techniques have been reported so far for the fabrication of silicon nanospheres (100–200 nm in diameter) which are resonant in the visible, for example, laser ablation of a silicon wafer[190], [191], decomposition of trisilane in supercritical *n*-hexane[192], thermal annealing of silicon suboxide,[193], [194] grinding of silicon lump[195], *etc.*[188] Among them, the thermal annealing of silicon suboxide is the only approach which can obtain a colloidal solution of high

sphericity, crystallinity, size purity, and dispersity silicon nanospheres. [193], [194] The development of such a high-quality silicon nanosphere colloid opened a new avenue toward scalable fabrication of nanophotonic devices including metasurfaces, application for color inks, facile integration with fragile materials, syntheses of novel structures using liquid phase chemical processes, and realization of metafluids.

In Chapter 5, we briefly summarize the fabrication process and structural and optical properties of the colloiddally synthesized silicon nanosphere developed in our group. Additionally, conventional measurement technique of such small scatterers is explained. The data in this chapter are partly adopted from a publication [4: H. Sugimoto, T. Hinamoto, and M. Fujii, Adv. Opt. Mat., 7, 2900591 (2019)] in the publication list.

## 5.2. Fabrication, optical measurement, and simulation methods

**Fabrication of colloidal silicon nanospheres.** The formation of silicon nanosphere is accomplished by the disproportionation of silicon-rich silicon oxide into silicon nanoparticles and a silicon dioxide matrix in high-temperature above the melting point of silicon (1414°C). [193] The procedure is schematically shown in Figure 5-1. First, silicon, silicon dioxide, boron trioxide, and phosphorus pentaoxide were co-sputtered on a thin stainless-steel plate to obtain a borophosphosilicate (BPSG) film with 10–20  $\mu\text{m}$  in thickness. The film was then annealed at 1500°C for 30 minutes to grow silicon nanospheres in the matrix. The nanospheres were extracted from the matrix by etching in hydrofluoric acid (46 wt%) for one hour and transferred into solvents such as methanol or ethanol. The nanospheres were finally dispersed with the help of ultrasonication. Note that the boron (B) and phosphorus (P) were doped for better colloidal

stability by electrostatic repulsion induced in a negatively charged heavily-B and P doped layer on the nanosphere surface.

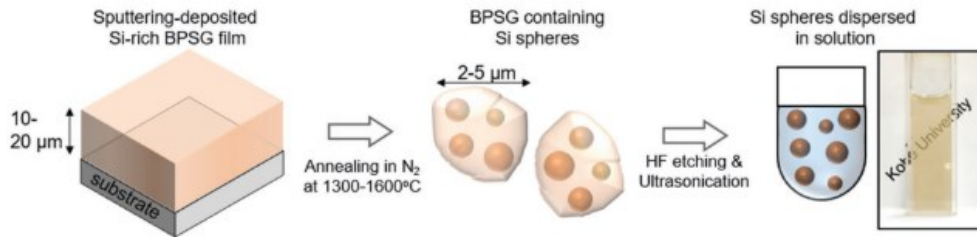


Figure 5-1. Fabrication procedure of the colloidal solution of silicon nanospheres.[193]

The procedure provides the nanosphere with pretty good crystallinity as discussed later, while it engages time consuming sputter-deposition process. For better scalability, commercially available silicon monoxide powder can substitute for the BPSG film.[194]

Finally, the obtained solution was drop-cast on a silica substrate or a home-made thin silica membrane supported by a copper TEM mesh grid. The optically thin (8 nm in thickness) silica membrane enables us to characterize optical responses without undesired effects induced by the substrate. It also makes it possible to carry out precise comparison between optical and structural properties at a single particle level by tracking the same particle in optical microscopy and TEM observation.

The nanosphere fabricated in this method has inevitable size distribution (typical coefficient of variation  $C.V.$ : ~40%), but it convenient to measure size dependent optical properties as shown later. For applications which require small size distribution, a density gradient centrifugation method can be applied to obtain monodispersed nanospheres ( $C.V.$  < 6%).[194]

**Optical measurements.** To characterize optical properties of single nanoantennas, an optical microscope coupled with a spectrometer is utilized. The scattering spectrum can be

measured in a dark-field mode. In this configuration, the specular reflection by a substrate does not come into the collection angle, enabling detection of photons purely scattered the nanoantenna.

The schematic illustration of the conventional measurement setup with an inverted microscope is shown in Figure 5-2. In order to evaluate directional scattering behavior of the single silicon nanosphere, we measured the forward and backward scattering spectra in different illumination configurations. For forward scattering measurement, the white light from a halogen lamp was illuminated via dark-field condenser (N.A. = 0.8–0.95) sitting on the top, and the scattered light was collected using a 50x objective from the bottom (Figure 5-2a). For the backward one, both illumination and collection was done via the objective (Figure 5-2b). The collected light was relayed to and focus at the entrance slit of a monochromator equipped with a charge-coupled device (CCD).

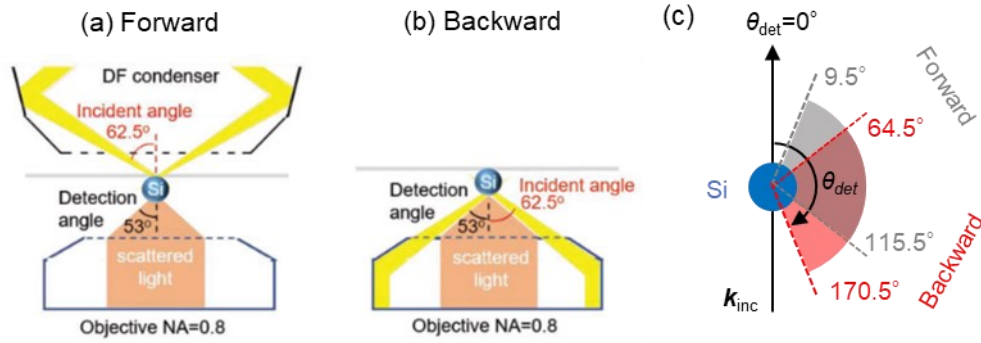


Figure 5-2. (a,b) Conventional setup for a dark-field spectrum measurement of a single nanoantenna using a microscope. [196] (c) Detection angles (cones) corresponding to forward (red) and backward (black) scattering measurements.

It is important to note that in both configuration the light scattered within the certain angle determined by the numerical aperture (N.A.) of the objective is integrated and detected as the scattering intensity. Besides, some portion of the forward and backward angular range overlaps each other. In Figure 5-2c, the detection angles  $\theta_{det}$  against the illumination direction ( $k_{inc}$ ) is

shown, under the assumption that the illumination angles are the same in both cases and is  $62.5^\circ$  (i.e., average of N.A. 0.8–0.95). Therefore, the angular ranges of detection are from  $9.5^\circ$  to  $115.5^\circ$  for the forward and  $64.5^\circ$  to  $170.5^\circ$  for the backward.

**FDTD Simulation.** In this chapter, the optical responses of a single silicon nanospheres was calculated using the finite-difference time-domain (FDTD) method (Lumerical Inc.). As mentioned above, the dark-field measurement only collects light purely scattered by the nanoantenna. This setup can be reproduced by a total-field scattered-field (TFSF) method in the simulation. It utilizes the relationship  $\mathbf{E}_{\text{tot}} = \mathbf{E}_{\text{sca}} + \mathbf{E}_{\text{inc}}$  between total ( $\mathbf{E}_{\text{tot}}$ ), scattered ( $\mathbf{E}_{\text{sca}}$ ), and incident ( $\mathbf{E}_{\text{inc}}$ ) fields, and only the scattered field exist outside the TFSF boundaries. A TFSF source from which plane-wave is launched was placed so as it surrounds the nanosphere. The scattered light was collected by a box monitor in the scattered field region (i.e., outside the TFSF boundaries). The entire simulation region was surrounded by the perfect matched layer boundary. This is the typical simulation setup for single nanoantennas. Scattering cross sections can be simulated by integrating the all the scattered power, followed by normalization by the incident power.

In order to reproduce the measured scattering spectra, the scattered power has to be integrated over the solid angle defined by the numerical aperture of the objective, following near-to-far-field-transformation (NFFT). The scattered power  $P_{\text{sca}}$  can be obtained by

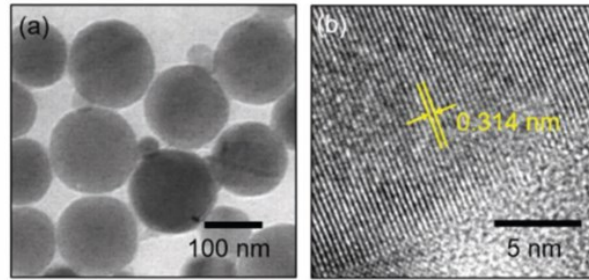
$$P_{\text{sca}} = \frac{1}{2} \iint^{N.A.} \text{Re} \left[ n \sqrt{\frac{\epsilon_0}{\mu_0}} |\mathbf{E}_{\text{sca}}^{\text{ff}}(\mathbf{r}, \theta, \phi)|^2 \right] r^2 \sin \theta d\theta d\phi \quad (5-1)$$

, where  $\mathbf{E}_{\text{sca}}^{\text{ff}}(\mathbf{r}, \theta, \phi)$  is the scattered field after the NFFT in the spherical coordinate system defined by the position vector  $\mathbf{r}$ , radial angle  $\theta$ , and azimuthal angle  $\phi$ . In the Lumerical FDTD

solutions, convenient scripts such as `farfield3dintegrate` can carry out the NFFT and following integration. Finally, by averaging the scattered power calculated for s- and p-polarization, the simulated spectrum was obtained.

### 5.3. Structural and optical characterization

A TEM image of the fabricated silicon nanospheres is shown in Figure 5-3a. The image shows that the synthesized particles are highly spherical and are not forming agglomerates. In the high-resolution TEM image shown in Figure 5-3b, the lattice fringes correspond to the  $\{111\}$  plane of crystalline silicon are seen clearly, indicating the high crystallinity of this material. Note that no thick oxide layers are observed at the surface. From these observations, our silicon nanosphere with highly spherical surface and high crystallinity is expected to work as an ideal spherical Mie resonator.



*Figure 5-3. (a) TEM and (b) high-resolution TEM images of the fabricated silicon nanospheres.[193]*

The forward and backward scattering spectrum of a single silicon nanosphere on the thin silica membrane is shown in Figure 5-4a. The TEM image in the inset is that of the measured nanosphere, and the diameter is  $\sim 143$  nm. In both forward and backward spectra, prominent peaks appear around 480 and 580 nm, which correspond to electric and magnetic Mie resonances. The

ratio of forward and backward scattering (blue dashed line) reaches  $\sim 4$  around 650 nm at which the first Kerker condition is satisfied. The simulated spectra for a nanosphere of 143 nm in diameter are shown in Figure 5-4b. The measured and simulated spectra show almost perfect qualitative and quantitative agreement each other. This proves the quality of the nanosphere, because the simulation is performed for an ideal geometry, that is, perfectly spherical particle with the refractive index of bulk single crystalline silicon.[7] The small deviation such as broader peaks may originate from the slightly higher losses due to imperfection in the crystallinity or the doping of B and P.

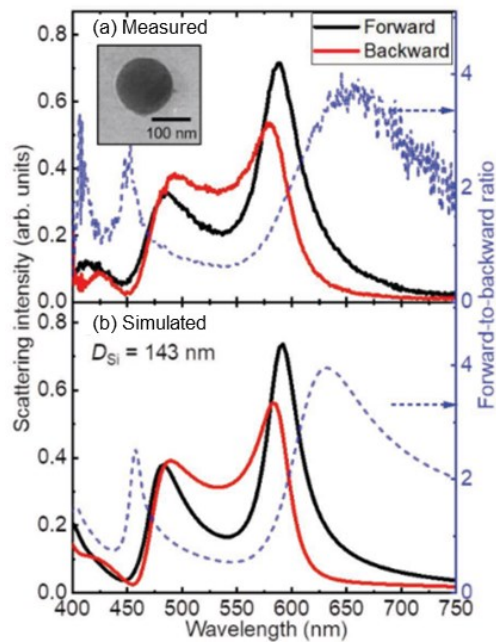


Figure 5-4. (a) Measured and (b) simulated scattering spectra of a single silicon nanosphere on an 8 nm thickness silica membrane. The black and red solid lines show forward and backward spectra, respectively. The blue dashed line is the spectrum of the forward-to-backward ratio.[196]

Because the Mie resonance is highly sensitive to the sphere size, the resonance wavelength can be controlled across the visible and near-infrared ranges by the diameter, which is the strong contrast to the LSPR. The scattering spectra of the silicon nanospheres with different

diameters on the silica substrate are shown in Figure 5-5. Color images of the forward and backward scattering are shown in between the forward and backward spectra together with the nanosphere diameter estimated from the peak positions of backward scattering spectra. The peaks in forward (left) and backward spectra shifts to the longer wavelength as the nanosphere gets larger. Corresponding to the shift of the resonance, the color of the sphere changes from blue, green, yellow, to red. For the nanosphere larger than  $\sim 150$  nm, higher order modes also appear in the short wavelength range. Because the higher order modes have higher quality factors than the lower ones, they are useful for applications which require strongly localized field. In this size range, roughly from 100 nm to 200 nm, the resonance wavelength of the magnetic dipole mode can be shifted over almost entire visible spectrum. This is the typical size range of the nanosphere fabricated with this method, while larger particles up to  $\sim 300$  nm can be obtained using the silicon suboxide as the starting material.

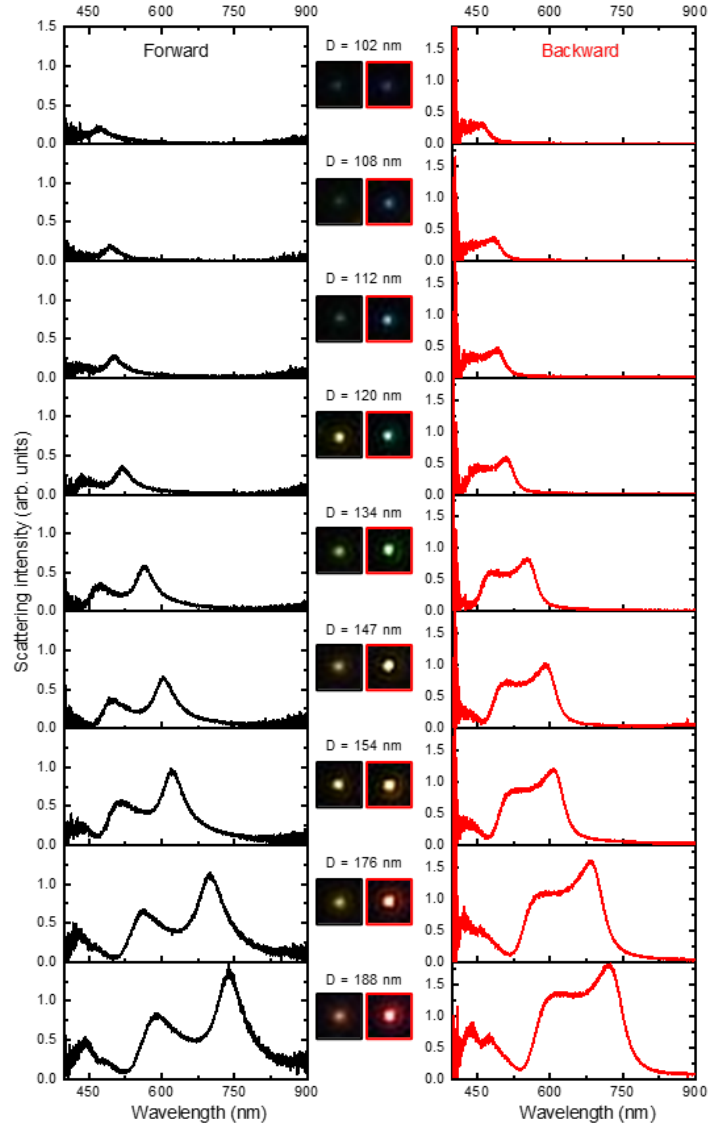


Figure 5-5. Size dependence of the forward (left panel, black line) and backward (right panel, red line) scattering spectra of single silicon nanospheres on a silica substrate. The corresponding color images are shown together. The estimated diameters are shown in between the panels. They are estimated from the peak position of the magnetic dipole mode in backward scattering spectra by comparing with that of simulation.

#### 5.4. Conclusion

In this chapter, information about the silicon nanosphere which is utilized in the following chapters was provided. Through the explanation of fabrication method and TEM images, we

described the characteristics of the nanosphere, which is high sphericity and crystallinity. Additionally, the measurement and simulation methods, which are generally employed for evaluation of single nanoantennas, were briefly described.

## Chapter 6

# Angular Scattering Measurement of a Single Mie resonant Nanoantenna Using Fourier-plane spectroscopy

### 6.1. Introduction

Optical nanoantennas enable efficient manipulation of electromagnetic field at optical frequencies. They have been developed as building blocks of functional metamaterials and metasurfaces.[86], [176], [178], [179], [197]–[200] Recently, dielectric nanoantennas made of high-refractive-index semiconductors are energetically studied due to the possession of Mie resonances which exhibit high scattering efficiencies with low-losses.[89] The developments have greatly pushed up the efficiency of planar metasurface devices, and nowadays the transmission efficiencies are reaching the value equivalent to that of a glass plate ( $>90\%$ ).[94], [95]

Thanks to the possession of electric and magnetic multipole resonances, the dielectric nanoantenna has a degree of freedom to tailor scattering radiation patterns.[201] For example, unidirectional scattering occurs due to the interference of electric and magnetic dipole resonances, which has improved the efficiency of transmission type metasurfaces by suppressing reflection losses.[93], [95], [202] Various directional nanoantennas have been proposed using interference of multiple resonances, for example, dielectric or Janus dimer[106], [203]–[207], Yagi-Uda[208], and more.[209]–[211] Besides, transverse scattering, which means the nanostructure does not scatter light in both forward and backward directions but does in-plane, has been proposed by the interference between electric dipole and off-resonant quadrupoles.[212] Furthermore,

nanoantennas which show asymmetric radiation patterns are reported, and the application for metalens with near-unity numerical aperture ( $>0.99$ ) has been demonstrated.[213]

The evaluation of scattering patterns and directionality of single nanoantennas is essential to maximize the performance of metasurfaces; however, it is not straightforward for such small nanostructures. Typically, the scattering behavior of a single nanoparticle is characterized with an optical microscope in the dark-field geometry. The directionality is measured by illuminating light from top and bottom and collecting the scattering directed within the numerical aperture (N.A.) of an objective.[93] On the other hand, the high magnification objective with large N.A. collects light over large light cone, leading to under estimation of the directionality due to the detection of not only forward/backward but also transverse scattering, or the overlapping of the light cones. In addition, the ring-shaped illumination used for the dark-field makes it difficult to analyze polarization dependence.

Fourier-plane imaging, in other words, back-focal plane imaging and spectroscopy is a technique which resolves information in a Fourier-plane of lens. In contrast to conventional image-plane imaging, the Fourier-plane has an angular information of light, and thus angular radiation patterns can be obtained by looking at the plane. In nanophotonics field, it is often utilized to measure angular emission patterns from quantum emitters[18], [214], cathodoluminescence[104], [215]–[218], and lasing[103], and to visualize propagation of surface plasmon polaritons[219]–[221]. The technique has also demonstrated the directional scattering of planewave by dielectric nanoantennas[19], [209], but angle-resolved scattering spectrum over a wide angular range from backward to forward is merely studied.

In this work, we develop the dark-field optical microscopy setup which is capable of angle- and spectrally resolved scattering measurements over wide angular range from  $22^\circ$  to  $158^\circ$  against the incident direction, based on a conventional microscope. This is enabled by limiting azimuthal angle of illumination and resolving scattered angle by the Fourier-plane imaging. Using the constructed setup, we measure angular scattering spectra of a single silicon nanosphere and demonstrate the capability to evaluate the directionality of single directional nanoantennas. Furthermore, as another advantage of the setup, the selective detection of electric and magnetic dipole resonances is demonstrated using polarization resolved measurement.

## 6.2. Measurement setup

In order to carry out the angle- and spectrally resolved scattering measurement with a conventional optical microscope, both the illumination and detection setups need to be updated. To address this, we start from a typical inverted microscope equipped with a epi-illumination dark-field objective (x50, N.A. = 0.80) on the bottom and an upper dark-field condenser (N.A. = 0.8-0.95) as shown in Figure 6-1 a and c. In the transmission mode (Figure 6-1 a), white light from a halogen lamp was shone via the upper condenser at incident angle  $\theta_{\text{inc}} = 75^\circ$ , while white light from another lamp house shone via the lower objective in the reflection mode (Figure 6-1 c) at  $\theta_{\text{inc}} = 105^\circ$ . The scattered light was then collected by the lower objective and relayed to a spectrometer coupled with a charge coupled device (CCD). Although the inverted microscope was adopted here, the methodology developed in this work is general regardless of whether it is inverted or upright-type.

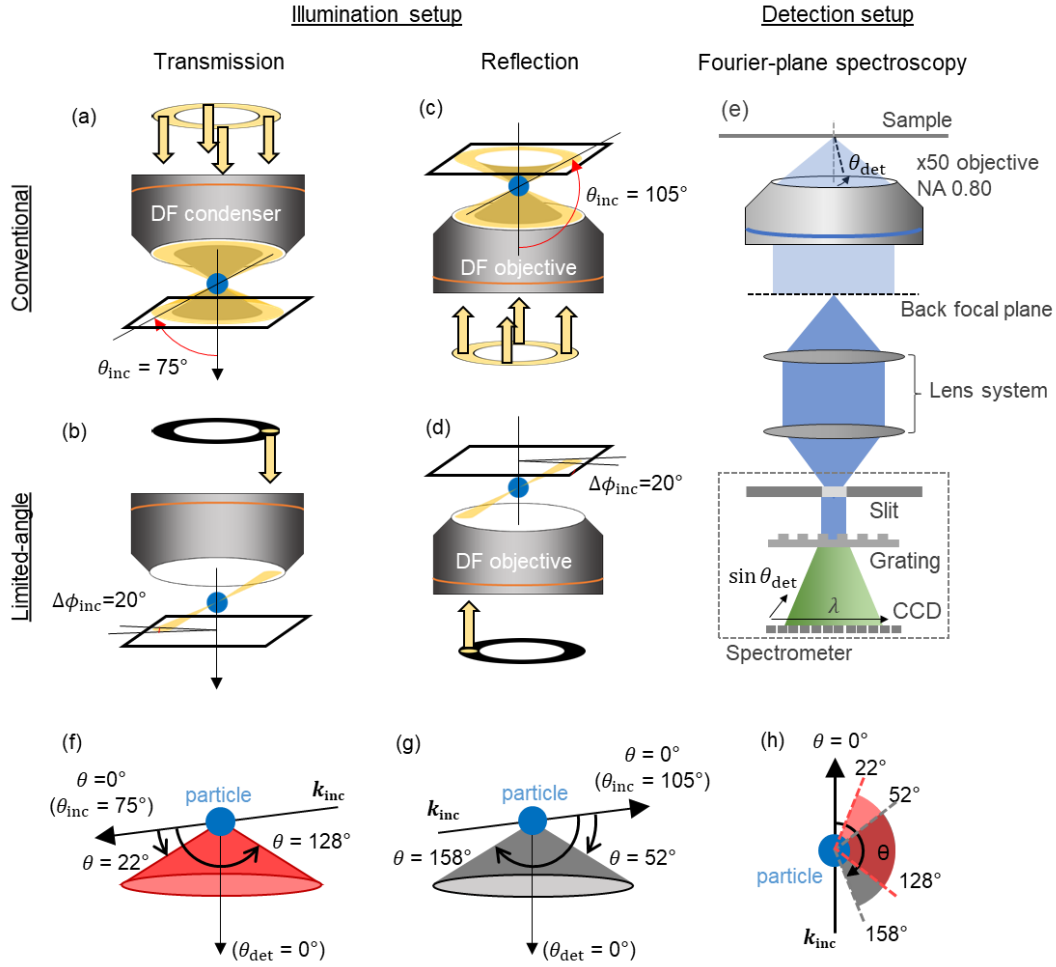


Figure 6-1. Schematics of measurement configurations. (a-d) Illumination setups in (a,b) Transmission- and (c,d) reflection modes. (a,c) and (b,d) are Conventional ring-shape and limited azimuthal angle ( $\phi$ ) illumination, respectively. (e) Detection setup using Fourier-plane spectroscopy. (f-h) Detectable angles in (f) transmission and (g) reflection modes, (h) both of them against the illumination direction ( $\theta=0^\circ$ ).

In the conventional setup, the dark-field condenser has ring-shaped aperture and illuminates from all azimuths. Therefore, we first limited the azimuthal angle ( $\phi_{inc}$ ) by placing an aperture at the position of pupil to fix an incident angle, enabling us to define scattering polar ( $\theta$ ) and azimuthal ( $\phi$ ) angles against the direction and the polarization of the incidence (Figure 6-1b,d). In both transmission and reflection modes, the width of the azimuth ( $\Delta\phi$ ) was limited to  $\sim 20^\circ$ .

As a next step, we constructed the detection setup based on the Fourier-plane spectroscopy. As shown in Figure 6-1e, the scattered light was collected by the lower objective, forming an angular distribution image in the back-focal plane (*i.e.*, the Fourier-plane). The plane was then imaged onto the entrance slit (slit width =  $\Delta\phi_{\text{inc}}$ ) of the spectrometer using some relay lenses. During the relay, a pinhole was inserted in an image plane to eliminate signals not coming from the target particle. The illumination plane and the orientation of the slit were aligned to be orthogonal each other. Therefore, the scattering intensity image on the CCD has the vertical and horizontal axes which correspond to  $\theta$  and wavelength, respectively. Note that the vertical axis of the raw data is proportional to  $\sin\theta$ , so the data shown in this paper was calibrated so the axis to be linear.

The angular range which can be obtained in our setup is schematically shown in Figure 6-1f-h. Given that N.A. = 0.8 corresponds to  $53^\circ$ , the objective collects the scattered light from  $22^\circ$  to  $128^\circ$  and from  $52^\circ$  to  $158^\circ$  to the incident axis in the transmission and reflection mode, respectively. Thus, the angular range  $\theta = 22^\circ - 158^\circ$  (*i.e.*,  $136^\circ$  in total) can be measured (Figure 6-1h) with an overlap range  $\theta = 52^\circ - 158^\circ$ .

### 6.3. Results and discussion

We apply the angle- and spectrally resolved scattering measurement to the directional scattering of a crystalline silicon nanosphere.[193] In order to eliminate substrate induced effects, the nanosphere is placed on an 8 nm thickness thin silica film supported by a TEM mesh grid. First, we discuss the measurement results carried out with unpolarized light illumination. Afterwards, the result of s- and p-polarization illumination will be discussed.

Figure 6-2a,b show two-dimensional (2D) maps of angle-resolved scattering spectra for unpolarized light in transmission and reflection modes. As can be seen in Figure 6-2a, strong scattering peaks appear around 700, 550, and 400 nm around  $\theta = 35^\circ$ . To investigate the origin of these peaks, we have simulated angular scattering spectra for a silicon nanosphere with 150 nm in diameter using finite-difference time-domain (FDTD) method as shown in Figure 6-2c. The observed features in the experiment show overall agreement with the simulation, that is, the emergence of peaks and their blue-shift trend for large  $\theta$ . There is fluctuation of the scattering intensity in the vertical direction in the measurement data, but it may be caused by the undesirable filtering of some angular component due to lens relay or the aperture.

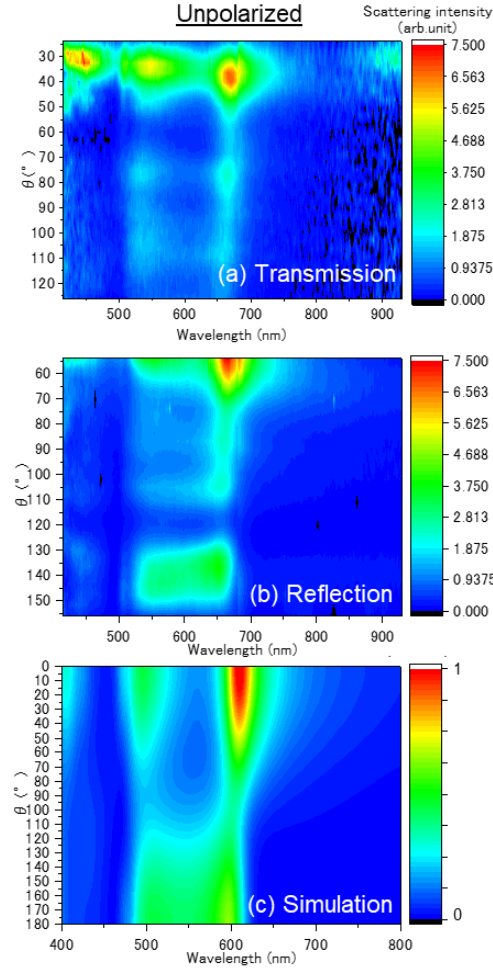


Figure 6-2. (a,b) Measured and (c) simulated angular-scattering intensities under unpolarized-light illumination as a function of wavelength and scattered angle ( $\theta$ ). (a) and (b) are measured in transmission and reflection modes, respectively.

From the simulation, the first and second lowest peaks can be assigned to magnetic and electric Mie resonances. The angular distribution of the electric dipole becomes strong around the edge of the numerical aperture edges around 30° and 140°, which is a typical dipolar pattern. On the other hand, the magnetic dipole is asymmetric, and the forward scattering is particularly strong in the long wavelength side of the peak. This unidirectional scattering originates from the far-field interference between the electric and magnetic dipoles, so-called the Kerker condition. We stress here that the unidirectional behavior is captured well in the measured data. The peak at the

shortest wavelength can be assigned to the electric quadrupole mode, while it is not obvious prominent in this wavelength range where silicon has relatively large absorption. From these observations, the measurement setup has successfully measured the angle-resolved scattering spectra of the single silicon nanosphere.

The advantage of this measurement method is that the directionality, forward and backward scattering can be evaluated at more ideal condition than the conventional setup by selecting the particular angles as shown in Figure 6-3a. Although it is still impossible to measure scattering at  $\theta = 0^\circ$  and  $180^\circ$  in the dark-field setup, this method enables us to exclude transverse scattering. The measured forward and backward scattering spectra at  $\theta = 50^\circ$  and  $130^\circ$ , where the strongest forward-to-backward (F/B) ratio is obtained, is shown in Figure 6-3b. The corresponding F/B ratio spectrum is shown in Figure 6-3c. The spectra show prominent peaks in forward and broadened ones in backward, and the spectra are very similar to them at  $\theta = 0^\circ$  and  $180^\circ$ . The measured F/B ratio reaches  $\sim 9$  at the peak wavelength. The spectral shapes qualitatively agree very well with those obtained by simulation shown in Figure 6-3e,f.

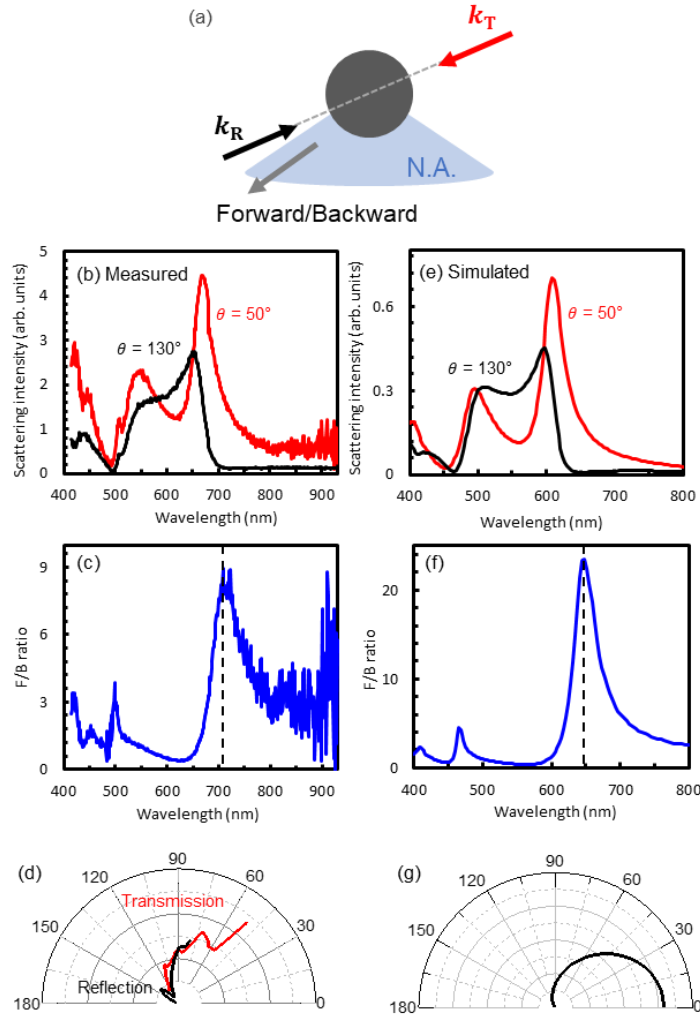


Figure 6-3. Evaluation of the directionality under unpolarized-light illumination. (a) Schematic illustration of forward and backward scattering. (b-d) Measured and (e-g) simulated (b,e) scattering spectra at  $\theta = 50^\circ$  (forward, red) and  $\theta = 130^\circ$  (backward, black), forward-to-backward ratios, and (d,g) radiation patterns.

The radiation pattern at the peak wavelengths of the F/B ratio spectra are extracted from the 2D maps and shown in Figure 6-3d,g. Note that a certain angular region where reasonable intensities could be obtained are plotted for the experimental data. The measured radiation patterns clearly indicate that the scattering is suppressed steeply when  $\theta > 90^\circ$ , indicating successful measurement of the scattering pattern of the single nanosphere.

From here, we move on to the measurement under the s- and p-polarized light illumination, which is enabled by the limitation of  $\phi_{\text{inc}}$ . In Figure 6-4, measured and simulated polarization maps are shown. The overall spectra are similar to those obtained for unpolarized, but the modes to be excited are different between polarization states. Both in transmission and reflection modes, the shorter wavelength peak is preferably detected in s-polarization especially near  $\theta = 90^\circ$ , and opposite for the longer one. This behavior is also reproduced in the simulated spectra, proving the validity of this polarization dependent measurement.

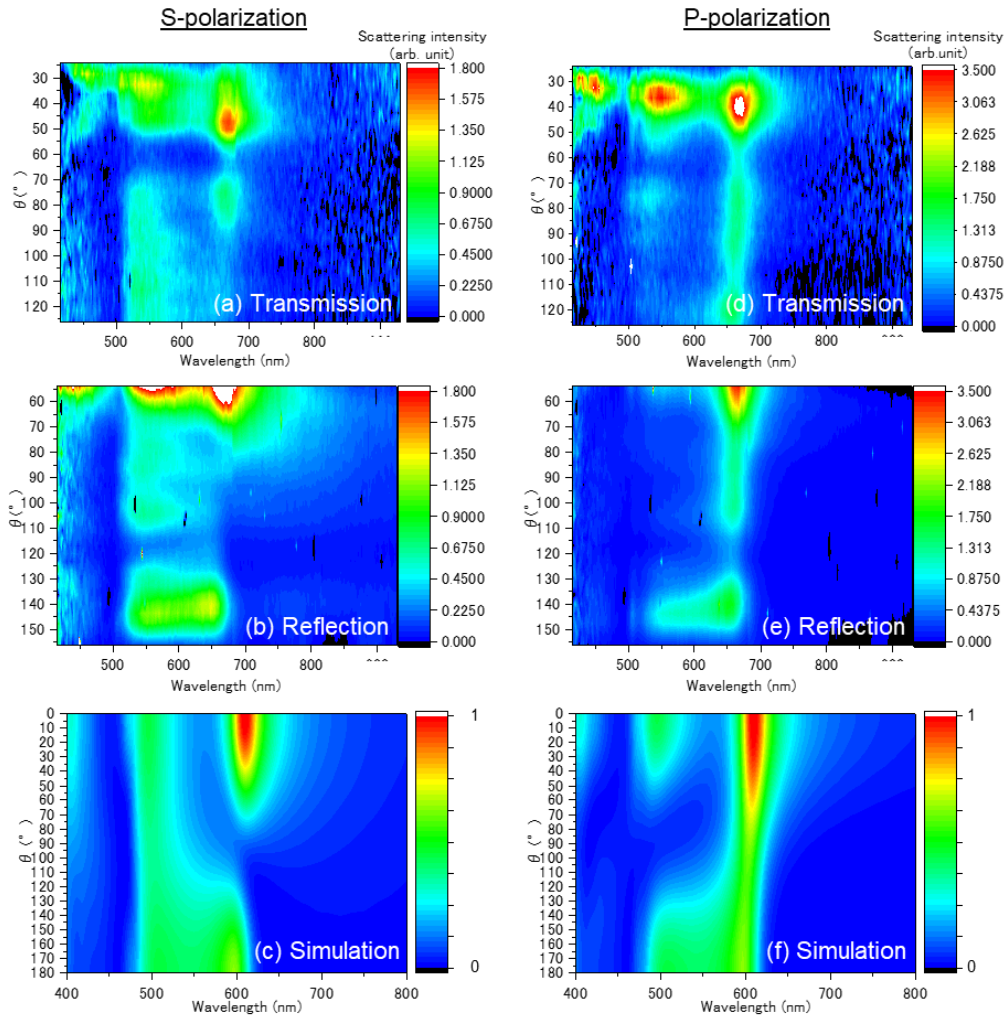


Figure 6-4. (a,b,d,e) Measured and (c,f) simulated angular-scattering intensities under (a-c) s- and (d-f) p-polarized light illumination as a function of wavelength and scattered angle ( $\theta$ ). (a,d) and (b,e) are measured in transmission and reflection modes, respectively.

The mechanism of the selective detection can be explained by the orientation and the radiation pattern of the electric and magnetic dipole resonances. In Figure 6-5, the radiation patterns of them under s- and p-polarized light are schematically illustrated. When the s-polarized light is illuminated, the electric dipole is excited with the orientation perpendicular to the illumination plane and thus has a circular radiation profile. On the other hand, the magnetic dipole is induced in an in-plane alignment with a dipolar radiation profile ( $\propto \cos^2 \theta$ ). Therefore, only the contribution from the electric dipole is detected at  $\theta = 90^\circ$ . The relationship is opposite in p-polarized light illumination, leading to the detection of contribution only from the magnetic dipole.

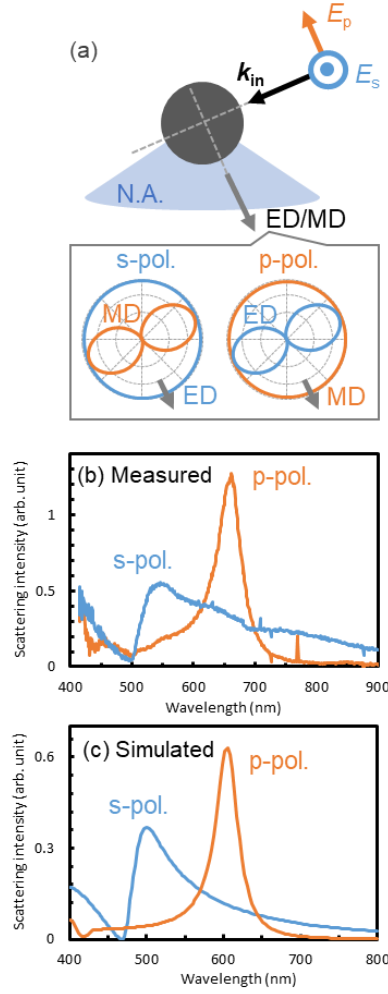


Figure 6-5. Selective detection of electric and magnetic dipole Mie resonances. (a) Schematics showing how the selective detection can be achieved. The bottom panels are radiation patterns of electric and magnetic dipoles under *s*- and *p*-polarized light illumination. (b) Measured and (c) simulated scattering spectra.

Theoretically, the behavior can be described using the Mie theory.[90] In the Mie theory, the multipolar contributions can be expressed using Mie coefficients of  $n$ -th order  $a_n$  and  $b_n$  which corresponds to electric and magnetic resonances, respectively. The normalized scattered field  $E_s$  by a sphere with size parameter  $\rho$  in free space is given by

$$E_{s\theta} = \frac{\cos \phi}{\rho} \sum_{n=1}^{\infty} E_n (ia_n \xi'_n \tau_n(\cos \theta) - b_n \xi_n \pi_n(\cos \theta)) \quad (6-1)$$

$$E_{s\phi} = \frac{\sin \phi}{\rho} \sum_{n=1}^{\infty} E_n (b_n \xi_n \tau_n(\cos \theta) - i a_n \xi'_n \pi_n(\cos \theta))$$

, where  $a_n$  and  $b_n$  are the Mie coefficients of  $n$ -th order,  $E_n = i^n(2n+1)/n(n+1)$ ,  $\xi_n$  is the Riccati-Bessel function,  $\pi_n$  and  $\tau_n$  are the angle dependent functions.[27]  $E_{s\theta}$  and  $E_{s\phi}$  denote the scattered field with polarizations orthogonal each other. Because now we are interested in the case of  $\theta = 90^\circ$  and dipole modes ( $n = 1$ ), the angle dependent functions are given by  $\pi_n = 1$  and  $\tau_n = 0$ . Also, s- and p-polarization corresponds to  $\phi = 90^\circ$  and  $\phi = 0^\circ$ , respectively. We thus get the scattering intensity by  $I_{sca} = |E_{s\theta}|^2 + |E_{s\phi}|^2$ , and it can be written as

$$\begin{aligned} I_{sca}^s &= \left| \frac{1}{\rho} E_1 (-i a_1 \xi'_1) \right|^2 \\ I_{sca}^p &= \left| \frac{1}{\rho} E_1 (-b_1 \xi_1) \right|^2. \end{aligned} \tag{6-2}$$

Therefore, the scattering intensities in the measurement condition have only contribution from the electric ( $a_1$ ) or magnetic ( $b_1$ ) dipole depending on the polarization states s- or p-, respectively.

Supported by the theoretical description, we found that we can determine the contributions of electric and magnetic dipoles separately in the scattering spectrum. The scattering spectra at  $\theta = 90^\circ$  are extracted from the Figure 6-4a,d and shown in Figure 6-5b. The corresponding simulated spectra are also shown in Figure 6-5c. We see that the measured spectra of s- and p-polarization have features of electric and magnetic dipoles in good agreement with the simulation.

## 6.4. Conclusion

In conclusion, we have demonstrated the angle- and spectrally resolved scattering measurement on a single Mie resonant nanoantenna using Fourier-plane spectroscopy. By adding facile modification on a conventional dark-field optical microscope and spectroscopy equipment, the measurement setup which is capable of the angle-resolved spectroscopy for the single nanoparticle has been developed. The constructed setup has been applied to the directionality measurement of a silicon nanosphere, and the capability to evaluate angular information in wide angular range has been demonstrated. As another advantage of this method, we experimentally and theoretically proposed that electric and magnetic dipole contributions to the scattering spectrum of the single nanosphere can be separately measured by our setup. To the best of our knowledge, this is the first report on the selective detection of electric and magnetic dipole contributions of a single Mie resonator in the scattering spectrum and under incoherent planewave excitation. Because it does not require any special equipment such as laser or prism but just apertures and some additional lenses, the developed method may be utilized for optical characterization of various nanoantennas.

## Chapter 7

# Controlling Emission Directionality of monolayer WS<sub>2</sub> with Spherical Mie Resonator

One of the most important function of optical nanoantennas is directionality control of emission from nearby emitters. Recently emerged Mie resonators has drawn much attention due to the possession of magnetic resonances in addition to electric ones and resultant Kerker type directional scattering under plane wave illumination. However, little has been reported on the control of emission directionality by individual Mie resonators, especially three dimensionally sub-wavelength structure such as nanospheres.

In Chapter 7, we give an in-depth study on the emission directionality of emitters below Mie resonant silicon nanospheres. We start from theoretical analysis for the ideal system consisting of a silicon nanosphere and a point dipole source on the sphere surface by rigorously evaluating radiated field in the same manner with the classical Mie theory. We then demonstrate the directional emission experimentally by placing the colloidally synthesized silicon nanospheres on monolayer WS<sub>2</sub> which is as an ideal emitter. From theoretical and experimental results, it is shown that the directional emission occurs due to the cancellation of emission in bottom direction as a result of far-field interference between the source dipole and coherently excited electric and magnetic dipole Mie resonances.

### 7.1. Introduction

Atomically thin transition metal dichalcogenides (TMDCs) are attracting great attentions for photonic, electronic, and optoelectronic devices because of their unique physical properties such as the strong, stable, and tunable excitonic behaviors, high electron mobility, and valley selectivity.[222]–[229] Among those phenomena, the emergence of strong photoluminescence (PL) in some monolayer TMDCs (1L-TMDCs; *e.g.*, MoS<sub>2</sub>, MoSe<sub>2</sub>, WS<sub>2</sub>, WSe<sub>2</sub>) make them extremely fascinating and has been widely studied in recent years.[230]–[232] The strong PL which lays in visible and near-infrared spectrum originates from the direct band gap transition governed by bounded excitons with two-dimensional quantum confinement.[233] Because the two-dimensional excitons are strictly oriented in-plane, and exhibit strong oscillator strength, 1L-TMDCs not only work as an alternative of conventional emitters, such as organic dye or quantum dots, but also ideal emitters to study electromagnetic coupling with various photonic structures.[231], [234]

A variety of coupled systems consisting of 1L-TMDCs and photonic structures are reported to improve the performance and/or give new functionalities. For example, several optical microcavities, such as Fabry-Perot[235], [236], distributed Bragg reflectors (DBRs)[237], [238], photonic crystal[239], and Whispering gallery mode[240], [241], have been proposed to demonstrate the control of radiative lifetime and lasing action. Nano-resonators made of noble metals and high-index semiconductors have been also utilized to study the interaction with 1L-TMDCs in the subwavelength scale. Employing their advantages developed as plasmonics, such as the ultrasmall mode volume, the hybrid structure consisting of metal nanostructures and 1L-TMDCs have demonstrated plasmon-exciton couplings ranging from weak to strong couplings.[231], [234] Likewise, recently emerged high-index semiconductor nanostructures

have been coupled with 1L-TMDCs, and the interaction with Mie resonances and resultant effects, for example PL enhancement, has been reported.[214], [242], [243] In contrary to the plasmonic ones, the Mie resonance offers the low-loss optical resonances of electric and magnetic dipoles and higher order modes. The possession of the multipole resonances makes it particularly unique due to the ability to control emission directionality of nearby emitters even by a single resonator.[105], [108], [244] So far, the emission directivity control of the 1L-TMDCs by Mie resonators have been experimentally demonstrated using the silicon nanowire and the metasurface made of nanocylinder array.[108], [214]

Contrary to previous works engaging one- (nanowire) or two- (metasurface) dimensional systems, which require optically finite structure in at least one dimension, here we study the ability of a single spherical Mie resonator to control the emission directionality of the 1L-TMDC with the three-dimensionally subwavelength footprint. The emission directionality by a silicon nanosphere has been theoretically predicted in ref.[105] for the ideal case, that is, an electric dipole emitter is transversely coupled to a sphere that is dominantly characterized by electric and magnetic dipolar response. Go beyond their prediction, we start from analyzing the emission directionality by modifying the classical Mie theory[90] for the excitation by an electric dipole source. Through the rigorous calculation including multipolar contribution, it is shown that the coherent excitation of the electric and magnetic dipole modes suppresses the emission in bottom direction and redirects into top. Based on the theoretical analysis, we then experimentally demonstrate the emission directionality in the system fabricated by placing colloiddally synthesized silicon nanospheres of 50–100 nm in radius on a monolayer  $\text{WS}_2$  (1L- $\text{WS}_2$ ) covering a silica substrate. Due to the coupling of the exciton emission with Mie resonances, the

enhancement factor of top-to-bottom (T/B) ratio reaches 3.2 when the radius of the nanosphere matches the directionality condition. Although we demonstrate the emission directionality of the 1L-WS<sub>2</sub> in this work, the proposed directionality mechanism can be applied to various emitters because the resonances of the silicon nanosphere can be tuned over the visible and near-infrared spectrum.

## 7.2. Results and discussion

**Theoretical analysis.** According to the classical Mie theory, the scattering efficiency of a nanosphere of radius  $R$  is given as

$$Q_{\text{scat}}^{\text{Planewave}} = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1)(|a_n|^2 + |b_n|^2) \quad (7-1)$$

, where  $x = \frac{2\pi}{\lambda}R$ , and  $a_n$  and  $b_n$  are the Mie coefficients which describe contributions from electric and magnetic multipoles.[27], [90] Similarly, the scattered field under excitation of a point dipole can also be calculated by modifying the Mie theory.[245], [246] The calculation model for the modified Mie theory is shown in Figure 7-1a. The sphere is excited by a point dipole ( $\mathbf{p}_{\text{inc}} = p\mathbf{e}_x$ ) located on the z-axis with a distance  $d$  to the surface of the sphere. The dipole moment is oriented along the x-axis, which corresponds to a dipole in the plane of the 1L-TMDCs. The scattering efficiency can be obtained by dividing the scattered power by the incident power as well as the classical Mie theory:

$$Q_{\text{scat}}^{\text{Dipole}} = \frac{3}{4x_s^2} \sum_{n=1}^{\infty} (2n+1)(|a_n|^2|\xi_n(x_s)|^2 + |b_n|^2|\xi'_n(x_s)|^2) \quad (7-2)$$

, where  $x_s = \frac{2\pi}{\lambda}(R + d)$ , and  $\xi_n(z) = zh_n^1(z)$  is the Riccati-Bessel function ( $h_n^1(z)$  denotes the spherical Hankel function of first order). For the dipole case, each of the electric and magnetic resonant contribution has the Riccati-Bessel function as a distance-dependent weighting factor.

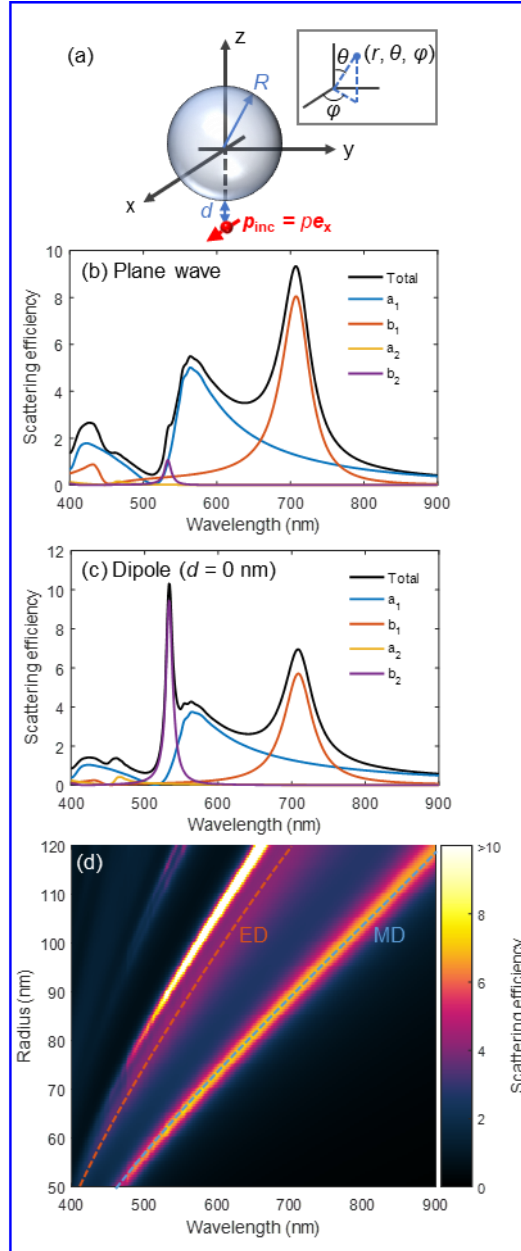


Figure 7-1. Scattering properties of a silicon nanosphere under plane wave and dipole excitations. (a) Calculation setup, consisting of a nanosphere of radius  $R$  and a dipole at distance  $d$  from the nanosphere surface, for dipole excitation. The definition of the spherical coordinate is shown in the inset. (b,c) Scattering efficiencies and the multipolar contributions, the electric dipole  $p$ , magnetic

dipole  $m$ , electric quadrupole  $q_e$ , magnetic quadrupole  $q_m$ , of a nanosphere with  $R = 90$  nm and  $d = 0$  nm under (b) plane wave and (c) dipole excitations. (d) Two-dimensional map of scattering efficiency as a function of  $R$  and wavelength under dipole excitation.

The calculated scattering spectra of a silicon sphere ( $R = 90$  nm) for plane wave and dipole ( $d = 0$  nm) excitation are shown in Figure 7-1b and c together with the contributions of multipole resonances, electric dipole ( $a_1$ ), electric quadrupole ( $a_2$ ), magnetic dipole ( $b_1$ ), and magnetic quadrupole ( $b_2$ ). The refractive index of silicon is taken from literature.[7] As expected from eq. 1 and 2, the resonances are excited at the same wavelengths, while the amplitudes are different. For example, the magnetic quadrupole mode is excited efficiently when the dipole is placed very close to the sphere. The radius dependence of the scattering efficiency under dipole excitation is shown in Figure 7-1d. As well as the case of plane wave excitation, the resonance wavelengths goes longer for larger sphere.

In order to study the emission directionality of this dipole-nanosphere system, we calculate the angular emission intensity in the far-field as a total of the incident ( $\mathbf{E}_{\text{inc}}$ ) and scattered field ( $\mathbf{E}_{\text{sca}}$ ). Within the modified Mie theory, the total emission intensity is written as

$$I_{\text{tot}}(\theta, \phi) = |\mathbf{E}_{\text{inc}} + \mathbf{E}_{\text{sca}}|^2$$

$$= \left| \frac{k^2 p}{4\pi\epsilon_0 x_s} \sum_n E_n \{ \cos\phi (\beta_n \pi_n + i\alpha_n \tau_n) \mathbf{e}_\theta \right. \quad (7-3)$$

$$\left. - \sin\phi (\beta_n \tau_n + i\alpha_n \pi_n) \mathbf{e}_\phi \} \right|^2$$

, where  $\pi_n$  and  $\tau_n$  are the angle-dependent function of the classical Mie theory.[27] Modified Mie coefficients defined as  $\alpha_n = \psi'_n(x_s) - a_n \xi'_n(x_s)$  and  $\beta_n = \psi_n(x_s) - a_n \xi_n(x_s)$ , where  $\psi_n(z) = z j_n(z)$  is the Riccati-Bessel function ( $j_n(z)$  is the spherical Bessel function), are used

for better understanding of the formula. In this work, we evaluate the directionality as the ratio of the top ( $I_{\text{tot}}(0, 0)$ ) to bottom ( $I_{\text{tot}}(\pi, 0)$ ) emission intensity; (T/B) ratio. Two-dimensional color plot of the T/B ratio as a function of wavelength and radius is shown in Figure 7-2a. The first band of high T/B ratio appears across whole visible wavelength range for different radii. Several additional bands also appear in 400 to 500 nm wavelength range, but they cannot be accessed by the emission of 1L-WS<sub>2</sub> (shaded wavelength range in Figure 7-2a) on which we are focusing in this work. Given that the emission peak of the monolayer WS<sub>2</sub> is at ~630 nm as will be shown later, the silicon nanosphere with radius of 90 nm would result in the highest directionality (T/B ratio ~6). At this condition, the point marked with a star in Figure 7-2a, the radiation pattern of  $I_{\text{tot}}(\theta, \phi)$  is calculated in Figure 7-2b, revealing the directional emission into top direction. Although we are not focusing in this work, we note that the directionality can be boosted more than an order of magnitude by tuning the distance between the dipole and the nanosphere.

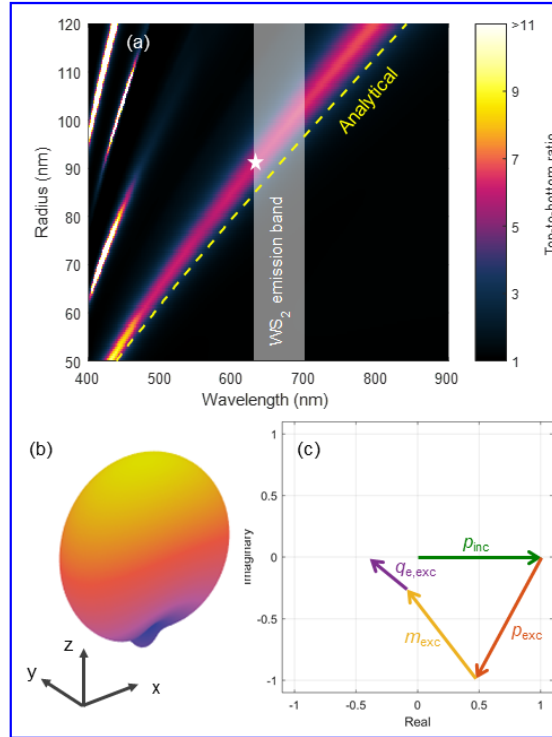


Figure 7-2. Directional emission of a point dipole under a nanosphere ( $d = 0$  nm). (a) Top-to-bottom emission ratio (T/B ratio) as a function of  $R$  and wavelength. Analytically obtained directionality condition is plotted by yellow dashed line. The vertical shaded area indicates the emission band of  $WS_2$ . (b) Radiation pattern and (c) phasor diagram of electric field in the backward direction of the dipole-sphere pair at the point indicated by a star in (a):  $R = 90$  nm and emission wavelength of 630 nm. Labels indicates the contribution of each multipoles: source dipole  $p_{inc}$  and excited electric dipole  $p_{exc}$ , magnetic dipole  $m_{exc}$ , and electric quadrupole  $q_{e,exc}$ .

The mechanism of this directionality can be analyzed by decomposing the total electric field in backward direction ( $\theta = \pi$ ) in the far-field. The phasor diagram of the complex electric field from relevant contributions in Figure 7-2c shows that the incident electric dipole ( $p_{inc}$ ) is cancelled out in backward direction mainly by the coherently excited electric and magnetic dipoles of the nanosphere. The excitation of electric quadrupole also has certain influence, but the disturbance by it is trivial. It is worth to note that the cancellation of the incident electric dipole only by the excited electric dipole, which is the first mechanism of the directionality reported on a silicon nanowire[108], does not happen in the case of nanosphere because the magnetic dipole is the lowest order resonance in the nanosphere.

Based on the above observation, we analytically derive the directionality condition of the nanosphere using the modified Mie theory. From eq. (7-3), the top-to-bottom ratio ( $\eta$ ) is expressed by

$$\eta = \frac{I_{tot}(0, 0)}{I_{tot}(\pi, 0)} = \frac{|\sum_n E_n \{\beta_n \pi_n(-1) + i\alpha_n \tau_n(-1)\}|^2}{|\sum_n E_n \{\beta_n \pi_n(0) + i\alpha_n \tau_n(0)\}|^2}. \quad (7-4)$$

Thus, the maximum in  $\eta$  occurs when

$$\sum_n E_n \{\beta_n \pi_n(0) + i\alpha_n \tau_n(0)\} = 0 \quad (7-5)$$

is satisfied. Since only the dipole resonances are matters as the above discussion, the directionality condition in dipolar approximation:

$$\beta_1 = -i\alpha_1 \quad (7-6)$$

can be obtained. This is the form of the generalized first Kerker condition.[105], [247] Go beyond this simple expression, we expand the equation in order to explore, for example,  $x_s$  dependence more easily:

$$\arg \left[ x_s^3 \exp(-i2x_s) + \frac{3}{2}a_1(ix_s^2 - x_s - i) \right] = \arg \left[ \frac{3}{2}b_1x_s(ix_s - 1) \right]. \quad (7-7)$$

This analytically obtained directionality condition is plotted in Figure 7-2a with yellow dashed line. It clearly captures the trend of the high T/B band. A bit of discrepancy would be resulted by the excitation of the electric quadrupole as shown in Figure 7-2c. The condition reproduces the high T/B band more accurately when the source dipole is moved away from the sphere surface and the contribution of the electric quadrupole is smaller.

**Experimental Demonstration of the Directional Emission.** Based on the theoretical analysis above, here we apply the spherical Mie resonator to exciton emission of the 1L-TMDC and demonstrate the directional emission. Figure 7-3a shows the schematic illustration of the experimental configuration. We use commercially available 1L-WS<sub>2</sub> covering the full area of SiO<sub>2</sub> substrate (10×10 mm<sup>2</sup>; 2D Semiconductors Inc.) as the 1L-TMDC emitter. A colloidal solution of silicon nanospheres (100 – 200 nm in diameter) is drop-cast over the 1L-WS<sub>2</sub>. In order to remove the uncoupled emitters around the nanosphere, Ar<sup>+</sup> plasma etching is applied using the nanosphere itself as an etching mask.

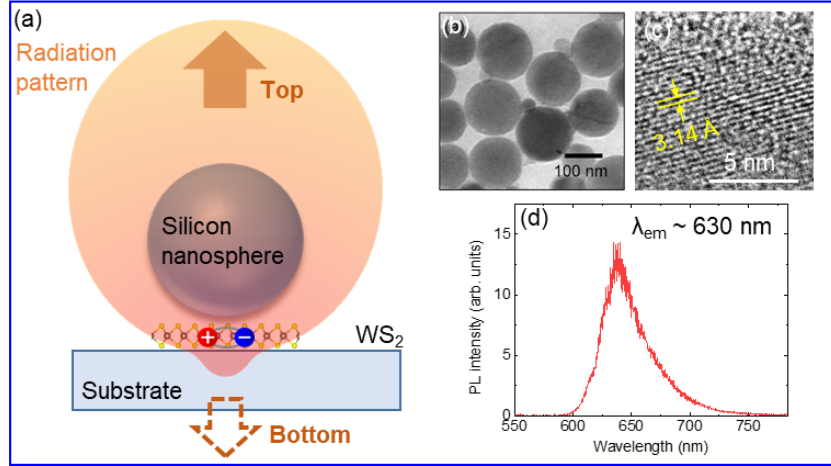


Figure 7-3. (a) Schematic of a silicon nanosphere on a monolayer  $WS_2$  coated substrate. (b) TEM and (c) HRTEM images of colloidal silicon nanospheres. (d) PL spectrum of a monolayer  $WS_2$  coated on silica substrate before etching.

Shown in Figure 7-3b is a transmission electron microscope (TEM) image of the silicon nanospheres. We can see that the shape of them are perfectly spherical. Additionally, a high-resolution TEM image in Figure 7-3c shows the lattice fringes corresponds to  $\{1\ 1\ 1\}$  plane of the silicon crystal, indicating high crystallinity of this material. These results prove that this silicon nanosphere is an ideal spherical Mie resonator, allowing us to predict the scattering and emission behavior including the directionality using the Mie theory into which the refractive index of bulk crystalline silicon is incorporated. The PL spectrum of reference 1L- $WS_2$ , *i.e.*, without the nanosphere, was measured using a confocal microscope via objective in top direction under excitation with 485 nm semiconductor laser (see METHOD) and is shown in Figure 7-3d. The strong emission peak is observed at 630 nm. The spectral feature agrees with that of 1L- $WS_2$  in literature[248], and it can be assigned to the A-exciton peak of the 1L- $WS_2$ . Hereafter, the PL signals were detected with avalanche photo diodes (APDs) via two objectives situated in top and bottom direction, integrating over the whole A-exciton peak.

Figure 7-4a shows a dark-field microscope image of the fabricated structure. Each hybrid structure consisting of the nanosphere and 1L-WS<sub>2</sub> strongly scatters light at the resonance wavelength depending on the nanosphere radius, for example, the blue, green, and red scattering colors correspond to the radii around 60, 75, and 100 nm, respectively. As will be shown later, this size variation of the nanospheres provides information on size dependence of the emission directionality. The PL mapping (top direction) of the same view is shown in Figure 7-4b. In good agreement with the position of the nanospheres on the dark-field scattering image, the bright spots appear in the PL mapping, proving successful removal of uncoupled emitters around nanospheres. In order to discuss optical responses of the coupled structure, we chose a typical nanosphere as marked in Figure 7-4a. The measured backward scattering spectrum is shown in Figure 7-4c by a black line. The scanning electron microscope (SEM) image is also shown in the inset. In accord with the scattering spectrum obtained by the classical Mie theory (Figure 7-1b), two dominant peaks appear in the long wavelength range, which can be assigned to magnetic (760 nm) and electric (650 nm) dipole modes. The higher order modes ( $n > 2$ ) are also excited in the short wavelength range. The measured spectrum is compared to the calculated backward scattering spectrum obtained by FDTD simulation for a silicon nanosphere of 99.5 nm in radius on a silica substrate (red dashed line alongside the measured data in Figure 7-4c), showing overall agreement each other.

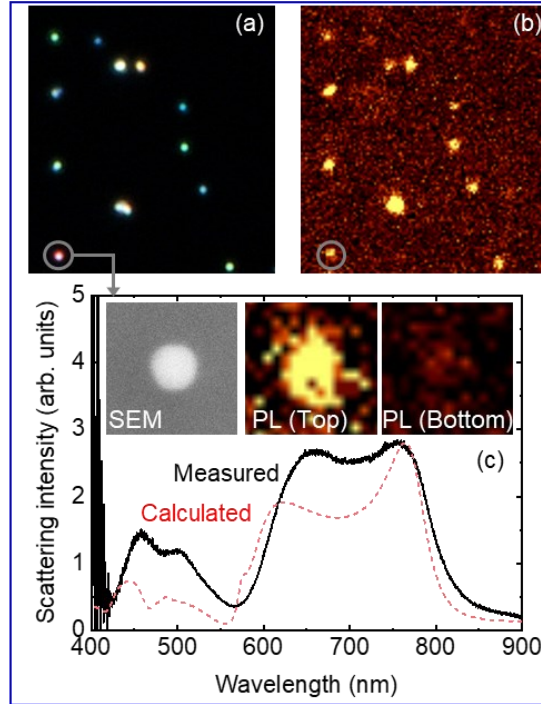


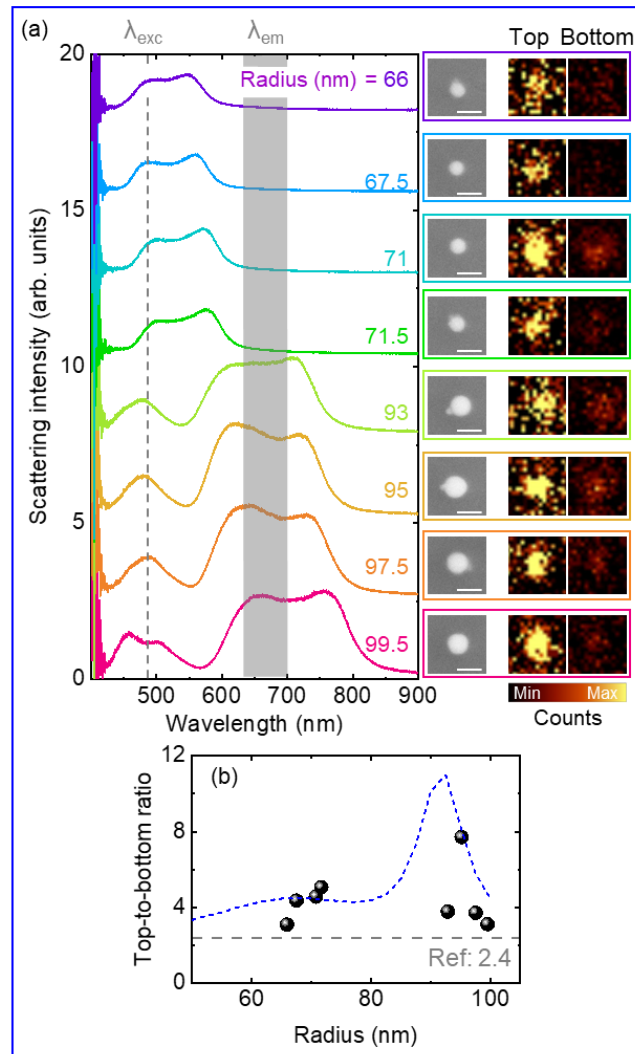
Figure 7-4. Experimentally measured scattering and PL properties of a silicon nanosphere on monolayer  $WS_2$  system. (a) Dark field scattering image. (b) PL mapping in the top direction at the same area corresponding to (a). (c) Measured and calculated scattering spectra of a single silicon nanosphere. Insets are the SEM, PL (Top), PL (Bottom) images of the particle.

The emission directionality of the nanosphere is evaluated by measuring top and bottom PL mappings via top and bottom objectives (both of them are  $50\times$  and N.A. = 0.55) and calculating T/B ratio by dividing them after integration of the PL signals (see METHOD). Note that the N.A. of the top and bottom objectives are same, but there is inherent asymmetry in the top and bottom detection due to different detection setups and the substrate induced refraction. We thus corrected the system response so that the T/B ratio of reference 1L- $WS_2$  (without nanospheres) to be 2.4, which had been obtained by FDTD simulation for a point dipole placed on a silica substrate (see METHOD). The top and bottom PL mappings of the same nanosphere whose scattering spectrum were measured are shown in insets of Figure 7-4c. As can be seen

clearly, the PL intensity taken from the top is stronger than that of the bottom. The T/B ratio reaches 3.1, while that of the reference 1L-WS<sub>2</sub> is 2.4. This is the indication of the PL enhancement in the top and the suppression in the bottom due to the coupling of 1L-WS<sub>2</sub> with the nanosphere.

From the above discussion based on analytical calculation (Figure 7-2a), the directionality is dependent on the nanosphere radius. To explore the radius dependence experimentally, we carried out scattering and PL measurement on many nanospheres with various radii (Figure 7-5). The scattering spectra are shown in Figure 7-5a with SEM images and top and bottom PL mappings. The radii were determined by comparing the measured and simulated peak wavelengths of magnetic dipole resonances, and they were from 66 to 99.5 nm. For small nanospheres, both of the electric and magnetic dipole resonances appear in shorter wavelengths than the 1L-WS<sub>2</sub> emission wavelength. As the nanosphere radius is increased, the resonances red-shift across the emission wavelength. The top and bottom PL images of each nanosphere are also shown next to the spectra. Note that each set of top and bottom PL images have the same color scale, while the contrast is adjusted for every nanosphere for better visualization. In the whole radius range, PL spots from the 1L-WS<sub>2</sub> are observed in the top, while the emission is barely detected in the bottom. In order to quantitatively evaluate the directionality, T/B ratios are calculated and plotted by black dots in Figure 7-5b. As can be seen, the T/B ratio exceeds the reference line (2.4, gray dashed line) in all measurement points due to the redirection of emission by the nanosphere. The highest T/B ratio reaches 7.7 (*i.e.*, 3.2-fold enhancement) when the nanosphere radius is 95 nm, at which the electric and magnetic dipole resonances overlap each other. These results agree with the analytical calculation on ideal configuration (*i.e.*, a silicon

nanosphere with a point dipole in free space) as discussed above and the FDTD simulation on experimental configuration (blue dashed line in Figure 7-5b), that is, including the substrate and the asymmetry of our detection system. Therefore, it can be concluded that we observed the directional emission by the interference of electric and magnetic dipole resonances. The small deviation between the experiment and simulation can be resulted by the imperfection of the fabricated structure, for example, adhesion of small silicon particles and the inhomogeneity in the etching process as the non-spherical PL spots imply.



*Figure 7-5. (a) Scattering spectra of silicon nanospheres with various radii on WS<sub>2</sub> and corresponding SEM images and PL mappings measured in top (left panel) and bottom (right panel) directions. The gray dashed line and shaded area indicate excitation wavelength (485 nm) and emission band of 1L-WS<sub>2</sub>. The scale bars in SEM images are 250 nm. (b) Measured (scatter) and simulated (blue dashed line) top-to-bottom (T/B) PL ratios of nanospheres as a function of the diameter. The measured data are normalized as the T/B ratio without nanosphere to be 2.4 (gray dashed line).*

### 7.3. Conclusion

In conclusion, we have proposed the directional control of the emission of a monolayer WS<sub>2</sub> with a single spherical Mie resonator. Based on the Mie theory modified for a dipole excitation, it is derived that the directional emission occurs by the interference of the electric and magnetic dipole resonances. The proposed directionality has also been demonstrated experimentally by integrating colloidally synthesized silicon nanospheres onto the monolayer WS<sub>2</sub>. The observed enhancement factor of T/B ratio reaches 3.2 with a nanosphere whose directionality condition matches the emission wavelength. The resonance wavelengths and the resultant directionality condition can be easily tuned by the nanosphere radius spanning visible and near-infrared spectrum, suggesting the applicability of the spherical Mie resonators to a wide range of materials including quantum emitters and their application, such as single-photon sources.

### 7.4. Method

**Sample fabrication.** The silicon nanosphere was synthesized with the previously reported method.[193] Briefly, a boron and phosphorus doped silicon rich-silicon oxide film was deposited by sputtering. The film was then annealed at 1500°C for 30 minutes in nitrogen

atmosphere to grow silicon nanospheres in silicon dioxide matrix. By etching the matrix by HF and transferring into methanol, the colloidal solution of silicon nanosphere was obtained. The silicon nanosphere was placed on 1L-WS<sub>2</sub> by drop-casting the colloidal solution on a silica substrate covered by 1L-WS<sub>2</sub> (2D Semiconductors Inc.). The sample was then exposed to Ar<sup>+</sup> plasma (Oxford PlasmaPro 80) in order to remove uncoupled excitons around the nanospheres.

**Scattering and PL spectroscopy.** Scattering spectra were measured by a Nikon C1 confocal microscope equipped with a halogen light. The light was epi-illuminated on the sample through 50x objective (N.A. = 0.80). The scattered light was collected by the same objective and transferred to a fiber coupled monochromator (Princeton Instruments) with a CCD after spatial filtering by an aperture in the confocal head. The PL measurement was performed with a WiTec alpha 300 confocal microscope equipped with two objectives (50x, N.A. = 0.55) in top and bottom directions. For the excitation, 485 nm picosecond pulsed laser (PicoQuant) was used via the top objective. The laser power was reduced to 140  $\mu$ W to avoid heating effects. The system in top direction path consists of the objective (Nikon), a long pass filter, a fiber with a 25  $\mu$ m core diameter, and an APD (Micro Photon Devices). That in bottom direction path consists of the objective (Zeiss), a long pass filter, and a free-space-coupled APD (Micro Photon Devices). The PL spectrum was measured in top direction path with a fiber-coupled monochromator (Princeton Instruments) and CCD (Andor). Given the inherent asymmetry of the detection system, the top and bottom PL intensities were calibrated as the T/B ratio of the 1L-WS<sub>2</sub> without nanospheres to be 2.4, which is the value simulated by the FDTD method for a point dipole on a SiO<sub>2</sub> substrate as explained in the following paragraph. The T/B ratio of the 1L-WS<sub>2</sub> with the silicon nanosphere

was calculated by integrating top and bottom PL intensities over the area of  $2 \times 2 \mu\text{m}^2$  and dividing them.

**FDTD simulation.** Commercially available software (FDTD Solutions, Lumerical Inc.) was used for FDTD simulations. The refractive index of silicon was taken from the literature[7], and the indices of 1L-WS<sub>2</sub> and silica substrate were set to 4.5 and 1.46. In order to simulate emission directionality, the radiated field of a dipole source placed in WS<sub>2</sub> layer of 1 nm in thickness was captured by two 2D monitors in the top and bottom direction. The T/B ratio was obtained by integrating the Poynting vector over detection angle corresponds to N.A. = 0.55 after the near to far-field transformation of the captured fields. The T/B ratio of a dipole on a substrate without nanosphere, which was used to calibrate the asymmetry of the measurement setup, was simulated in the same manner but without the nanosphere.

## Chapter 8

# A Colloidal Solution of Silicon Nanospheres toward All-Dielectric Metafluids

### 8.1. Introduction

Permittivity ( $\epsilon$ ), permeability ( $\mu$ ), and their product, refractive index ( $n$ ), are key parameters which describe macroscopic response of materials to electromagnetic fields. At the optical frequencies, natural materials lack responses to magnetic component of light (*i.e.*,  $\mu = 1$ ), limiting a degree of freedom to manipulate light. Tackling on this issue, recent advancements in the field of metamaterials revealed that artificially fabricated structures enable us to regulate magnetic component of light and to address negative permittivity and/or permeability via displacement currents in, for example, metallic split-ring resonators or dielectric structures.[185], [249] In visible and near-infrared frequencies, two-dimensional arrays of nanostructures which support such optical magnetism are intensively studied as metasurfaces and demonstrated the capabilities to control various properties of light, that is, amplitude, phase, polarization, and wavefront. Such three- or two-dimensional solid-state devices have succeeded in surpassing natural and bulky materials, and interesting phenomena including negative refraction has been demonstrated.

As another research direction, metafluids, artificial fluids in which subwavelength photonic structures are dispersed to tailor light-matter interaction, has been proposed. The central interest in this topic is to achieve unnaturally high, low, or even negative effective refractive indices by designing meta-atoms or meta-molecules which exhibit isotropic optical magnetism

and can control permeability.[250]–[255] A pioneer work was on a composite nanoparticle made of circularly assembled plasmonic nanospheres which exhibits isotropic electric and magnetic dipolar behavior in 2002.[256] Using the *meta-atom*, it was theoretically proposed that negative values of both effective permittivity and permeability can be realized in a meta-atoms dispersed material. Since then, various types of meta-atoms or molecules with optical magnetism have been proposed. So far, most reports on metafluids are about plasmonic ones, including metallic nanoclusters,[257], [258] dielectric nanoparticles decorated with metal nanospheres,[250], [253]–[255], [259]–[261] self-assembled nanorod dimers.[251], [262] Although they show excellent optical behavior theoretically, complicated structures, aggregates in other words, are required for plasmonic nanostructures to have optical magnetism. Due to this limitation, previously reported plasmonic metafluids are suffering from broadening due to inhomogeneity, and their experimentally measured extinction or scattering spectra in most cases deviates from the simulation. Also, the broadening degrades their magnetic responses, and the strengths of magnetic dipole (MD) is much weaker than the electric (D) ones (typically MD/ED ratio < 0.3).

Here in this work, we propose to add a colloidal solution of nanospheres made of high-index semiconductor represented by silicon into a library of optical metafluid which operates in visible and near-infrared spectra. As shown in Figure 8-1, a silicon nanosphere exhibit prominent magnetic dipole Mie resonance whose strength is comparable to electric dipole one. In stark contrast to plasmonic counterparts, the magnetic the Mie resonance naturally occurs in spherical particles without a specific arrangement of constitutions. Several groups have partly proposed the concept of all-dielectric metafluids composed of colloidal dielectric nanoparticles. For example, Cho *et. al.* reported the smooth selenium colloids for optical metafluids. Such a moderate

refractive index material ( $n \sim 3$ ) may work as building blocks for solid state devices; however, it is not suitable for metafluids due to the requirement of the effective medium theory and broad Mie resonance feature as will be discussed later.[252] As most of metasurfaces, silicon is one of the best materials for Mie resonators and is we believe only a candidate which satisfy criteria for optical metafluids.

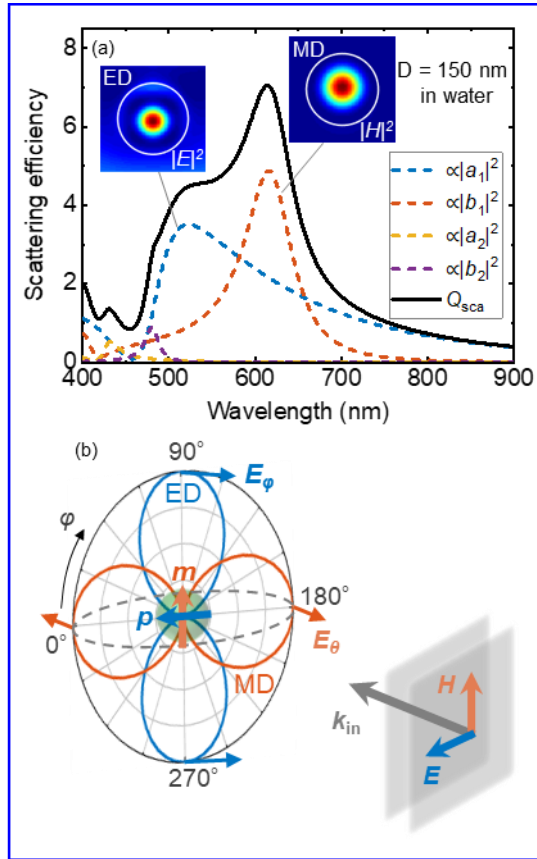


Figure 8-1. Electric and magnetic responses of a single silicon Mie resonator. (a) Scattering efficiency (solid) and its multipolar decomposition (dashed) of a single silicon nanosphere with 150 nm in diameter in water (solid line). The contributions of electric and magnetic dipoles ( $a_1$ ,  $b_1$ ) and quadruples ( $a_2$ ,  $b_2$ ) are shown. (b) Schematic illustration of scattering patterns and orientations of their electric fields of electric ( $p$ , blue) and magnetic ( $m$ , orange) dipoles.

Very recently, we have developed the highly uniform and stable colloidal solution of crystalline silicon nanospheres with a diameter range from 90 to 200 nm.[193], [194] Using the

solution, which is scalable for gram-scale production, we report the selective measurement of electric and magnetic dipolar scattering from bulky all-dielectric metafluids in liquid phase for the first time. Besides, we discuss the controllability of effective permittivity, permeability, and refractive index with all-dielectric metafluids by the effective medium theory, which have seldom studied so far in the optical frequencies.

## 8.2. Theory

The key for the selective measurement of electric and magnetic dipolar contributions stems from the different scattering pattern of them as shown in Figure 8-1b. Because the proposed inclusion has spherical shape, we can predict their optical response with the Mie theory.[90] According to a reference, the scattered electric field polarized along polar ( $E_\theta$ ) and azimuthal ( $E_\varphi$ ) angles at distance  $r$  from a sphere with diameter  $D$  can be written as

$$\begin{aligned} E_{s\theta} &= \frac{\cos \varphi}{\rho} \sum_{n=1}^{\infty} E_n (ia_n \xi'_n \tau_n(\cos \theta) - b_n \xi_n \pi_n(\cos \theta)) \\ E_{s\varphi} &= \frac{\sin \varphi}{\rho} \sum_{n=1}^{\infty} E_n (b_n \xi_n \tau_n(\cos \theta) - ia_n \xi'_n \pi_n(\cos \theta)) \end{aligned} \quad (8-1)$$

, where  $a_n$  and  $b_n$  are the Mie coefficients of  $n$ -th order modes,  $\rho = kr$  with a free space wavenumber in the surrounding medium  $k$ ,  $E_n = i^n E_0 (2n+1)/n(n+1)$ , and  $\xi_n$  is the Riccati-Bessel function.[27] When we consider only dipolar contributions, the angle dependent function  $\pi_n = P_n^1 / \sin \theta$  and  $\tau_n = dP_n^1 / d\theta$  become  $\pi_1 = 1$  and  $\tau_1 = \cos \theta$ . Additionally, if we observe the scattering from  $\theta = \pi/2$ , the latter vanishes. Therefore, equation (8-1) can be simplified, and following equations are led

$$E_{s\theta} = \frac{\cos \varphi}{\rho} E_1(-b_1 \xi_1) \quad (8-2)$$

$$E_{s\varphi} = \frac{\sin \varphi}{\rho} E_1(-ia_1 \xi'_1).$$

Because  $a_1$  and  $b_1$  denote the contributions due to electric and magnetic dipoles, their contribution can be separately determined by measuring scattered light with  $\theta$  - and  $\varphi$  - polarization. Also, equation (8-2) show that they have orthogonal radiation patterns expressed by  $\cos^2 \varphi$  and  $\sin^2 \varphi$ .

### 8.3. Experimental results

The fabrication procedure of the silicon nanosphere forming our metafluid is schematically shown in Figure 8-2a-d. The nanosphere is grown from a commercially available silicon mono-oxide powder by a high-temperature annealing (1450°C) at the temperature higher than the melting point of silicon. Following etching of a silicon dioxide matrix with hydrofluoric acid, they can be dispersed in solutions such as water and alcohol. Finally, almost mono-dispersed colloidal solution is obtained by a size separation process using a density-gradient centrifugation method. A TEM image of typical nanosphere, with average diameter 129 nm, is shown in Figure 8-2e. One can see the highly spherical surface of the synthesized silicon nanospheres (circularity factor~0.97[194]).

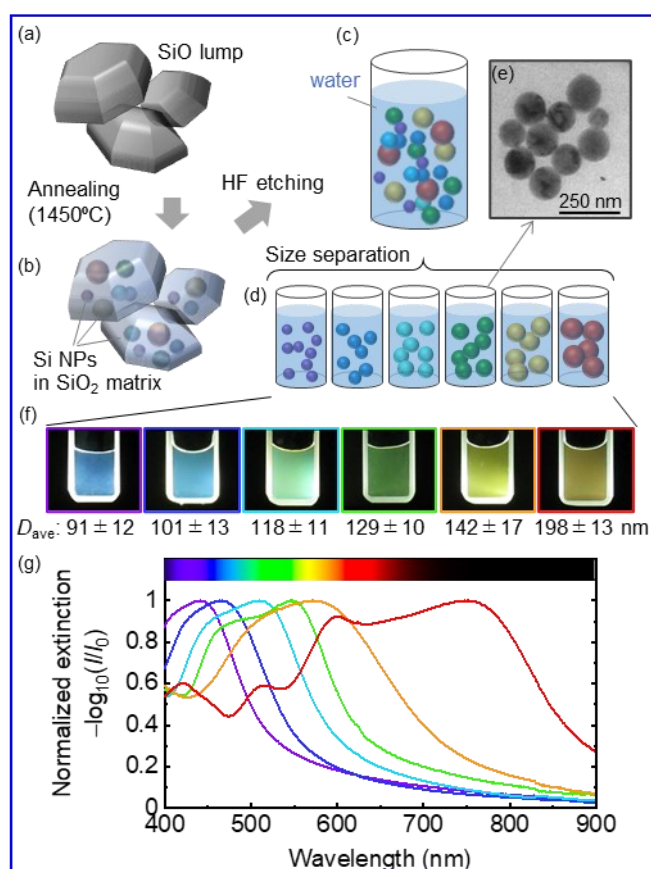


Figure 8-2. Fabrication of colloidal silicon nanospheres. (a-d) Schematics of the fabrication procedure. (e) TEM image of the silicon nanospheres with average diameter of 129 nm. (f) Images of the colloidal silicon nanospheres with different diameters. Corresponding average diameters ( $D_{ave}$ ) and the standard deviations are shown together. (g) Extinction spectra of the solutions. The samples are same as (f), and the line colors correspond to the image's borders.

Figure 8-2f are color images of the produced metafluids, exhibiting beautiful scattering colors by size-dependent Mie scattering depending on the size of silicon nanospheres. Corresponding extinction spectra of the metafluids are shown in Figure 8-2g with line colors same as the borders of the images in Figure 8-2f. We can see that the peak wavelengths can be controlled spanning visible and near-infrared spectra. Note that in addition to scattering, there is slight contribution from absorption. This feature is one advantage to utilize the Mie resonator as a building block of metafluids. Because the resonance wavelengths are determined by the

diameter with approximately linear relationship (e.g.,  $D/(\lambda/n) \sim 1$  for a magnetic dipole resonance), the operation frequencies of all-dielectric metafluids can be easily tuned over range in contrast to plasmonic ones whose resonance is ruled by a plasma frequency of a constituting metal. Here we determined the average diameter and standard deviation of the containing nanospheres by fitting the measured extinction spectra with calculated ones using the Mie theory and show them below images of Figure 8-2f. The size distributions are less than 13 % over all samples. For the following experiments, we have chosen three typical metafluids which works at blue ( $D_{\text{ave}} = 101$  nm), green ( $D_{\text{ave}} = 129$  nm), and red ( $D_{\text{ave}} = 198$  nm) spectral ranges.

The angle- and polarization-resolved scattering measurement was carried out to demonstrate the Mie scattering of the macroscopic amount metafluid using the setup shown in Figure 8-3a. The metafluid in a quartz cuvette with a light path length of 10 mm is illuminated by collimated white light from a tungsten-halogen lamp (Ocean Optics LS-1) through a polarizing prism. The light scattered within a half-angle of  $3.6^\circ$  in the perpendicular direction ( $\theta = 90^\circ$ ) is collected by an infinity-corrected lens system and led to a spectrometer equipped with a charge-coupled device (Acton Research Corporation SpectraPro-300i). The polarization of the scattered light was selected by an analyzer inserted in the lens relay. This setup allow us to selectively measure angular distribution ( $\varphi = 0 - 360^\circ$ ) of scattering intensities  $I_\varphi(\varphi) \propto |E_{s\varphi}|^2$  and  $I_\theta(\varphi) \propto |E_{s\theta}|^2$  which correspond to electric and magnetic dipoles, respectively, as was discussed above.

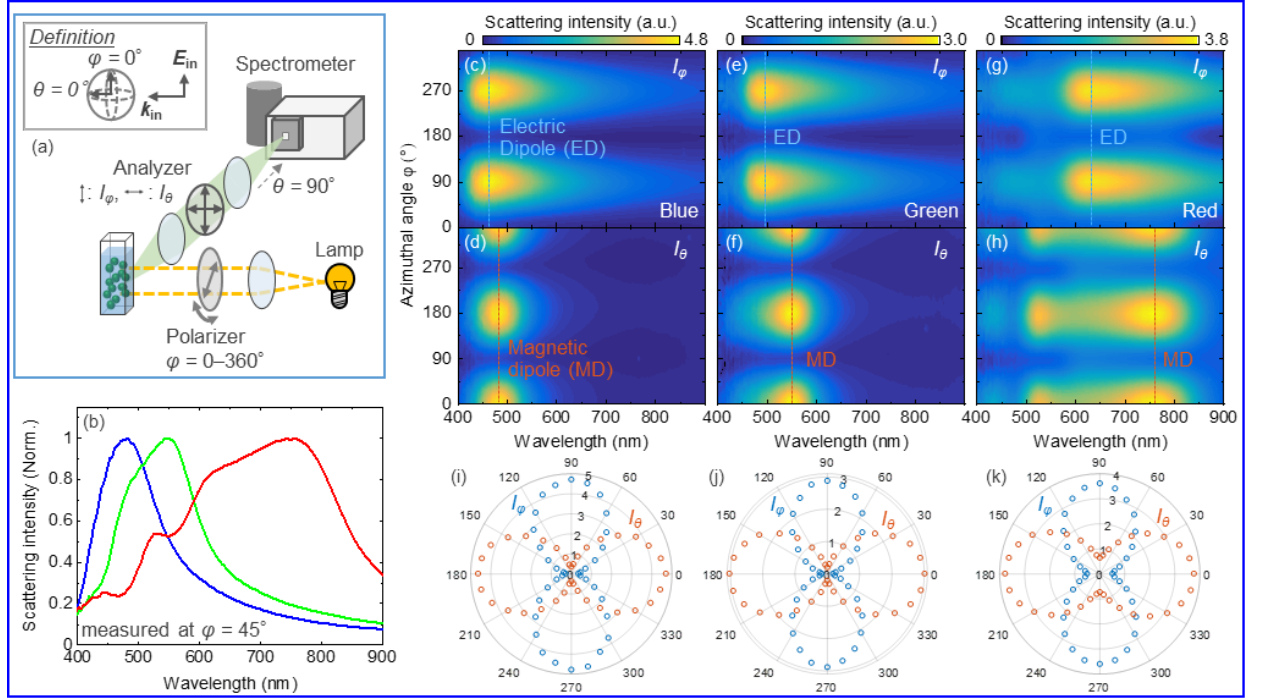


Figure 8-3. Angle- and polarization-resolved scattering spectroscopy. (a) Illustration of the measurement setup. An azimuth ( $\phi$ ) can be changed from  $0^\circ$  to  $360^\circ$  by rotating a polarizer, while a polar angle ( $\theta$ ) is fixed at  $90^\circ$ . (b) Scattering spectra measured at  $\phi = 45^\circ$ . Line colors corresponds to blue, green, and red metafluids. (c-h) Angular scattering maps of  $I_\phi$  (c,e,g) and  $I_\theta$  (d,f,h) for blue (c,d), green (e,f), and red (g,h) as a function of wavelength and azimuthal angle. (i-k) Scattering patterns obtained by slicing the two-dimensional maps of blue (i), green (j), and red (k) metafluids at the peak wavelengths of electric and magnetic dipoles as indicated by blue and orange dashed lines, respectively.

Before proceeding to polarization-resolved measurement, we characterize the blue, green, and red metafluids by scattering spectra measured at  $\phi = 45^\circ$  without the analyzer (Figure 8-3b). Based on the Mie theory, the scattering spectra in this configuration are supposed to be proportional to those of scattering cross section as long as multipoles ( $n > 2$ ) are omitted. As the contribution of absorption does not exist, the spectral shapes are sharper than those in Figure 8-2g, and features of the Mie resonances can be observed more clearly. Note that scattering

measurements throughout this letter is carried out in the regime established by a Lambert-Beer law to exclude disturbance due to multiple scattering.

Two-dimensional scattering maps as a function of azimuthal angle and wavelength are shown in Figure 8-3c-h. For all metafluids, their angular and spectral responses are different between  $I_\varphi$  (Figure 8-3c,e,g) and  $I_\theta$  (Figure 8-3d,f,h). The scattering maps of  $I_\varphi$  have peaks at  $90^\circ$  and  $270^\circ$  with long tail in longer wavelengths, while that of  $I_\theta$  are strongest at  $0^\circ$  and  $180^\circ$ . These features agree with the theoretical prediction and prove that electric and magnetic dipolar scattering have been successively detected in  $I_\varphi$  and  $I_\theta$ , respectively. The rich spectral feature of the red metafluid will be discussed later. To further confirm the electric and magnetic nature of the observed peaks, angular distributions are plotted in Figure 8-3i-k at the peak wavelengths, 465 and 487 nm for blue, 495 and 550 nm for green, and 623 and 757 nm for red metafluids, indicated by dashed lines in the maps. The plots exhibit dipolar radiation patterns which are orthogonal each other, reproducing theoretical prediction perfectly.

Such a high quality metafluid with bulky amount allows us to visually recognize their spectral differences of electric and magnetic nature even with our eyes. Figure 8-4a-c show photographs of the blue, green, and red metafluids taken with a commercial CMOS camera through the analyzer. When  $I_\varphi$  (left) is captured, slightly whitish colors are observed in agreement with broad nature of the electric dipole mode. On the other hand, colors of  $I_\theta$  (right) exhibit highly saturated colors which correspond to the magnetic dipole mode. We further provide detailed analysis of their spectral response in Figure 8-4d-i by comparing measured spectra with theoretical calculation. In the theoretical calculation, we used the Mie theory under the assumption that the size distribution of the silicon nanospheres follows a log-normal function. We find

excellent quantitative agreement between experimental and theoretical spectra on all metafluids, proving the existence of building blocks in ideal situation (*i.e.*, no agglomerates). Trivial deviations of them such as a slight broadening of the measured spectra may come from differences in the size distribution function. The accord allows us to assign peaks with certainty with the help of multipole decomposition of the scattering spectra for a single silicon nanosphere. For the blue and green metafluids, dipolar contributions are dominant, and the assignment is straightforward as shown in the figure. Whereas, the spectrum of the red one is rather rich due to higher order modes ( $n > 2$ ). Nonetheless, the lowest order peaks in each polarization ( $I_\varphi$  and  $I_\theta$ ) are still dominated by dipolar resonances, while additional strong peak at 530 nm arises from electric quadrupole.

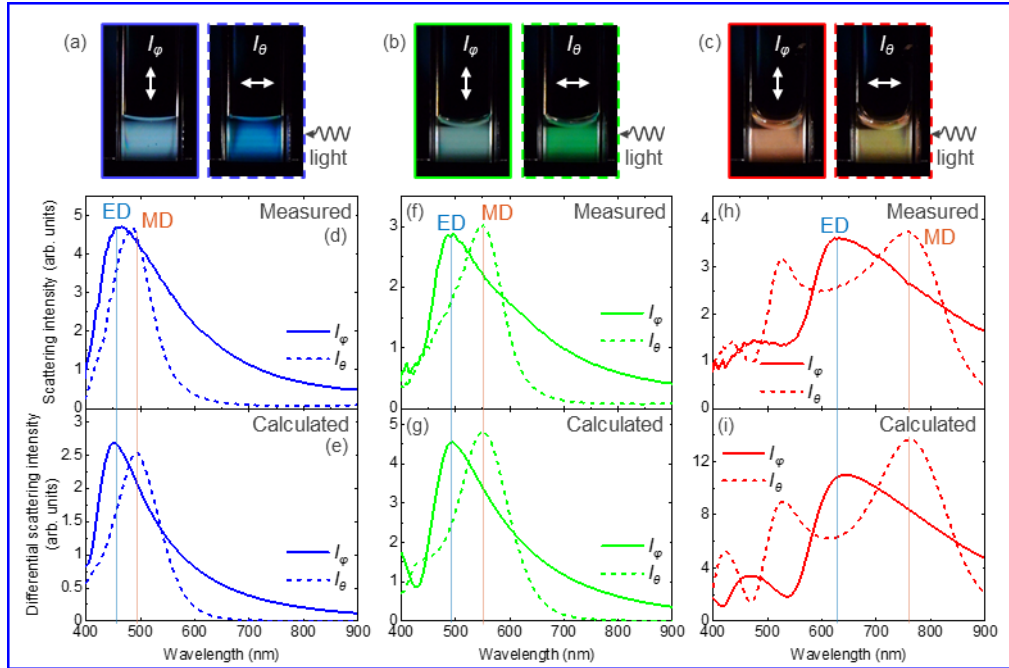


Figure 8-4. Spectral response of metafluids with different sizes. (a-c) Photographs of the blue, green, and red metafluids, exhibiting colors due to electric ( $I_\varphi$ ) and magnetic ( $I_\theta$ ) dipole scattering. (d-h) Measured and (e-i) calculated scattering spectra at detection angles  $(\theta, \varphi) = (90^\circ, 90^\circ)$  for electric dipole and  $(\theta, \varphi) = (90^\circ, 0^\circ)$  for magnetic dipole modes.

So far in this letter, we have demonstrated strong magnetic nature in addition to electric one of our all-dielectric metafluids. Spectrally resolved selective measurements of electric and magnetic dipole strengths in macroscopic amount solution has so far, to the best of our knowledge, not been reported in such a good match between theory and experiment. Also, in most cases, such selective measurements have been carried out at a single wavelength, lacking reliability because electric (magnetic) dipole and magnetic (electric) quadrupole have the same angular and polarization dependences and cannot be separated. Besides, experimentally measured intensity ratios of magnetic-to-electric dipoles (MD/ED ratio) of metafluids are much lower than theoretically predicted values in the previous reports,[251], [254], [255] except for report on a spectrally broadened result[250]. Up to now, the highest MD/ED ratio is about 0.28 on a metafluid made of silver raspberry nanoparticles, even though strong optical magnetism is the key to manipulate effective refractive index in a wide range.[259] As an important achievement of this work, we report the highest MD/ED ratio 1.00, 1.05, and 1.04 for blue, green, and red metafluids (Figure 8-4d-h), which are almost unity and more than three times higher than previous reports. From these experimental results, we claim the first realization of all-dielectric metafluids consisting of silicon nanospheres in solution with excellent performance and feasibility compared to plasmonic counterparts.

#### 8.4. Perspective: optical metafluids as effective media

Having demonstrated electric and magnetic responses of the all-dielectric metafluids as a hallmark, we discuss the possibility to control effective parameters based on an effective medium theory. It is known that the effective medium theory is valid under the condition where a size

parameter ( $x = kD/2$ ) is less than 1, that is, the dimension of inclusion must be smaller than the operation wavelength. Considering a resonant condition of the lowest Mie resonance,  $D/(\lambda/n) \sim 1$ , a lower limit of refractive index for the inclusion of all-dielectric metafluids can be derived as  $n > \pi$ . Accordingly, we argue that nanospheres made of high-refractive-index materials are necessary for all-dielectric metafluids, and silicon is the best one in visible because of its high refractive index  $>3.5$  across visible and near-infrared spectra and even higher index in the wavelength range below 570 nm. Besides, for this reason previously reported meta-atoms made of moderate-refractive-index dielectrics such as selenium[195], [252] and copper oxide[263] are not suitable to control effective parameters of solution in liquid phase.

Justified the use of the effective theory, we estimate effective permittivity  $\epsilon_{eff}$ , permeability  $\mu_{eff}$ , and refractive index  $n_{eff}$  of the all-dielectric metafluid based on the extended Maxwell-Garnett (EMG) theory, which is commonly used for artificial composites where meta-atoms or meta-molecules are randomly dispersed.[264], [265] The calculated results are shown in Figure 8-5. We assumed that silicon nanospheres of 129 nm in diameter, which corresponds to the green metafluid, are randomly dispersed in water ( $n = 1.33$ ) and that near-field interaction and multipolar effects are negligible. In Figure 8-5a, polarizabilities of electric and magnetic dipoles are shown. In agreement with previously reported features, the electric one has long tail, while magnetic one exhibit almost symmetric line shape. It is worth noting here that the polarizability of our inclusion takes a diagonal form thanks to the spherical shape and resultant completely isotropic responses, which is important nature for metafluid. Effective refractive index is plotted in Figure 8-5b as a function of volume fraction ( $f$ ) and wavelength. As can be seen, the metafluid exhibit unnaturally low refractive index (e.g.,  $n = 1.33$ – $1.55$  for naturally occurring fluids) in a

wide volume fraction range around 450–550 nm where electric and magnetic dipole resonances are excited. In particular, we highlight that even near zero index ( $n_{eff} < 1$ ) is achieved in the region  $f < 0.5$  where the inclusion are not assembled into ordered crystals (fluid+crystalline phase) but still in a fluid phase.[258] Note that beyond the  $f$  of 0.5, the EMG calculation is not accurate, and a different approach such as dressed polarizability need to be adopted. The origin of such a notable tunability can be understood by exploring spectral profiles of each effective parameter at  $f = 0.5$  in Figure 8-5c-e. The figures show that the lowest and highest refractive indices coincide with the sweep of permeability, evidencing the indispensable role of strong magnetism supported by the Mie resonance of the high-index semiconductor. Besides, the operation wavelengths of our metafluids can be adjusted across whole visible range by the size (Figure 8-5f), demonstrating stark contrast against plasmonic counterparts.

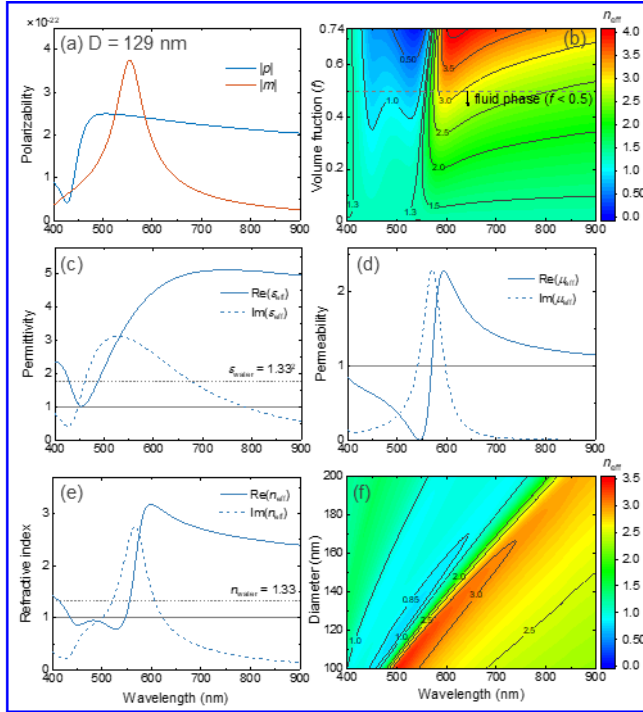


Figure 8-5. Effective medium calculations for the metafluid based on the extended Maxwell-Garnett theory. (a) Polarizabilities of electric ( $p$ , blue line) and magnetic ( $m$ , orange line) dipoles for a 129

*nm silicon nanosphere in water. (b) Effective refractive index as a function of wavelength and volume fraction. (c-e) Effective permittivity (c), permeability (d), and refractive index of the metafluid with volume fraction  $f = 0.5$ . (f) Effective refractive index as a function of wavelength and diameter of the nanosphere ( $f = 0.5$ ).*

## 8.5. Summary

In summary, a concept of all-dielectric metafluid composed of high-refractive-index Mie resonators as building blocks is proposed. We experimentally and theoretically demonstrated a colloidal solution of silicon nanospheres can be an excellent candidate for it in visible and near-infrared spectra. Through the macroscopic measurement of azimuthal angle and polarization resolved scattering spectra, it is directly demonstrated in a bulky solution that the metafluid possesses strong electric and magnetic dipolar responses with comparable strengths (MD/ED = 1). As a stark contrast to previous works on plasmonic metafluids, the measured spectra exhibit perfect agreement with theoretical ones. We also investigated the artificial optical responses of bulk solution under the effective medium theory and found that unnaturally low and even near-zero index ( $< 1$ ) material can be achieved with a reasonable concentration. To the best of our knowledge, this is the first report that experimentally evidences optical magnetism of artificial solution in visible excluding contribution of quadrupoles. In visible and near-infrared frequencies, the investigation is also for the first time on macroscopic effective medium parameters of materials in which Mie resonant building blocks are randomly dispersed. The all-dielectric metafluid may break recent stagnation of plasmonic metafluids, resulted from difficulty of homogeneous production and structural complexity, and open a new way toward tunable index fluids which comport very well with optofluidic devices. The proposed metafluid would also work

as a novel platform to investigate phenomena in fundamental physics which require dual scatterer, for example, Kerker-type multipolar interferences and helicity conservation.[266]

## Chapter 9

### Summary and outlook

In summary, we have developed novel optical nanoantennas including plasmonic and dielectric ones. The plasmonic nanoantennas have been studied based on the metal nanocap structure, and the potential as an antenna was greatly expanded by the coverage control technique, introduction of anisotropy, and hybridization with another plasmonic structure. I believe that the performance of the plasmonic nanocomposite for upconversion enhancement will be further enhanced by combining the approaches developed in this thesis. Besides, we have succeeded in the demonstration of directional scattering and emission with single silicon spherical particles. We have also suggested another research direction which utilize silicon nanospheres as building blocks for bulky effective media, enabling us to realize unnatural optical materials thanks to their optical magnetism.

For the demonstration of the emission directionality, we have utilized the two-dimensional semiconductor as the emitter, but the interference of electric and magnetic dipole Mie resonances is a general approach to achieve the directional emission. One of the interesting strategies in the future is to combine the silicon nanosphere with the upconversion and plasmonic nanocomposites. For example, the plasmon-enhanced upconversion emission may gain directionality due to the coupling with the Mie resonances, suggesting its great potential for spectrum conversion layer of photovoltaics. Such that, we still have several ideas which has never reported so far. Here are some of them which have been found in this Ph.D. study.

- A) Although we did not focus on the illumination direction of upconversion nanocomposites, the asymmetry of the nanocap would result in different multipole contributions depending on the direction which illumination light comes in. Although the difference does not significantly affect the linear response (*i.e.*, scattering cross section), the effect can be boosted in the non-linear response (*i.e.*, upconversion emission).
- B) When we were conducting analytical calculation on the directionality by the modified Mie theory, it was found that the T/B ratio is strongly dependent on the dipole-to-sphere distance by the factor  $>10^2$ . We propose to fabricate thin a silicon dioxide layer on the emitter or around the Mie resonator and maximize the directionality. It is also worthy to note about the experimental setup for directionality measurement. Although two objectives in top and bottom direction have been utilized in this thesis, it would be possible to utilize one objective and measure twice from one and the other side by flipping over the sample.

## References

- [1] L. Novotny and N. van Hulst, “Antennas for light,” *Nat. Photonics*, vol. 5, no. 2, pp. 83–90, Feb. 2011.
- [2] A. E. Krasnok *et al.*, “Optical nanoantennas,” *Uspekhi Fiz. Nauk*, vol. 183, no. 6, pp. 561–589, 2013.
- [3] E. Hecht, *Optics*, 5th ed. Pearson Education, 2017.
- [4] P. Biagioni, J.-S. Huang, and B. Hecht, “Nanoantennas for visible and infrared radiation,” *Reports Prog. Phys.*, vol. 75, no. 2, p. 024402, Feb. 2012.
- [5] M. Agio and A. Alú, Eds., *Optical Antennas*, 1st ed. Cambridge University Press, 2013.
- [6] P. B. Johnson and R. W. Christy, “Optical Constants of the Noble Metals,” *Phys. Rev. B*, vol. 6, no. 12, pp. 4370–4379, Dec. 1972.
- [7] Edward D. Palik, *Handbook of Optical Constants of Solids*. Academic Press, 1997.
- [8] A. F. Koenderink, “Single-Photon Nanoantennas,” *ACS Photonics*, vol. 4, no. 4, pp. 710–722, Apr. 2017.
- [9] S. Bidault, M. Mivelle, and N. Bonod, “Dielectric nanoantennas to manipulate solid-state light emission,” *J. Appl. Phys.*, vol. 126, no. 9, p. 094104, Sep. 2019.
- [10] P. Lalanne, W. Yan, K. Vynck, C. Sauvan, and J.-P. Hugonin, “Light Interaction with Photonic and Plasmonic Resonances,” *Laser Photon. Rev.*, vol. 12, no. 5, p. 1700113, May 2018.
- [11] T. Ming, H. Chen, R. Jiang, Q. Li, and J. Wang, “Plasmon-Controlled Fluorescence: Beyond the Intensity Enhancement,” *J. Phys. Chem. Lett.*, vol. 3, no. 2, pp. 191–202, Jan. 2012.
- [12] E. H. Synge, “XXXVIII. A suggested method for extending microscopic resolution into the ultra-microscopic region,” *London, Edinburgh, Dublin Philos. Mag. J. Sci.*, vol. 6, no. 35, pp. 356–362, Aug. 1928.
- [13] L. Novotny and B. Hecht, *Principles of Nano-Optics*, 2nd ed. Cambridge University Press, 2012.
- [14] J. Wessel, “Surface-enhanced optical microscopy,” *J. Opt. Soc. Am. B*, vol. 2, no. 9, p. 1538, Sep. 1985.
- [15] D. W. POHL, “Near Field Optics Seen as an Antenna Problem,” in *Near-Field Optics*, WORLD SCIENTIFIC, 2000, pp. 9–21.
- [16] A. Alù and N. Engheta, “Hertzian plasmonic nanodimer as an efficient optical nanoantenna,” *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 78, no. 19, pp. 1–6, 2008.
- [17] C. Balanis, *Antenna Theory: Analysis and Design*, 4th ed. Wiley, 2016.
- [18] A. G. Curto, G. Volpe, T. H. Taminiau, M. P. Kreuzer, R. Quidant, and N. F. van Hulst, “Unidirectional Emission of a Quantum Dot Coupled to a Nanoantenna,” *Science*, vol. 329, no. 5994, pp. 930–933, Aug. 2010.
- [19] T. Kosako, Y. Kadoya, and H. F. Hofmann, “Directional control of light by a nano-optical Yagi–Uda antenna,” *Nat. Photonics*, vol. 4, no. 5, pp. 312–315, May 2010.
- [20] S. A. Maier, *Plasmonics: Fundamentals and Applications*. New York, NY: Springer US, 2007.

- [21] 佐藤勝昭, “プラズモンの基礎.” [Online]. Available: [http://home.sato-gallery.com/research/plasmons\\_slide.pdf](http://home.sato-gallery.com/research/plasmons_slide.pdf).
- [22] M. L. Brongersma and P. G. Kik, *Surface Plasmon Nanophotonics*. Springer, 2007.
- [23] 梶川浩太郎, 岡本隆之, 高原淳一, and 岡本晃一, アクティブ・プラズモニクス. コロナ社, 2013.
- [24] S. A. Safiabadi Tali and W. Zhou, “Multiresonant plasmonics with spatial mode overlap: overview and outlook,” *Nanophotonics*, vol. 8, no. 7, pp. 1199–1225, Jul. 2019.
- [25] 岡本隆之 and 梶川浩太郎, プラズモニクス—基礎と応用. 講談社, 2010.
- [26] J. D. Jackson, *Classical Electrodynamics*, 3rd ed. Wiley, 1998.
- [27] C. F. Bohren and D. R. Huffman, Eds., *Absorption and Scattering of Light by Small Particles*. Weinheim, Germany: Wiley-VCH Verlag GmbH, 1998.
- [28] H. Chen, L. Shao, Q. Li, and J. Wang, “Gold nanorods and their plasmonic properties,” *Chem. Soc. Rev.*, vol. 42, no. 7, pp. 2679–2724, 2013.
- [29] T. S. van Zanten, M. J. Lopez-Bosque, and M. F. Garcia-Parajo, “Imaging Individual Proteins and Nanodomains on Intact Cell Membranes with a Probe-Based Optical Antenna,” *Small*, vol. 6, no. 2, pp. 270–275, Jan. 2010.
- [30] J. J. Mock, M. Barbic, D. R. Smith, D. A. Schultz, and S. Schultz, “Shape effects in plasmon resonance of individual colloidal silver nanoparticles,” *J. Chem. Phys.*, vol. 116, no. 15, pp. 6755–6759, Apr. 2002.
- [31] P. Ghenuche, S. Cherukulappurath, T. H. Taminiau, N. F. van Hulst, and R. Quidant, “Spectroscopic Mode Mapping of Resonant Plasmon Nanoantennas,” *Phys. Rev. Lett.*, vol. 101, no. 11, p. 116805, Sep. 2008.
- [32] M. H. Chowdhury, J. Pond, S. K. Gray, and J. R. Lakowicz, “Systematic Computational Study of the Effect of Silver Nanoparticle Dimers on the Coupled Emission from Nearby Fluorophores,” *J. Phys. Chem. C*, vol. 112, no. 30, pp. 11236–11249, Jul. 2008.
- [33] T.-S. Deng, J. Parker, Y. Yifat, N. Shepherd, and N. F. Scherer, “Dark Plasmon Modes in Symmetric Gold Nanoparticle Dimers Illuminated by Focused Cylindrical Vector Beams,” *J. Phys. Chem. C*, vol. 122, no. 48, pp. 27662–27672, Dec. 2018.
- [34] O. L. Muskens, V. Giannini, J. a. Sánchez-Gil, and J. Gómez Rivas, “Strong enhancement of the radiative decay rate of emitters by single plasmonic nanoantennas,” *Nano Lett.*, vol. 7, no. 9, pp. 2871–2875, 2007.
- [35] F. Todisco *et al.*, “Toward Cavity Quantum Electrodynamics with Hybrid Photon Gap-Plasmon States,” *ACS Nano*, vol. 10, no. 12, pp. 11360–11368, Dec. 2016.
- [36] S. Bidault *et al.*, “Picosecond Lifetimes with High Quantum Yields from Single-Photon-Emitting Colloidal Nanostructures at Room Temperature,” *ACS Nano*, vol. 10, no. 4, pp. 4806–4815, Apr. 2016.

- [37] R. Chikkaraddy *et al.*, “How Ultranarrow Gap Symmetries Control Plasmonic Nanocavity Modes: From Cubes to Spheres in the Nanoparticle-on-Mirror,” *ACS Photonics*, vol. 4, no. 3, pp. 469–475, Mar. 2017.
- [38] J. Mertens, M. E. Kleemann, R. Chikkaraddy, P. Narang, and J. J. Baumberg, “How Light Is Emitted by Plasmonic Metals,” *Nano Lett.*, vol. 17, no. 4, pp. 2568–2574, 2017.
- [39] F. Benz *et al.*, “Single-molecule optomechanics in ‘picocavities,’” *Science*, vol. 354, no. 6313, pp. 726–729, Nov. 2016.
- [40] J. J. Baumberg, J. Aizpurua, M. H. Mikkelsen, and D. R. Smith, “Extreme nanophotonics from ultrathin metallic gaps,” *Nat. Mater.*, vol. 18, no. 7, pp. 668–678, Jul. 2019.
- [41] D. O. Sigle *et al.*, “Monitoring Morphological Changes in 2D Monolayer Semiconductors Using Atom-Thick Plasmonic Nanocavities,” *ACS Nano*, vol. 9, no. 1, pp. 825–830, Jan. 2015.
- [42] B. de Nijs *et al.*, “Unfolding the contents of sub-nm plasmonic gaps using normalising plasmon resonance spectroscopy,” *Faraday Discuss.*, vol. 178, pp. 185–193, 2015.
- [43] M.-E. Kleemann *et al.*, “Strong-coupling of WSe<sub>2</sub> in ultra-compact plasmonic nanocavities at room temperature,” *Nat. Commun.*, vol. 8, no. 1, p. 1296, Dec. 2017.
- [44] A. Lombardi *et al.*, “Anomalous spectral shift of near- and far-field plasmonic resonances in nano-gaps,” *ACS Photonics*, vol. 3, no. 3, pp. 471–477, Feb. 2016.
- [45] J. Mertens *et al.*, “Controlling Subnanometer Gaps in Plasmonic Dimers Using Graphene,” *Nano Lett.*, vol. 13, no. 11, pp. 5033–5038, Nov. 2013.
- [46] J. Peng *et al.*, “Scalable electrochromic nanopixels using plasmonics,” *Sci. Adv.*, vol. 5, no. 5, p. eaaw2205, May 2019.
- [47] R. Chikkaraddy *et al.*, “Single-molecule strong coupling at room temperature in plasmonic nanocavities,” *Nature*, vol. 535, no. 7610, pp. 127–130, Jul. 2016.
- [48] M. E. Kleemann *et al.*, “Revealing Nanostructures through Plasmon Polarimetry,” *ACS Nano*, vol. 11, no. 1, pp. 850–855, 2017.
- [49] C. Carnegie *et al.*, “Flickering nanometre-scale disorder in a crystal lattice tracked by plasmonic flare light emission,” *Nat. Commun.*, vol. 11, no. 1, p. 682, Dec. 2020.
- [50] G. V. Naik, J. L. Schroeder, X. Ni, A. V. Kildishev, T. D. Sands, and A. Boltasseva, “Titanium nitride as a plasmonic material for visible and near-infrared wavelengths,” *Opt. Mater. Express*, vol. 2, no. 4, p. 478, Apr. 2012.
- [51] J. Mertens, Y. Shi, A. Molina-Sánchez, L. Wirtz, H. Y. Yang, and J. J. Baumberg, “Excitons in a mirror: Formation of ‘optical bilayers’ using MoS<sub>2</sub> monolayers on gold substrates,” *Appl. Phys. Lett.*, vol. 104, no. 19, p. 191105, May 2014.
- [52] G. M. Akselrod *et al.*, “Probing the mechanisms of large Purcell enhancement in plasmonic nanoantennas,” *Nat. Photonics*, vol. 8, no. 11, pp. 835–840, 2014.
- [53] M. E. Sykes *et al.*, “Enhanced generation and anisotropic Coulomb scattering of hot electrons in an ultra-broadband plasmonic nanopatch metasurface,” *Nat. Commun.*, vol. 8, no. 1, p. 986, Dec. 2017.
- [54] A. Rose *et al.*, “Control of Radiative Processes Using Tunable Plasmonic Nanopatch Antennas,” *Nano Lett.*, vol. 14, no. 8, pp. 4797–4802, Aug. 2014.

- [55] P. Kolchin *et al.*, “High Purcell Factor Due To Coupling of a Single Emitter to a Dielectric Slot Waveguide,” *Nano Lett.*, vol. 15, no. 1, pp. 464–468, Jan. 2015.
- [56] T. B. Hoang, G. M. Akselrod, and M. H. Mikkelsen, “Ultrafast Room-Temperature Single Photon Emission from Quantum Dots Coupled to Plasmonic Nanocavities,” *Nano Lett.*, vol. 16, no. 1, pp. 270–275, 2016.
- [57] W. M. Wilson, J. W. Stewart, and M. H. Mikkelsen, “Surpassing Single Line Width Active Tuning with Photochromic Molecules Coupled to Plasmonic Nanoantennas,” *Nano Lett.*, vol. 18, no. 2, pp. 853–858, Feb. 2018.
- [58] J. Huang, A. J. Traverso, G. Yang, and M. H. Mikkelsen, “Real-Time Tunable Strong Coupling: From Individual Nanocavities to Metasurfaces,” *ACS Photonics*, vol. 6, no. 4, pp. 838–843, Apr. 2019.
- [59] T. B. Hoang, G. M. Akselrod, C. Argyropoulos, J. Huang, D. R. Smith, and M. H. Mikkelsen, “Ultrafast spontaneous emission source using plasmonic nanoantennas,” *Nat. Commun.*, vol. 6, p. 7788, Jul. 2015.
- [60] G. M. Akselrod *et al.*, “Leveraging nanocavity harmonics for control of optical processes in 2d semiconductors,” *Nano Lett.*, vol. 15, no. 5, pp. 3578–3584, 2015.
- [61] J. Zhang, Y. Fu, M. H. Chowdhury, and J. R. Lakowicz, “Single-Molecule Studies on Fluorescently Labeled Silver Particles: Effects of Particle Size,” *J. Phys. Chem. C*, vol. 112, no. 1, pp. 18–26, Jan. 2008.
- [62] W. Ge, X. R. Zhang, M. Liu, Z. W. Lei, R. J. Knize, and Y. Lu, “Distance Dependence of Gold-Enhanced Upconversion luminescence in Au/SiO<sub>2</sub>/Y<sub>2</sub>O<sub>3</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> Nanoparticles,” *Theranostics*, vol. 3, no. 4, pp. 282–288, 2013.
- [63] A. Inoue, H. Sugimoto, H. Yaku, and M. Fujii, “DNA assembly of silicon quantum dots/gold nanoparticle nanocomposites,” *RSC Adv.*, vol. 6, no. 68, pp. 63933–63939, 2016.
- [64] A. Inoue, M. Fujii, H. Sugimoto, and K. Imakita, “Surface Plasmon-Enhanced Luminescence of Silicon Quantum Dots in Gold Nanoparticle Composites,” *J. Phys. Chem. C*, vol. 119, no. 44, pp. 25108–25113, Nov. 2015.
- [65] Y. Song, G. Liu, X. Dong, J. Wang, W. Yu, and J. Li, “Au Nanorods@NaGdF<sub>4</sub>/Yb<sup>3+</sup>, Er<sup>3+</sup> Multifunctional Hybrid Nanocomposites with Upconversion Luminescence, Magnetism, and Photothermal Property,” *J. Phys. Chem. C*, vol. 119, no. 32, pp. 18527–18536, Aug. 2015.
- [66] Y. Huang, F. Rosei, and F. Vetrone, “A single multifunctional nanoplatform based on upconversion luminescence and gold nanorods,” *Nanoscale*, vol. 7, no. 12, pp. 5178–5185, 2015.
- [67] F. Kang, J. He, T. Sun, Z. Y. Bao, F. Wang, and D. Y. Lei, “Plasmonic Dual-Enhancement and Precise Color Tuning of Gold Nanorod@SiO<sub>2</sub> Coupled Core-Shell-Shell Upconversion Nanocrystals,” *Adv. Funct. Mater.*, p. 1701842, Aug. 2017.
- [68] H. Li, Q. Deng, B. Liu, J. Yang, and B. Wu, “Fabrication of core@spacer@shell Au nanorod @mSiO<sub>2</sub>@Y<sub>2</sub>O<sub>3</sub>:Er nanocomposites with enhanced upconversion fluorescence,” *RSC Adv.*, vol. 6, no. 16, pp. 13343–13348, 2016.
- [69] J. He *et al.*, “Plasmonic enhancement and polarization dependence of nonlinear upconversion emissions from single gold nanorod@SiO<sub>2</sub>@CaF<sub>2</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> hybrid core-shell-satellite

- nanostructures,” *Light Sci. Appl.*, vol. 6, no. 5, p. e16217, May 2017.
- [70] J. Zhang, I. Gryczynski, Z. Gryczynski, and J. R. Lakowicz, “Dye-Labeled Silver Nanoshell–Bright Particle,” *J. Phys. Chem. B*, vol. 110, no. 18, pp. 8986–8991, May 2006.
- [71] M. Fujii, T. Nakano, K. Imakita, and S. Hayashi, “Upconversion Luminescence of Er and Yb Codoped NaYF<sub>4</sub> Nanoparticles with Metal Shells,” *J. Phys. Chem. C*, vol. 117, no. 2, pp. 1113–1120, Jan. 2013.
- [72] C. Ayala-Orozco *et al.*, “Fluorescence Enhancement of Molecules Inside a Gold Nanomatryoshka,” *Nano Lett.*, vol. 14, no. 5, pp. 2926–2933, May 2014.
- [73] B. Khlebtsov, V. Khanadeev, and N. Khlebtsov, “Surface-enhanced Raman scattering inside Au@Ag core/shell nanorods,” *Nano Res.*, vol. 9, no. 8, pp. 2303–2318, Aug. 2016.
- [74] J. G. Hinman, A. J. Stork, J. A. Varnell, A. A. Gewirth, and C. J. Murphy, “Seed mediated growth of gold nanorods: towards nanorod matryoshkas,” *Faraday Discuss.*, vol. 191, pp. 9–33, 2016.
- [75] K. Yamamoto, M. Fujii, S. Sowa, K. Imakita, and K. Aoki, “Upconversion Luminescence of Rare-Earth-Doped Y<sub>2</sub>O<sub>3</sub> Nanoparticle with Metal Nano-Cap,” *J. Phys. Chem. C*, vol. 119, no. 2, pp. 1175–1179, Jan. 2015.
- [76] T. Hinamoto, H. Takashina, H. Sugimoto, and M. Fujii, “Controlling Surface Plasmon Resonance of Metal Nanocap for Upconversion Enhancement,” *J. Phys. Chem. C*, vol. 121, no. 14, pp. 8077–8083, Apr. 2017.
- [77] D. Bang *et al.*, “Asymmetric Nanocrescent Antenna on Upconversion Nanocrystal,” *Nano Lett.*, vol. 17, no. 11, pp. 6583–6590, Nov. 2017.
- [78] M. Ringler *et al.*, “Shaping Emission Spectra of Fluorescent Molecules with Single Plasmonic Nanoresonators,” *Phys. Rev. Lett.*, vol. 100, no. 20, p. 203002, May 2008.
- [79] A. Das, C. Mao, S. Cho, K. Kim, and W. Park, “Over 1000-fold enhancement of upconversion luminescence using water-dispersible metal-insulator-metal nanostructures,” *Nat. Commun.*, vol. 9, no. 1, p. 4828, Dec. 2018.
- [80] Y. Qin, Z. Dong, D. Zhou, Y. Yang, X. Xu, and J. Qiu, “Modification on populating paths of  $\beta$ -NaYF<sub>4</sub>:Nd/Yb/Ho@SiO<sub>2</sub>@Ag core/double-shell nanocomposites with plasmon enhanced upconversion emission,” *Opt. Mater. Express*, vol. 6, no. 6, pp. 1942–1955, Jun. 2016.
- [81] S. Liu, G. Chen, T. Y. Ohulchanskyy, M. T. Swihart, and P. N. Prasad, “Facile Synthesis and Potential Bioimaging Applications of Hybrid Upconverting and Plasmonic NaGdF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup>/Silica/Gold Nanoparticles,” *Theranostics*, vol. 3, no. 4, pp. 275–281, 2013.
- [82] P. Kannan *et al.*, “Au Nanorod Decoration on NaYF<sub>4</sub>:Yb/Tm Nanoparticles for Enhanced Emission and Wavelength-Dependent Biomolecular Sensing,” *ACS Appl. Mater. Interfaces*, vol. 5, no. 9, pp. 3508–3513, May 2013.
- [83] E. Prodan, “A Hybridization Model for the Plasmon Response of Complex Nanostructures,” *Science*, vol. 302, no. 5644, pp. 419–422, Oct. 2003.
- [84] P. Nordlander, C. Oubre, E. Prodan, K. Li, and M. I. Stockman, “Plasmon Hybridization in Nanoparticle Dimers,” *Nano Lett.*, vol. 4, no. 5, pp. 899–903, 2004.
- [85] S. Baur, S. Sanders, and A. Manjavacas, “Hybridization of Lattice Resonances,” *ACS Nano*, p. acsnano.7b08206, 2018.

- [86] R. Won, “Into the ‘Mie-tronic’ era,” *Nat. Photonics*, vol. 13, no. 9, pp. 585–587, Sep. 2019.
- [87] Q. Zhao, J. Zhou, F. Zhang, and D. Lippens, “Mie resonance-based dielectric metamaterials,” *Mater. Today*, vol. 12, no. 12, pp. 60–69, Dec. 2009.
- [88] T. Liu, R. Xu, P. Yu, Z. Wang, and J. Takahara, “Multipole and multimode engineering in Mie resonance-based metastructures,” *Nanophotonics*, Mar. 2020.
- [89] A. I. Kuznetsov, A. E. Miroshnichenko, M. L. Brongersma, Y. S. Kivshar, and B. Luk’yanchuk, “Optically resonant dielectric nanostructures,” *Science*, vol. 354, no. 6314, p. aag2472, Nov. 2016.
- [90] G. Mie, “Beiträge zur Optik trüber Medien, speziell kolloidaler Metallösungen,” *Ann. Phys.*, vol. 330, no. 3, pp. 377–445, 1908.
- [91] M. Kerker, D.-S. Wang, and C. L. Giles, “Electromagnetic scattering by magnetic spheres,” *J. Opt. Soc. Am.*, vol. 73, no. 6, p. 765, Jun. 1983.
- [92] J. M. Geffrin *et al.*, “Magnetic and electric coherence in forward- and back-scattered electromagnetic waves by a single dielectric subwavelength sphere,” *Nat. Commun.*, vol. 3, no. 1, p. 1171, Jan. 2012.
- [93] Y. H. Fu, A. I. Kuznetsov, A. E. Miroshnichenko, Y. F. Yu, and B. Luk’yanchuk, “Directional visible light scattering by silicon nanoparticles,” *Nat. Commun.*, vol. 4, p. 1527, Feb. 2013.
- [94] S. Kruk and Y. Kivshar, “Functional Meta-Optics and Nanophotonics Governed by Mie Resonances,” *ACS Photonics*, vol. 4, no. 11, pp. 2638–2649, Nov. 2017.
- [95] M. Decker *et al.*, “High-Efficiency Dielectric Huygens’ Surfaces,” *Adv. Opt. Mater.*, vol. 3, no. 6, pp. 813–820, Jun. 2015.
- [96] D. M. Wu, A. García-Etxarri, A. Salleo, and J. A. Dionne, “Plasmon-Enhanced Upconversion,” *J. Phys. Chem. Lett.*, vol. 5, no. 22, pp. 4020–4031, Nov. 2014.
- [97] E. M. Purcell, “Spontaneous Emission Probabilities at Radio Frequencies,” 1995, pp. 839–839.
- [98] M. Pelton, “Modified spontaneous emission in nanophotonic structures,” *Nat. Photonics*, vol. 9, no. 7, pp. 427–435, Jun. 2015.
- [99] V. Rutckaia, F. Heyroth, A. Novikov, M. Shaleev, M. Petrov, and J. Schilling, “Quantum Dot Emission Driven by Mie Resonances in Silicon Nanostructures,” *Nano Lett.*, vol. 17, no. 11, pp. 6886–6892, Nov. 2017.
- [100] K. Chen *et al.*, “High- Q , low-mode-volume and multiresonant plasmonic nanoslit cavities fabricated by helium ion milling,” *Nanoscale*, vol. 10, no. 36, pp. 17148–17155, 2018.
- [101] M. V. Rybin *et al.*, “High-Q Supercavity Modes in Subwavelength Dielectric Resonators,” *Phys. Rev. Lett.*, vol. 119, no. 24, p. 243901, Dec. 2017.
- [102] A. A. Bogdanov *et al.*, “Bound states in the continuum and Fano resonances in the strong mode coupling regime,” *Adv. Photonics*, vol. 1, no. 01, p. 1, Jan. 2019.
- [103] S. T. Ha *et al.*, “Directional lasing in resonant semiconductor nanoantenna arrays,” *Nat. Nanotechnol.*, vol. 13, no. 11, pp. 1042–1047, Nov. 2018.
- [104] T. Coenen, E. J. R. Vesseur, A. Polman, and A. F. Koenderink, “Directional Emission from Plasmonic Yagi–Uda Antennas Probed by Angle-Resolved Cathodoluminescence Spectroscopy,” *Nano Lett.*, vol. 11, no. 9, pp. 3779–3784, Sep. 2011.

- [105] B. Rolly, B. Stout, and N. Bonod, "Boosting the directivity of optical antennas with magnetic and electric dipolar resonant particles," *Opt. Express*, vol. 20, no. 18, p. 20376, Aug. 2012.
- [106] J. Ho *et al.*, "Highly Directive Hybrid Metal–Dielectric Yagi-Uda Nanoantennas," *ACS Nano*, vol. 12, no. 8, pp. 8616–8624, Aug. 2018.
- [107] A. E. Krasnok, A. E. Miroshnichenko, P. A. Belov, and Y. S. Kivshar, "All-dielectric optical nanoantennas," in *AIP Conference Proceedings*, 2012, vol. 22, no. 2012, pp. 22–24.
- [108] A. F. Cihan, A. G. Curto, S. Raza, P. G. Kik, and M. L. Brongersma, "Silicon Mie resonators for highly directional light emission from monolayer MoS<sub>2</sub>," *Nat. Photonics*, vol. 12, no. 5, pp. 284–290, May 2018.
- [109] J. Zhao *et al.*, "Single-nanocrystal sensitivity achieved by enhanced upconversion luminescence," *Nat. Nanotechnol.*, vol. 8, no. 10, pp. 729–734, Sep. 2013.
- [110] F. Wang *et al.*, "Simultaneous phase and size control of upconversion nanocrystals through lanthanide doping," *Nature*, vol. 463, no. 7284, pp. 1061–1065, Feb. 2010.
- [111] E. Downing, L. Hesselink, J. Ralston, and R. Macfarlane, "A Three-Color, Solid-State, Three-Dimensional Display," *Science*, vol. 273, no. 5279, pp. 1185–1189, Aug. 1996.
- [112] S. Fischer *et al.*, "Enhancement of silicon solar cell efficiency by upconversion: Optical and electrical characterization," *J. Appl. Phys.*, vol. 108, no. 4, p. 044912, Aug. 2010.
- [113] G. Chen, H. Qiu, P. N. Prasad, and X. Chen, "Upconversion Nanoparticles: Design, Nanochemistry, and Applications in Theranostics," *Chem. Rev.*, vol. 114, no. 10, pp. 5161–5214, May 2014.
- [114] G. Chen *et al.*, "(α-NaYbF<sub>4</sub>:Tm<sup>3+</sup>)/CaF<sub>2</sub> Core/Shell Nanoparticles with Efficient Near-Infrared to Near-Infrared Upconversion for High-Contrast Deep Tissue Bioimaging," *ACS Nano*, vol. 6, no. 9, pp. 8280–8287, Sep. 2012.
- [115] F. Zhang *et al.*, "Fabrication of Ag@SiO<sub>2</sub>@Y<sub>2</sub>O<sub>3</sub>:Er Nanostructures for Bioimaging: Tuning of the Upconversion Fluorescence with Silver Nanoparticles," *J. Am. Chem. Soc.*, vol. 132, no. 9, pp. 2850–2851, Mar. 2010.
- [116] C. Wang, L. Cheng, and Z. Liu, "Drug delivery with upconversion nanoparticles for multi-functional targeted cancer cell imaging and therapy," *Biomaterials*, vol. 32, no. 4, pp. 1110–1120, Feb. 2011.
- [117] F. Zhang, *Photon Upconversion Nanomaterials*, vol. 44. Berlin, Heidelberg: Springer Berlin Heidelberg, 2015.
- [118] A. El Halawany *et al.*, "Enhanced UV upconversion emission using plasmonic nanocavities," *Opt. Express*, vol. 24, no. 13, p. 13999, 2016.
- [119] W. Park, D. Lu, and S. Ahn, "Plasmon enhancement of luminescence upconversion," *Chem. Soc. Rev.*, vol. 44, no. 10, pp. 2940–2962, 2015.
- [120] T. Kodama, M. Fujii, T. Nakano, K. Imakita, and S. Hayashi, "Enhancement of upconversion luminescence of Er and Yb co-doped Y<sub>2</sub>O<sub>3</sub> nanoparticle by Ag half-shell," *Opt. Mater. (Amst.)*, vol. 35, no. 12, pp. 2394–2399, Oct. 2013.
- [121] T. Aisaka, M. Fujii, and S. Hayashi, "Enhancement of upconversion luminescence of Er doped Al<sub>2</sub>O<sub>3</sub> films by Ag island films," *Appl. Phys. Lett.*, vol. 92, no. 13, p. 132105, 2008.

- [122] M. Haase and H. Schäfer, "Upconverting Nanoparticles," *Angew. Chemie Int. Ed.*, vol. 50, no. 26, pp. 5808–5829, Jun. 2011.
- [123] S. Han, R. Deng, X. Xie, and X. Liu, "Enhancing luminescence in lanthanide-doped upconversion nanoparticles," *Angew. Chemie - Int. Ed.*, vol. 53, no. 44, pp. 11702–11715, 2014.
- [124] B. Zhou, B. Shi, D. Jin, and X. Liu, "Controlling upconversion nanocrystals for emerging applications," *Nat. Nanotechnol.*, vol. 10, no. 11, pp. 924–936, Nov. 2015.
- [125] Z. Q. Li *et al.*, "Plasmon-enhanced upconversion fluorescence in NaYF<sub>4</sub>:Yb/Er/Gd nanorods coated with Au nanoparticles or nanoshells," *J. Appl. Phys.*, vol. 111, no. 1, p. 014310, 2012.
- [126] E. He *et al.*, "Facile fabrication and upconversion luminescence enhancement of LaF<sub>3</sub>:Yb<sup>3+</sup>/Ln<sup>3+</sup>@SiO<sub>2</sub> (Ln = Er, Tm) nanostructures decorated with Ag nanoparticles," *Nanotechnology*, vol. 25, no. 4, pp. 045603–11, 2014.
- [127] P. Yuan, Y. H. Lee, M. K. Gnanasammandhan, Z. Guan, Y. Zhang, and Q.-H. Xu, "Plasmon enhanced upconversion luminescence of NaYF<sub>4</sub>:Yb,Er@SiO<sub>2</sub>@Ag core-shell nanocomposites for cell imaging," *Nanoscale*, vol. 4, no. 16, p. 5132, 2012.
- [128] J. Kümmerlen, A. Leitner, H. Brunner, F. R. Aussenegg, and A. Wokaun, "Enhanced dye fluorescence over silver island films: analysis of the distance dependence," *Mol. Phys.*, vol. 80, no. 5, pp. 1031–1046, Dec. 1993.
- [129] K. Sokolov, G. Chumanov, and T. M. Cotton, "Enhancement of Molecular Fluorescence near the Surface of Colloidal Metal Films," *Anal. Chem.*, vol. 70, no. 18, pp. 3898–3905, Sep. 1998.
- [130] Y. Zhang, A. Barhoumi, J. B. Lassiter, and N. J. Halas, "Orientation-Preserving Transfer and Directional Light Scattering from Individual Light-Bending Nanoparticles," *Nano Lett.*, vol. 11, no. 4, pp. 1838–1844, Apr. 2011.
- [131] M. Cortie and M. Ford, "A plasmon-induced current loop in gold semi-shells," *Nanotechnology*, vol. 18, no. 23, p. 235704, Jun. 2007.
- [132] C. Charnay *et al.*, "Reduced Symmetry Metallodielectric Nanoparticles: Chemical Synthesis and Plasmonic Properties †," *J. Phys. Chem. B*, vol. 107, no. 30, pp. 7327–7333, Jul. 2003.
- [133] B. Ding, C. Hrelescu, N. Arnold, G. Isic, and T. A. Klar, "Spectral and Directional Reshaping of Fluorescence in Large Area Self-Assembled Plasmonic-Photonic Crystals," *Nano Lett.*, vol. 13, no. 2, pp. 378–386, Feb. 2013.
- [134] J. B. Lassiter, M. W. Knight, N. A. Mirin, and N. J. Halas, "Reshaping the Plasmonic Properties of an Individual Nanoparticle," *Nano Lett.*, vol. 9, no. 12, pp. 4326–4332, Dec. 2009.
- [135] N. A. Mirin and N. J. Halas, "Light-Bending Nanoparticles," *Nano Lett.*, vol. 9, no. 3, pp. 1255–1259, Mar. 2009.
- [136] J. Ye, L. Lagae, G. Maes, G. Borghs, and P. Van Dorpe, "Symmetry breaking induced optical properties of gold open shell nanostructures," *Opt. Express*, vol. 17, no. 26, p. 23765, Dec. 2009.
- [137] T. Wu, S. Yang, and X. Li, "Tunable plasmon resonances and two-dimensional anisotropy of angular optical response of overlapped nanoshells," *Opt. Express*, vol. 21, no. 6, p. 7811, 2013.
- [138] J. Ye *et al.*, "Plasmonic Modes of Metallic Semishells in a Polymer Film," *ACS Nano*, vol. 4, no. 3, pp. 1457–1464, Mar. 2010.
- [139] J. Ye *et al.*, "Fabrication and Optical Properties of Gold Semishells," *J. Phys. Chem. C*, vol. 113,

- no. 8, pp. 3110–3115, Feb. 2009.
- [140] Y. Yu, L. Gan, G. Zhang, and B. Yang, “Asymmetric microparticles and heterogeneous microshells via angled colloidal lithography,” *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 405, pp. 51–58, 2012.
  - [141] U. Hohenester and A. Trügler, “MNPBEM – A Matlab toolbox for the simulation of plasmonic nanoparticles,” *Comput. Phys. Commun.*, vol. 183, no. 2, pp. 370–381, 2012.
  - [142] R. Fujimura, R. Zhang, Y. Kitamoto, M. Shimojo, and K. Kajikawa, “Modeling of semi-shell nanostructures formed by metal deposition on dielectric nanospheres and numerical evaluation of plasmonic properties,” *Jpn. J. Appl. Phys.*, vol. 53, no. 3, p. 035201, Mar. 2014.
  - [143] H. S. Yoo, H. S. Jang, W. Bin Im, J. H. Kang, and D. Y. Jeon, “Particle size control of a monodisperse spherical  $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$  phosphor and its photoluminescence properties,” *J. Mater. Res.*, vol. 22, no. 07, pp. 2017–2024, Jul. 2007.
  - [144] R. McGill, J. W. Tukey, and W. A. Larsen, “Variations of Box Plots,” *Am. Stat.*, vol. 32, no. 1, p. 12, Feb. 1978.
  - [145] D. Lu, S. K. Cho, S. Ahn, L. Brun, C. J. Summers, and W. Park, “Plasmon enhancement mechanism for the upconversion processes in  $\text{NaYF}_4\text{:Yb}^{3+}, \text{Er}^{3+}$  nanoparticles: Maxwell versus Förster,” *ACS Nano*, vol. 8, no. 8, pp. 7780–7792, 2014.
  - [146] S. Hayashi and T. Okamoto, “Plasmonics: visit the past to know the future,” *J. Phys. D. Appl. Phys.*, vol. 45, no. 43, p. 433001, Oct. 2012.
  - [147] V. Giannini, A. I. Fernández-Domínguez, S. C. Heck, and S. A. Maier, “Plasmonic Nanoantennas: Fundamentals and Their Use in Controlling the Radiative Properties of Nanoemitters,” *Chem. Rev.*, vol. 111, no. 6, pp. 3888–3912, Jun. 2011.
  - [148] J. R. Lakowicz *et al.*, “Plasmon-controlled fluorescence: a new paradigm in fluorescence spectroscopy,” *Analyst*, vol. 133, no. 10, pp. 1308–1346, 2008.
  - [149] H. Sugimoto, T. Chen, R. Wang, M. Fujii, B. M. Reinhard, and L. Dal Negro, “Plasmon-Enhanced Emission Rate of Silicon Nanocrystals in Gold Nanorod Composites,” *ACS Photonics*, vol. 2, no. 9, pp. 1298–1305, Sep. 2015.
  - [150] T. Hinamoto, H. Sugimoto, and M. Fujii, “Metal-Core/Dielectric-Shell/Metal-Cap Composite Nanoparticle for Upconversion Enhancement,” *J. Phys. Chem. C*, vol. 122, no. 30, pp. 17465–17472, Aug. 2018.
  - [151] N. S. King, Y. Li, C. Ayala-Orozco, T. Brannan, P. Nordlander, and N. J. Halas, “Angle- and spectral-dependent light scattering from plasmonic nanocups,” *ACS Nano*, vol. 5, no. 9, pp. 7254–7262, 2011.
  - [152] N. S. King, M. W. Knight, N. Large, A. M. Goodman, P. Nordlander, and N. J. Halas, “Orienting Nanoantennas in Three Dimensions To Control Light Scattering Across a Dielectric Interface,” *Nano Lett.*, vol. 13, no. 12, pp. 5997–6001, Dec. 2013.
  - [153] F. J. García de Abajo, “Multiple scattering of radiation in clusters of dielectrics,” *Phys. Rev. B*, vol. 60, no. 8, pp. 6086–6102, Aug. 1999.
  - [154] C. Geuzaine and J.-F. Remacle, “Gmsh: A 3-D finite element mesh generator with built-in pre- and post-processing facilities,” *Int. J. Numer. Methods Eng.*, vol. 79, no. 11, pp. 1309–1331, Sep.

2009.

- [155] G. Lu, T. Zhang, W. Li, L. Hou, J. Liu, and Q. Gong, "Single-Molecule Spontaneous Emission in the Vicinity of an Individual Gold Nanorod," *J. Phys. Chem. C*, vol. 115, no. 32, pp. 15822–15828, Aug. 2011.
- [156] M. Kaiser, C. Würth, M. Kraft, I. Hyppänen, T. Soukka, and U. Resch-Genger, "Power-dependent upconversion quantum yield of NaYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> nano- and micrometer-sized particles – measurements and simulations," *Nanoscale*, vol. 9, no. 28, pp. 10051–10058, 2017.
- [157] J.-C. Boyer and F. C. J. M. van Veggel, "Absolute quantum yield measurements of colloidal NaYF<sub>4</sub>: Er<sup>3+</sup>, Yb<sup>3+</sup> upconverting nanoparticles," *Nanoscale*, vol. 2, no. 8, pp. 1417–1419, 2010.
- [158] F. Wang and X. Liu, "Recent advances in the chemistry of lanthanide-doped upconversion nanocrystals," *Chem. Soc. Rev.*, vol. 38, no. 4, p. 976, 2009.
- [159] K. Pavani *et al.*, "Highly efficient upconversion of Er<sup>3+</sup> in Yb<sup>3+</sup> codoped non-cytotoxic strontium lanthanum aluminate phosphor for low temperature sensors," *Sci. Rep.*, vol. 7, no. 1, p. 17646, Dec. 2017.
- [160] A. C. Atre, A. García-Etxarri, H. Alaeian, and J. a Dionne, "Toward high-efficiency solar upconversion with plasmonic nanostructures," *J. Opt.*, vol. 14, no. 2, p. 024008, Feb. 2012.
- [161] R. Deng, F. Qin, R. Chen, W. Huang, M. Hong, and X. Liu, "Temporal full-colour tuning through non-steady-state upconversion," *Nat. Nanotechnol.*, vol. 10, no. 3, pp. 237–242, Jan. 2015.
- [162] F. Auzel, "Upconversion and Anti-Stokes Processes with f and d Ions in Solids," *Chem. Rev.*, vol. 104, no. 1, pp. 139–174, Jan. 2004.
- [163] J. Zhou, Q. Liu, W. Feng, Y. Sun, and F. Li, "Upconversion Luminescent Materials: Advances and Applications," *Chem. Rev.*, vol. 115, no. 1, pp. 395–465, Jan. 2015.
- [164] F. Auzel and C. R. Acad, "Compteur Quantique par Transfert Denergie Entre Deux Ions De Terres Rares Dans Un Tungstate Mixte Et Dans Un Verre," *Sci.*, vol. 262, no. 15, p. 1016, 1966.
- [165] S. Fischer, B. Fröhlich, H. Steinkemper, K. W. Krämer, and J. C. Goldschmidt, "Absolute upconversion quantum yield of  $\beta$ -NaYF<sub>4</sub> doped with Er<sup>3+</sup> and external quantum efficiency of upconverter solar cell devices under broad-band excitation considering spectral mismatch corrections," *Sol. Energy Mater. Sol. Cells*, vol. 122, pp. 197–207, Mar. 2014.
- [166] W. Xu, X. Chen, and H. Song, "Upconversion manipulation by local electromagnetic field," *Nano Today*, vol. 17, pp. 54–78, Dec. 2017.
- [167] Z. Yin *et al.*, "Local Field Modulation Induced Three-Order Upconversion Enhancement: Combining Surface Plasmon Effect and Photonic Crystal Effect," *Adv. Mater.*, vol. 28, no. 13, pp. 2518–2525, Apr. 2016.
- [168] X. Chen *et al.*, "Large Upconversion Enhancement in the 'Islands' Au-Ag Alloy/NaYF<sub>4</sub>: Yb<sup>3+</sup>, Tm<sup>3+</sup>/Er<sup>3+</sup> Composite Films, and Fingerprint Identification," *Adv. Funct. Mater.*, vol. 25, no. 34, pp. 5462–5471, Sep. 2015.
- [169] D. Zhou *et al.*, "Observation of Considerable Upconversion Enhancement Induced by Cu<sub>2-x</sub>S Plasmon Nanoparticles," *ACS Nano*, vol. 10, no. 5, pp. 5169–5179, May 2016.
- [170] J. Qian, W. Wang, Y. Li, J. Xu, and Q. Sun, "Optical Extinction Properties of Perforated Gold-Silica-Gold Multilayer Nanoshells," *J. Phys. Chem. C*, vol. 116, no. 18, pp. 10349–10355, May 2012.

2012.

- [171] T. Wu, S. Yang, W. Tan, and X. Li, “Tunable Localized Hybrid Plasmon Modes and Fano Resonances in Au Core-Semishell,” *Plasmonics*, vol. 11, no. 5, pp. 1351–1359, Oct. 2016.
- [172] M. Jacquemet *et al.*, “Efficient laser action of Yb:LSO and Yb:YSO oxyorthosilicates crystals under high-power diode-pumping,” *Appl. Phys. B*, vol. 80, no. 2, pp. 171–176, Feb. 2005.
- [173] N. G. Bastús, J. Comenge, and V. Puentes, “Kinetically Controlled Seeded Growth Synthesis of Citrate-Stabilized Gold Nanoparticles of up to 200 nm: Size Focusing versus Ostwald Ripening,” *Langmuir*, vol. 27, no. 17, pp. 11098–11105, Sep. 2011.
- [174] W. Stöber, A. Fink, and E. Bohn, “Controlled growth of monodisperse silica spheres in the micron size range,” *J. Colloid Interface Sci.*, vol. 26, no. 1, pp. 62–69, 1968.
- [175] D.-C. Tien, L.-C. Chen, N. Van Thai, and S. Ashraf, “Study of Ag and Au Nanoparticles Synthesized by Arc Discharge in Deionized Water,” *J. Nanomater.*, vol. 2010, pp. 1–9, 2010.
- [176] R. Paniagua-Dominguez, S. T. Ha, and A. I. Kuznetsov, “Active and Tunable Nanophotonics With Dielectric Nanoantennas,” *Proc. IEEE*, vol. 108, no. 5, pp. 749–771, May 2020.
- [177] A. M. Shaltout, V. M. Shalaev, and M. L. Brongersma, “Spatiotemporal light control with active metasurfaces,” *Science*, vol. 364, no. 6441, p. eaat3100, May 2019.
- [178] R. Paniagua-Domínguez, B. Luk’yanchuk, A. Miroshnichenko, and J. A. Sánchez-Gil, “Dielectric nanoresonators and metamaterials,” *J. Appl. Phys.*, vol. 126, no. 15, p. 150401, Oct. 2019.
- [179] I. Staude, T. Pertsch, and Y. S. Kivshar, “All-Dielectric Resonant Meta-Optics Lightens up,” *ACS Photonics*, vol. 6, no. 4, pp. 802–814, Apr. 2019.
- [180] W. Liu and Y. S. Kivshar, “Generalized Kerker effects in nanophotonics and meta-optics [Invited],” *Opt. Express*, vol. 26, no. 10, p. 13085, May 2018.
- [181] Y. Kivshar, “All-dielectric meta-optics and non-linear nanophotonics,” *Natl. Sci. Rev.*, vol. 5, no. 2, pp. 144–158, Mar. 2018.
- [182] Z.-J. Yang, R. Jiang, X. Zhuo, Y.-M. Xie, J. Wang, and H.-Q. Lin, “Dielectric nanoresonators for light manipulation,” *Phys. Rep.*, vol. 701, pp. 1–50, Jul. 2017.
- [183] D. Tzarouchis, “Light Scattering by a Dielectric Sphere: Perspectives on the Mie Resonances,” *Appl. Sci.*, vol. 8, no. 2, p. 184, Jan. 2018.
- [184] H.-H. Hsiao, C. H. Chu, and D. P. Tsai, “Fundamentals and Applications of Metasurfaces,” *Small Methods*, vol. 1, no. 4, p. 1600064, Apr. 2017.
- [185] S. Jahani and Z. Jacob, “All-dielectric metamaterials,” *Nat. Nanotechnol.*, vol. 11, no. 1, pp. 23–36, Jan. 2016.
- [186] D. Smirnova and Y. S. Kivshar, “Multipolar nonlinear nanophotonics,” *Optica*, vol. 3, no. 11, p. 1241, Nov. 2016.
- [187] I. Staude and J. Schilling, “Metamaterial-inspired silicon nanophotonics,” *Nat. Photonics*, vol. 11, no. 5, pp. 274–284, 2017.
- [188] M. L. De Marco, S. Semlali, B. A. Korgel, P. Barois, G. L. Drisko, and C. Aymonier, “Silicon-Based Dielectric Metamaterials: Focus on the Current Synthetic Challenges,” *Angew. Chemie Int. Ed.*, pp. 2–23, Feb. 2018.
- [189] J. Cambiasso, G. Grinblat, Y. Li, A. Rakovich, E. Cortés, and S. A. Maier, “Bridging the Gap

- between Dielectric Nanophotonics and the Visible Regime with Effectively Lossless Gallium Phosphide Antennas,” *Nano Lett.*, vol. 17, no. 2, pp. 1219–1225, Feb. 2017.
- [190] A. B. Evlyukhin *et al.*, “Demonstration of Magnetic Dipole Resonances of Dielectric Nanospheres in the Visible Region,” *Nano Lett.*, vol. 12, no. 7, pp. 3749–3755, Jul. 2012.
- [191] A. I. Kuznetsov, A. E. Miroshnichenko, Y. H. Fu, J. Zhang, and B. Luk’yanchuk, “Magnetic light,” *Sci. Rep.*, vol. 2, no. 1, p. 492, Dec. 2012.
- [192] L. Shi *et al.*, “Monodisperse silicon nanocavities and photonic crystals with magnetic response in the optical region,” *Nat. Commun.*, vol. 4, no. 1, p. 1904, Oct. 2013.
- [193] H. Sugimoto and M. Fujii, “Colloidal Dispersion of Subquarter Micrometer Silicon Spheres for Low-Loss Antenna in Visible Regime,” *Adv. Opt. Mater.*, vol. 5, no. 17, p. 1700332, Sep. 2017.
- [194] H. Sugimoto, T. Okazaki, and M. Fujii, “Mie Resonator Color Inks of Monodispersed and Perfectly Spherical Crystalline Silicon Nanoparticles,” *Adv. Opt. Mater.*, vol. 2000033, p. 2000033, Apr. 2020.
- [195] Y. Cho, J. Huh, K. Kim, and S. Lee, “Scalable, Highly Uniform, and Robust Colloidal Mie Resonators for All-Dielectric Soft Meta-Optics,” *Adv. Opt. Mater.*, vol. 7, no. 3, p. 1801167, Feb. 2019.
- [196] H. Sugimoto, T. Hinamoto, and M. Fujii, “Forward to Backward Scattering Ratio of Dielectric–Metal Heterodimer Suspended in Almost Free-Space,” *Adv. Opt. Mater.*, vol. 1900591, p. 1900591, Aug. 2019.
- [197] J. Rho, “Metasurfaces: Subwavelength nanostructure arrays for ultrathin flat optics and photonics,” *MRS Bull.*, vol. 45, no. 3, pp. 180–187, Mar. 2020.
- [198] C. U. Hail, A. U. Michel, D. Poulikakos, and H. Eghlidi, “Optical Metasurfaces: Evolving from Passive to Adaptive,” *Adv. Opt. Mater.*, vol. 7, no. 14, p. 1801786, Jul. 2019.
- [199] A. Vaskin, R. Kolkowski, A. F. Koenderink, and I. Staude, “Light-emitting metasurfaces,” *Nanophotonics*, vol. 8, no. 7, pp. 1151–1198, Jul. 2019.
- [200] M. Taghinejad and W. Cai, “All-Optical Control of Light in Micro- and Nanophotonics,” *ACS Photonics*, vol. 6, no. 5, pp. 1082–1093, May 2019.
- [201] E. Poutrina and A. Urbas, “Multipole analysis of unidirectional light scattering from plasmonic dimers,” *J. Opt.*, vol. 16, no. 11, p. 114005, Nov. 2014.
- [202] L. Wang *et al.*, “Grayscale transparent metasurface holograms,” *Optica*, vol. 3, no. 12, p. 1504, 2016.
- [203] R. Guo *et al.*, “Multipolar Coupling in Hybrid Metal–Dielectric Metasurfaces,” *ACS Photonics*, vol. 3, no. 3, pp. 349–353, Mar. 2016.
- [204] A. Devilez, B. Stout, and N. Bonod, “Compact Metallo-Dielectric Optical Antenna for Ultra Directional and Enhanced Radiative Emission,” *ACS Nano*, vol. 4, no. 6, pp. 3390–3396, Jun. 2010.
- [205] P. Albella, T. Shibanuma, and S. A. Maier, “Switchable directional scattering of electromagnetic radiation with subwavelength asymmetric silicon dimers,” *Sci. Rep.*, vol. 5, no. August, pp. 1–8, 2015.
- [206] T. Shibanuma *et al.*, “Experimental Demonstration of Tunable Directional Scattering of Visible

- Light from All-Dielectric Asymmetric Dimers,” *ACS Photonics*, vol. 4, no. 3, pp. 489–494, Mar. 2017.
- [207] T. Shibanuma, P. Albella, and S. A. Maier, “Unidirectional light scattering with high efficiency at optical frequencies based on low-loss dielectric nanoantennas,” *Nanoscale*, vol. 8, no. 29, pp. 14184–14192, 2016.
- [208] W. Liu, A. E. Miroshnichenko, D. N. Neshev, and Y. S. Kivshar, “Broadband Unidirectional Scattering by Magneto-Electric Core–Shell Nanoparticles,” *ACS Nano*, vol. 6, no. 6, pp. 5489–5497, Jun. 2012.
- [209] J. Li, N. Verellen, D. Vercruysse, T. Bearda, L. Lagae, and P. Van Dorpe, “All-Dielectric Antenna Wavelength Router with Bidirectional Scattering of Visible Light,” *Nano Lett.*, vol. 16, no. 7, pp. 4396–4403, Jul. 2016.
- [210] C. Ma, J. Yan, Y. Huang, and G. Yang, “Directional Scattering in a Germanium Nanosphere in the Visible Light Region,” *Adv. Opt. Mater.*, vol. 5, no. 24, p. 1700761, Dec. 2017.
- [211] Y. Tsuchimoto, T. Yano, T. Hayashi, and M. Hara, “Fano resonant all-dielectric core/shell nanoparticles with ultrahigh scattering directionality in the visible region,” *Opt. Express*, vol. 24, no. 13, p. 14451, Jun. 2016.
- [212] H. K. Shamkhi *et al.*, “Transverse scattering and generalized kerker effects in all-dielectric mie-resonant metaoptics,” *Phys. Rev. Lett.*, vol. 122, no. 19, p. 193905, 2019.
- [213] R. Paniagua-Domínguez *et al.*, “A Metalens with a Near-Unity Numerical Aperture,” *Nano Lett.*, vol. 18, no. 3, pp. 2124–2132, 2018.
- [214] T. Bucher *et al.*, “Tailoring Photoluminescence from MoS<sub>2</sub> Monolayers by Mie-Resonant Metasurfaces,” *ACS Photonics*, vol. 6, no. 4, pp. 1002–1009, Apr. 2019.
- [215] T. Sannomiya *et al.*, “Cathodoluminescence Phase Extraction of the Coupling between Nanoparticles and Surface Plasmon Polaritons,” *Nano Lett.*, vol. 20, no. 1, pp. 592–598, Jan. 2020.
- [216] T. Matsukata *et al.*, “Selection and Visualization of Degenerate Magnetic and Electric Multipoles up to Radial Higher Orders by Cathodoluminescence,” *ACS Photonics*, vol. 6, no. 9, pp. 2320–2326, Sep. 2019.
- [217] C. Colliex, M. Kociak, and O. Stéphan, “Electron Energy Loss Spectroscopy imaging of surface plasmons at the nanometer scale,” *Ultramicroscopy*, vol. 162, pp. A1–A24, Mar. 2016.
- [218] P. Shekhar, M. Malac, V. Gaiand, N. Dalili, A. Meldrum, and Z. Jacob, “Momentum-Resolved Electron Energy Loss Spectroscopy for Mapping the Photonic Density of States,” *ACS Photonics*, vol. 4, no. 4, pp. 1009–1014, 2017.
- [219] A. Drezet *et al.*, “Leakage radiation microscopy of surface plasmon polaritons,” *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.*, vol. 149, no. 3, pp. 220–229, 2008.
- [220] A. Hohenau *et al.*, “Surface plasmon leakage radiation microscopy at the diffraction limit,” *Opt. Express*, vol. 19, no. 25, p. 25749, Dec. 2011.
- [221] P. E. Landreman and M. L. Brongersma, “Deep-Subwavelength Semiconductor Nanowire Surface Plasmon Polariton Couplers,” *Nano Lett.*, vol. 14, no. 2, pp. 429–434, Feb. 2014.
- [222] A. Kormányos, V. Zólyomi, N. D. Drummond, and G. Burkard, “Spin-Orbit Coupling, Quantum

- Dots, and Qubits in Monolayer Transition Metal Dichalcogenides,” *Phys. Rev. X*, vol. 4, no. 1, p. 011034, Mar. 2014.
- [223] D. Xiao, G.-B. Liu, W. Feng, X. Xu, and W. Yao, “Coupled Spin and Valley Physics in Monolayers of MoS<sub>2</sub> and Other Group-VI Dichalcogenides,” *Phys. Rev. Lett.*, vol. 108, no. 19, p. 196802, May 2012.
- [224] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, “Electronics and optoelectronics of two-dimensional transition metal dichalcogenides,” *Nat. Nanotechnol.*, vol. 7, no. 11, pp. 699–712, Nov. 2012.
- [225] F. Liu *et al.*, “Disassembling 2D van der Waals crystals into macroscopic monolayers and reassembling into artificial lattices,” *Science*, vol. 367, no. 6480, pp. 903–906, Feb. 2020.
- [226] H. Zeng and X. Cui, “An optical spectroscopic study on two-dimensional group-VI transition metal dichalcogenides,” *Chem. Soc. Rev.*, vol. 44, no. 9, pp. 2629–2642, 2015.
- [227] K. F. Mak and J. Shan, “Photonics and optoelectronics of 2D semiconductor transition metal dichalcogenides,” *Nat. Photonics*, vol. 10, no. 4, pp. 216–226, 2016.
- [228] J. Zhang *et al.*, “Reversible and selective ion intercalation through the top surface of few-layer MoS<sub>2</sub>,” *Nat. Commun.*, vol. 9, no. 1, p. 5289, Dec. 2018.
- [229] M. Koperski *et al.*, “Single photon emitters in exfoliated WSe<sub>2</sub> structures,” *Nat. Nanotechnol.*, vol. 10, no. 6, pp. 503–506, Jun. 2015.
- [230] A. Splendiani *et al.*, “Emerging Photoluminescence in Monolayer MoS<sub>2</sub>,” *Nano Lett.*, vol. 10, no. 4, pp. 1271–1275, Apr. 2010.
- [231] X. Yang and B. Li, “Monolayer MoS<sub>2</sub> for nanoscale photonics,” *Nanophotonics*, pp. 1–21, Feb. 2020.
- [232] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, “Atomically Thin MoS<sub>2</sub>: A New Direct-Gap Semiconductor,” *Phys. Rev. Lett.*, vol. 105, no. 13, p. 136805, Sep. 2010.
- [233] G. Wang *et al.*, “Colloquium : Excitons in atomically thin transition metal dichalcogenides,” *Rev. Mod. Phys.*, vol. 90, no. 2, p. 021001, Apr. 2018.
- [234] A. Krasnok, S. Lepeshov, and A. Alú, “Nanophotonics with 2D transition metal dichalcogenides [Invited],” *Opt. Express*, vol. 26, no. 12, p. 15972, Jun. 2018.
- [235] H. H. Fang *et al.*, “Control of the Exciton Radiative Lifetime in van der Waals Heterostructures,” *Phys. Rev. Lett.*, vol. 123, no. 6, p. 067401, Aug. 2019.
- [236] S. Wang *et al.*, “Coherent Coupling of WS<sub>2</sub> Monolayers with Metallic Photonic Nanostructures at Room Temperature,” *Nano Lett.*, vol. 16, no. 7, pp. 4368–4374, Jul. 2016.
- [237] J. Shang *et al.*, “Room-temperature 2D semiconductor activated vertical-cavity surface-emitting lasers,” *Nat. Commun.*, vol. 8, no. 1, p. 543, Dec. 2017.
- [238] S. Schwarz *et al.*, “Two-Dimensional Metal–Chalcogenide Films in Tunable Optical Microcavities,” *Nano Lett.*, vol. 14, no. 12, pp. 7003–7008, Dec. 2014.
- [239] S. Wu *et al.*, “Monolayer semiconductor nanocavity lasers with ultralow thresholds,” *Nature*, vol. 520, no. 7545, pp. 69–72, Apr. 2015.
- [240] Y. Ye *et al.*, “Monolayer excitonic laser,” *Nat. Photonics*, vol. 9, no. 11, pp. 733–737, Nov. 2015.
- [241] X. Fu *et al.*, “Optically Pumped Monolayer MoSe<sub>2</sub> Excitonic Lasers from Whispering Gallery

- Mode Microcavities,” *J. Phys. Chem. Lett.*, vol. 11, no. 2, pp. 541–547, Jan. 2020.
- [242] S. Lepeshov *et al.*, “Tunable Resonance Coupling in Single Si Nanoparticle–Monolayer WS<sub>2</sub> Structures,” *ACS Appl. Mater. Interfaces*, vol. 10, no. 19, pp. 16690–16697, May 2018.
- [243] H. Wang *et al.*, “Resonance Coupling in Heterostructures Composed of Silicon Nanosphere and Monolayer WS<sub>2</sub>: A Magnetic-Dipole-Mediated Energy Transfer Process,” *ACS Nano*, vol. 13, no. 2, p. 1739–1750, Jan. 2019.
- [244] S. Lepeshov, A. Krasnok, and A. Alù, “Enhanced excitation and emission from 2D transition metal dichalcogenides with all-dielectric nanoantennas,” *Nanotechnology*, vol. 30, no. 25, p. 254004, Jun. 2019.
- [245] M. Kerker, D.-S. Wang, and H. Chew, “Surface enhanced Raman scattering (SERS) by molecules adsorbed at spherical particles,” *Appl. Opt.*, vol. 19, no. 19, p. 3373, Oct. 1980.
- [246] R. Ruppin, “Decay of an excited molecule near a small metal sphere,” *J. Chem. Phys.*, vol. 76, no. 4, pp. 1681–1684, Feb. 1982.
- [247] R. Gómez-Medina, “Electric and magnetic dipolar response of germanium nanospheres: interference effects, scattering anisotropy, and optical forces,” *J. Nanophotonics*, vol. 5, no. 1, p. 053512, Jan. 2011.
- [248] W. Zhao *et al.*, “Evolution of Electronic Structure in Atomically Thin Sheets of WS<sub>2</sub> and WSe<sub>2</sub>,” *ACS Nano*, vol. 7, no. 1, pp. 791–797, Jan. 2013.
- [249] R. A. Shelby, “Experimental Verification of a Negative Index of Refraction,” *Science*, vol. 292, no. 5514, pp. 77–79, Apr. 2001.
- [250] Z. Qian *et al.*, “Raspberry-like metamolecules exhibiting strong magnetic resonances,” *ACS Nano*, vol. 9, no. 2, pp. 1263–1270, 2015.
- [251] S. Yang *et al.*, “Feedback-driven self-assembly of symmetry-breaking optical metamaterials in solution,” *Nat. Nanotechnol.*, vol. 9, no. 12, pp. 1002–1006, Dec. 2014.
- [252] Y. Cho, J.-H. Huh, K. J. Park, K. Kim, J. Lee, and S. Lee, “Using highly uniform and smooth selenium colloids as low-loss magnetodielectric building blocks of optical metafluids,” *Opt. Express*, vol. 25, no. 12, p. 13822, Jun. 2017.
- [253] C. Li, S. Lee, Z. Qian, C. Woods, S.-J. Park, and Z. Fakhraei, “Controlling Magnetic Dipole Resonance in Raspberry-like Metamolecules,” *J. Phys. Chem. C*, vol. 122, no. 12, pp. 6808–6817, Mar. 2018.
- [254] V. Many *et al.*, “High optical magnetism of dodecahedral plasmonic meta-atoms,” *Nanophotonics*, vol. 8, no. 4, pp. 549–558, Mar. 2019.
- [255] S. N. Sheikholeslami, H. Alaeian, A. L. Koh, and J. A. Dionne, “A Metafluid Exhibiting Strong Optical Magnetism,” *Nano Lett.*, vol. 13, no. 9, pp. 4137–4141, Sep. 2013.
- [256] A. Alù, A. Salandrino, and N. Engheta, “Negative effective permeability and left-handed materials at optical frequencies,” *Opt. Express*, vol. 14, no. 4, p. 1557, Feb. 2006.
- [257] J. Fontana *et al.*, “Virus-Templated Plasmonic Nanoclusters with Icosahedral Symmetry via Directed Self-Assembly,” *Small*, vol. 10, no. 15, pp. 3058–3063, Aug. 2014.
- [258] K. Kim, S. Yoo, J.-H. Huh, Q.-H. Park, and S. Lee, “Limitations and Opportunities for Optical Metafluids To Achieve an Unnatural Refractive Index,” *ACS Photonics*, vol. 4, no. 9, pp. 2298–

2311, Sep. 2017.

- [259] S. Gomez-Graña *et al.*, “Hierarchical self-assembly of a bulk metamaterial enables isotropic magnetic permeability at optical frequencies,” *Mater. Horizons*, vol. 3, no. 6, pp. 596–601, 2016.
- [260] S. Mühlig *et al.*, “Self-Assembled Plasmonic Core–Shell Clusters with an Isotropic Magnetic Dipole Response in the Visible Range,” *ACS Nano*, vol. 5, no. 8, pp. 6586–6592, Aug. 2011.
- [261] R. P. M. Höller *et al.*, “Protein-Assisted Assembly of Modular 3D Plasmonic Raspberry-like Core/Satellite Nanoclusters: Correlation of Structure and Optical Properties,” *ACS Nano*, vol. 10, no. 6, pp. 5740–5750, Jun. 2016.
- [262] S. Yang, Y. Wang, X. Ni, and X. Zhang, “Optical modulation of aqueous metamaterial properties at large scale,” *Opt. Express*, vol. 23, no. 22, p. 28736, Nov. 2015.
- [263] S. Zhang *et al.*, “Colloidal Moderate-Refractive-Index Cu<sub>2</sub>O Nanospheres as Visible-Region Nanoantennas with Electromagnetic Resonance and Directional Light-Scattering Properties,” *Adv. Mater.*, vol. 27, no. 45, pp. 7432–7439, Dec. 2015.
- [264] A.-G. Kussow, A. Akyurtlu, A. Semichaevsky, and N. Angkawisittpan, “MgB<sub>2</sub>-based negative refraction index metamaterial at visible frequencies: Theoretical analysis,” *Phys. Rev. B*, vol. 76, no. 19, p. 195123, Nov. 2007.
- [265] R. Ruppin, “Evaluation of extended Maxwell-Garnett theories,” *Opt. Commun.*, vol. 182, no. 4–6, pp. 273–279, Aug. 2000.
- [266] M. K. Schmidt, J. Aizpurua, X. Zambrana-Puyalto, X. Vidal, G. Molina-Terriza, and J. J. Sáenz, “Isotropically Polarized Speckle Patterns,” *Phys. Rev. Lett.*, vol. 114, no. 11, p. 113902, Mar. 2015.

## List of Achievements

### Publications

[1] (Chapter 2)

Tatsuki Hinamoto, Hiroyuki Takashina, Hiroshi Sugimoto, Minoru Fujii, “Controlling Surface Plasmon Resonance of Metal Nanocap for Upconversion Enhancement”, The Journal of Physical Chemistry C, vol. 121, pp. 8077-8083, 2017

[2] (Chapter 4)

Tatsuki Hinamoto, Hiroshi Sugimoto, and Minoru Fujii, "Metal-Core/Dielectric-Shell/Metal-Cap Composite Nanoparticle for Upconversion Enhancement", The Journal of Physical Chemistry C, vol. 122, pp. 174650-17472, 2018

[3] (Chapter 3)

Tatsuki Hinamoto, Tomoki Higashiura, Hiroshi Sugimoto, and Minoru Fujii, "Elongated Metal Nanocap with Two Magnetic Dipole Resonances and Its Application for Upconversion Enhancement", The Journal of Physical Chemistry C, vol. 123, pp. 25809-25815, 2019

[4] Hiroshi Sugimoto, Tatsuki Hinamoto, and Minoru Fujii, "Forward to Backward Scattering Ratio of Dielectric-Metal Heterodimer Suspended in Almost Free-Space", Advanced Optical Materials, vol. 7, pp. 1900591 (1-7), 2019

[5] Hiroto Yanagawa, Tatsuki Hinamoto, Takashi Kanno, Hiroshi Sugimoto, Masahiko Shioi, and Minoru Fujii, "Gold nanopillar array with sharp surface plasmon resonances and the application in immunoassay", Journal of Applied Physics, vol. 126, pp. 223104 (1-8), 2019

[6] Hiroshi Sugimoto, Ryosuke Imaizumi, Tatsuki Hinamoto, Takahiro Kawashima, and Minoru Fujii, “Silicon Nanowire on Mirror Nanoantennas -Engineering Hybrid Gap Mode for Light Sources and Sensing Platforms”, ACS Applied Nano Materials, 2020, *in press*

[7] Hiroaki Hasebe, Hiroshi Sugimoto, Tatsuki Hinamoto, and Minoru Fujii, “Coupled Toroidal Dipole Modes in Silicon Nanodisk Metasurface: Polarization Independent Narrow Band Absorption and Directional Emission”, *under review*

- [8] (Chapter 6)  
Tatsuki Hinamoto, Mikihiro Hamada, Hiroshi Sugimoto, and Minoru Fujii, “Fourier-Plane Spectroscopy for Characterization of Individual Mie-Resonant Optical Nanoantennas”, *in preparation*
- [9] (Chapter 7)  
Tatsuki Hinamoto, Yan Joe Lee, Søren Raza, Hiroshi Sugimoto, Minoru Fujii, and Mark L. Brongersma, “Controlling Emission of WS<sub>2</sub> Monolayer with a Spherical Silicon Mie Resonator”, *in preparation*
- [10] (Chapter 8)  
Tatsuki Hinamoto, Shinnosuke Hotta, Hiroshi Sugimoto, and Minoru Fujii, “A Colloidal Solution of Silicon Nanospheres toward All Dielectric Metafluids”, *in preparation*
- [11] Tatsuki Hinamoto, Junkyo Suh, Qitong Li, Minoru Fujii, and Mark L. Brongersma, “Boosting Spectral Response of Mie Resonators Against Surrounding Environment”, *in preparation*
- [12] Artyom Assadillayev, Tatsuki Hinamoto, Hiroshi Sugimoto, Minoru Fujii, Radu Malureanu, Tim Booth, Mark L. Brongersma, and Søren Raza, “Plasmon Launching and Scattering by Silicon Nanoparticles”, *in preparation*
- [13] (査読なし) 雛本樹生, 杉本泰, 藤井稔, “光の周波数で磁気応答を示す誘電体メタ原子の開発”, 第 30 回光物性研究会論文集, 光物性研究会, 論文番号 II-68 (pp. 1-4), 2019

## International Conferences

- [1] Tatsuki Hinamoto, Hiroyuki Takashina, and Minoru Fujii, “Surface Plasmon-Enhanced Upconversion in Rare-earth doped Nanoparticles with Au Nanocaps” 2016 MRS Fall Meeting & Exhibit, Number EM7.7.07, Boston (USA), November 2016 (Oral presentation)

- [2] Tatsuki Hinamoto, Kaoru Yamamoto, and Minoru Fujii, “Metal Core-Dielectric Shell-Metal Nanocap Structure for Surface Plasmon-Enhanced Upconversion” 2018 MRS Spring Meeting & Exhibit, Number NM09.06.03, Phoenix (USA), April 2018 (Poster presentation)
- [3] Tatsuki Hinamoto, Yan Joe Lee, Søren Raza, Hiroshi Sugimoto, Minoru Fujii, and Mark L. Brongersma, “Controlling Emission of WS<sub>2</sub> Monolayer with a Spherical Silicon Mie Resonator” 2019 MRS Fall Meeting & Exhibit, Number EL01.06.03, Boston (USA), December 2019 (Oral presentation)
- [4] Tatsuki Hinamoto, Mikihiro Hamada, Hiroshi Sugimoto, Minoru Fujii, “Engineering Directional Scattering of Mie Resonator”, The International Symposium on Plasmonics and Nanophotonics, Paper ID 17, Kobe (Japan), December 2019 (Poster presentation)
- [5] Tatsuki Hinamoto, 69<sup>th</sup> Lindau Nobel Laureate Meeting (dedicated to Physics), The Council for the Lindau Nobel Laureate Meetings, Lindau (Germany), June 2019  
The participation was supported by JSPS

## Award

- [1] 第 30 回光物性研究会奨励賞, 2019 年 12 月
- [2] Outstanding Student Award, Kobe University Premium Program, 2019 年 6 月
- [3] 第 7 回応用物理学会関西支部奨励賞, 2019 年 3 月
- [4] 応用物理学会関西支部第一回講演会 最優秀賞, 2018 年 4 月
- [5] 竹水会優秀論文賞 (副賞図書券 2 万円), 2018 年 3 月
- [6] 若手フロンティア研究会 2017 最優秀賞 (副賞 10 万円), 2017 年 12 月



Doctor Thesis, Kobe University

“Engineering Optical Nanoantennas based on Plasmonics and Mie Resonances”, 170 pages

Submitted on July 17, 2020

The date of publication is printed in cover of repository version published in Kobe University Repository Kernel.

© Tatsuki Hinamoto  
All Right Reserved, 2020