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Immobilization of Mie-Resonant Silicon Nanospheres on a Silica Substrate for Surface-Enhanced Fluorescence

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Abstract. A process to immobilize Mie resonant silicon nanospheres (Si NSs) on a large area substrate is developed for the application for surface-enhanced fluorescence (SEF) biosensors. The surface of size-purified Si NSs having the low-order Mie resonances in the visible to near-infrared range is functionalized with epoxy group, and the Si NSs are immobilized on the surface of an amino-terminated silica (SiO_2) substrate $1 \times 1 \text{ cm}^2$ in size by a fully wet process. The produced substrate exhibits clear Mie resonant color. The wavelength of the reflectance maximum is controlled by the size of Si NSs, and the highest reflectance value reaches over 40 %. In order to study the capability of the developed substrate as a SEF substrate, Lucifer Yellow CH dipotassium salt dye (LY) molecules are directly placed on the substrate and the photoluminescence (PL) properties are studied. The PL intensity is enhanced about 14-fold on a substrate on which Si NSs 129 nm in average diameters are immobilized. Theoretical calculations by taking into account the size distribution of Si NSs explain the observed size dependence of the enhancement factor.

Keywords: Silicon nanosphere, Mie resonance, Surface enhanced fluorescence

1. Introduction

Surface-enhanced fluorescence (SEF) biosensors known for their outstanding sensitivity and specificity have emerged as a powerful tool in the field of molecular detection.¹⁻³ One of the primary advantages of SEF biosensors is their ability to detect low-abundance targets, which is crucial in applications like early-stage disease diagnostics. In biomedical diagnostics, SEF biosensors can identify specific proteins, nucleic acids, or other biomarkers, providing rapid and accurate results that are essential for timely medical intervention. In environmental monitoring,

these biosensors are used to detect pollutants or toxins at very low concentrations, helping in the assessment and management of environmental health.⁴ Additionally, in drug development, SEF biosensors facilitate high-throughput screening of potential drug candidates by providing precise measurements of molecular interactions.⁵ The versatility of SEF biosensors extends their adaptability in various formats, such as handheld devices for point-of-care testing or integrated systems for laboratory-based assays. Their development continues to evolve, with ongoing research focused on enhancing their sensitivity, stability, and ease of use, making SEF biosensors a vital component in modern analytical science.¹

SEF leverages fluorescence enhancement that occurs when fluorescent molecules are in close proximity to metallic nanostructures, typically gold and silver nanostructures.⁶ These metallic surfaces with localized surface plasmon resonances (LSPR) can amplify the fluorescence signal, allowing for the detection of even minute quantities of biomolecules.⁷ However, they also present several disadvantages. Close proximity of fluorophores to metallic surfaces leads to photobleaching and photodegradation. This is because the enhanced electromagnetic field accelerates the decomposition of fluorescent molecules, reducing the longevity and reliability of the sensor. Moreover, fluorescence is quenched if fluorophores are too close to the metal surface. This quenching effect diminishes the signal-to-noise ratio, complicating the detection and quantification of target molecules.⁷⁻⁹ Other drawbacks might come from the expense, the complex fabrication techniques, and environmental implications during synthesis and disposal processes.¹⁰

To address these limitations, ongoing research aims to develop alternative materials to enhance SEF biosensor performance. Dielectric nanomaterials having low-order Mie resonances are considered promising candidates for improving the performance of SEF biosensors because they enable efficient light-matter interactions.¹¹⁻¹⁶ A silicon (Si) particle with the size of 100–250 nm is an almost ideal candidate of a Mie resonator because of the high reflective index ($n > 3$) and small extinction coefficient ($k < 0.5$) of crystalline Si in visible to near-infrared spectral ranges.¹⁷⁻²¹ For the construction of SEF biosensors from Si nanoparticles, they have to be immobilized on a substrate. This can be achieved by utilizing conventional nanofabrication technologies including electron beam lithography and reactive dry etching.^{22,23} However, these methods are expensive for the production of millimeter-scale nanoparticle arrays that can be used in naked-eye readable biosensors.

In this work, we develop a bottom-up process to produce a large area ($1 \times 1 \text{ cm}^2$) SEF substrate composed of a monolayer of Si nanospheres (NSs) having the Mie resonances in the visible to near-infrared spectral range by using the colloidal suspension as a precursor. We show that the produced substrates exhibit clear Mie resonances in the reflectance spectra, and that the resonance wavelength can be controlled in a wide wavelength range (480 - 800 nm) by changing the NS diameter from 115 to 255 nm. We study the fluorescence enhancement behavior of the produced SEF substrates by placing dye molecules directly on the surface. The fabricated substrate enhances the PL of the dye molecules at most 14-fold. Finally, we show that the observed size dependence of the PL enhancement factor can be well explained by theoretical calculations.

2. Results and Discussion

2.1. Immobilization of Mie-resonant Si NSs on a silica substrate

To fabricate a Si NS monolayer on a SiO_2 substrate, we use colloidal suspensions of Si NSs produced by thermal disproportionation of silicon monoxide (SiO).^{24,25} Details of the preparation procedure are shown in the experimental section. Briefly, SiO lumps are annealed at 1500°C for 30 minutes in an N_2 gas atmosphere to grow Si nanoparticles in SiO_2 matrices. Si nanoparticles are liberated from the matrices by hydrofluoric acid etching, and then transferred to methanol. Figure 1a shows the photograph of the solution. Figure 1b and c shows the transmission electron microscope (TEM) images of Si nanoparticles. The particles are almost perfectly spherical and the crystallinity is high.²⁴ Si NSs are then separated by size by the density-gradient centrifugation process.^{26,27} Figure 1d shows the Si NS suspensions after the size separation process. The brownish solution in Figure 1a is separated into colored solutions. The average diameter (D_{ave}) and the coefficients of variation of the size distribution (CV) defined by the standard deviation (σ) divided by D_{ave} are shown below the photos. In Figure 1e, the extinction spectra of these solutions are shown. Mie scattering peaks can be observed in the macroscopic scale suspensions and the peak red-shifts with increasing the size.

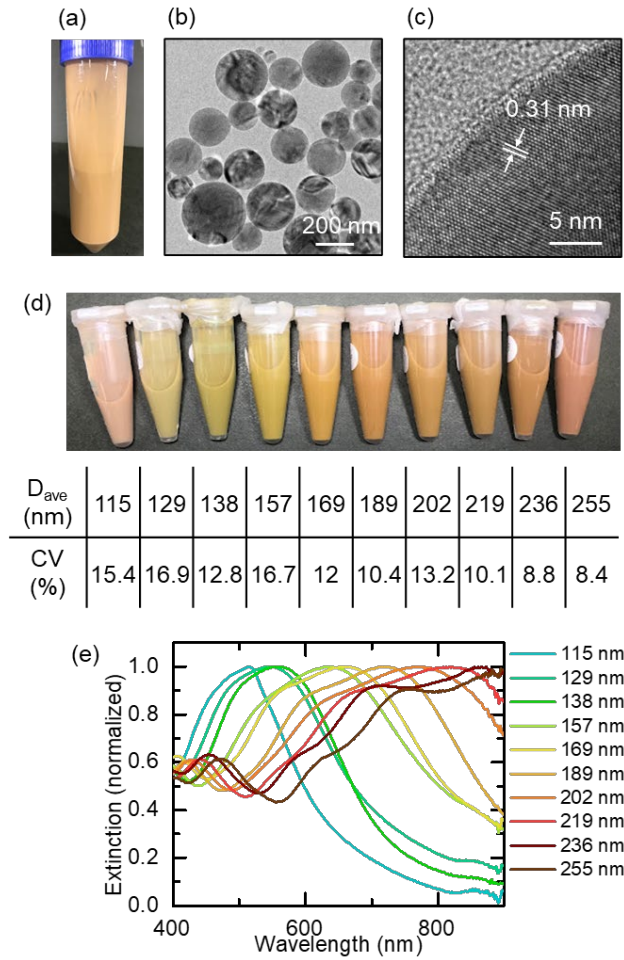


Figure 1. (a) Photograph of colloidal suspension of Si NSs before size separation. (b, c) TEM images of as-synthesized Si NSs. (d) Photograph of colloidal suspensions of size-separated Si NSs. The average diameters (D_{ave}) and the coefficients of variation of the size distribution (CV) defined by the standard deviation (σ) divided by D_{ave} are shown below the photograph. (e) Extinction spectra of colloidal suspensions of size-separated Si NSs.

The size-separated Si NSs are immobilized on a SiO_2 substrate by the epoxy-amine reaction by the procedure shown in Figure 2a. The surface of Si NSs is functionalized with (3-glycidypropyl) trimethoxysilane (GOPTS, >97%, TCI), and the surface of a SiO_2 substrate ($1 \times 1 \text{ cm}^2$ in size) is functionalized with 3-Aminopropyltriethoxylane (APTES, >98%, TCI). A Si NS suspension is dropped on the surface of the SiO_2 substrate to form a monolayer of Si NSs. Finally, unbonded Si NSs are washed out carefully by isopropyl alcohol (IPA, 99.7%, FUJIFILM Wako), and the sample

is dried by N₂ gun. In Figure 2b, photographs of Si NS-immobilized substrates produced from the suspensions in Figure 1d taken under white LED illumination are shown. The extinction spectra are shown in Supporting Information (Figure S2). Colors due to Mie scattering appear in the substrate despite the very small thickness, i.e., monolayers. The color is similar to those of the suspensions except for $D_{ave}=115$ nm. The color difference between the suspension and the monolayer in $D_{ave}=115$ nm is due to the multiple scattering and resulting blue light absorption in the suspension.²⁵ A typical dark-field microscope image and a scanning electron microscope (SEM) image of the fabricated substrate are shown in Figures 2c and 2d, respectively.

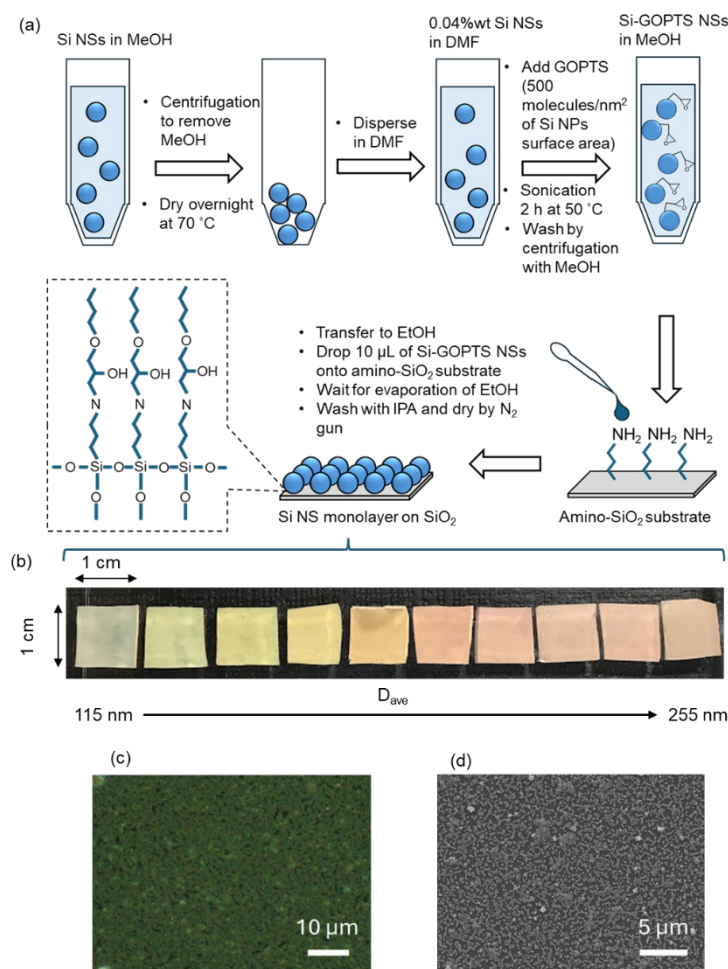


Figure 2. (a) Schematic illustration of Si NS monolayer fabrication process. (b) Photos of Si NS-immobilized SiO₂ substrates produced from the suspensions in Figure 1d taken under white LED illumination. (c, d) Typical dark-field optical microscope (c) and SEM (d) images of a Si NSs-immobilized substrate.

Figure 3a, b and c shows the specular, diffuse, and total reflectance spectra, respectively, of Si NS monolayers in Figure 2b. By comparing Figures 3a and 3b, we notice that the diffuse reflectance is stronger than the specular reflectance in most of the wavelength range. This is due to random alignment of Si NSs on the substrates. The total reflectance spectra obtained by adding the specular and diffuse reflectance spectra have single Mie-resonant peaks, and the peak shifts from 430 to 800 nm when D_{ave} is changed from 115 to 255 nm, demonstrating size-tunable Mie resonances in the Si NS-immobilized substrates. Therefore, depending on the excitation and emission wavelengths of dye molecules used for sensing, we can choose proper size Si NSs for the production of a SEF substrate. The values of the total reflectance and the extinction at 488 nm, i.e., the excitation wavelength in the next subsection, are shown in Supporting Information (Figure S3).

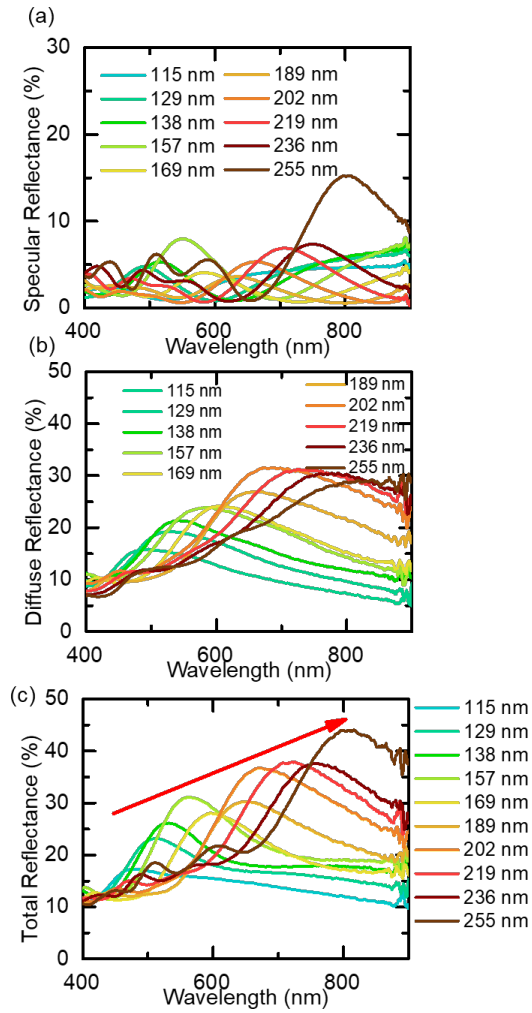


Figure 3. (a) Specular, (b) diffuse and (c) total reflectance spectra of Si NS-immobilized SiO₂ substrates shown in Figure 2b.

2.2. Fluorescence enhancement of dye molecules placed on Si NS-immobilized substrates

To study the capability of fluorescence enhancement, we directly placed Lucifer Yellow CH dipotassium salt dye (LY) on top of a Si NS monolayer by spin coating a 10 μ L water solution of 0.1 M LY and measured the photoluminescence (PL) and the PL decay properties. The size of the measurement area is about 25 μm^2 and 100 different points on a $1 \times 1 \text{ cm}^2$ size substrate are measured. Figure 4a shows the averaged PL spectrum of LY on a Si NS-immobilized substrate with $D_{\text{ave}} = 138 \text{ nm}$. The excitation wavelength is 488 nm. In Figure 4a, the reference spectrum obtained for a SiO_2 substrate coated with the same amount of LY is shown. The PL is strongly enhanced on the Si NS-immobilized substrate. Figure 4b shows the PL decay curves. The average lifetime (τ) estimated by fitting the decay curves with double exponential functions is shown in the graph. The lifetime is about 50 % shortened on the Si NS-immobilized substrate. We will quantitatively discuss this effect later. Figure 4c shows the PL enhancement factor at 600 nm as a function of the diameter of Si NSs. The error bar represents the maximum and minimum of the values obtained for 100 different points on a substrate. The enhancement factor has clear size dependence and is the largest when the diameter is 129 nm.

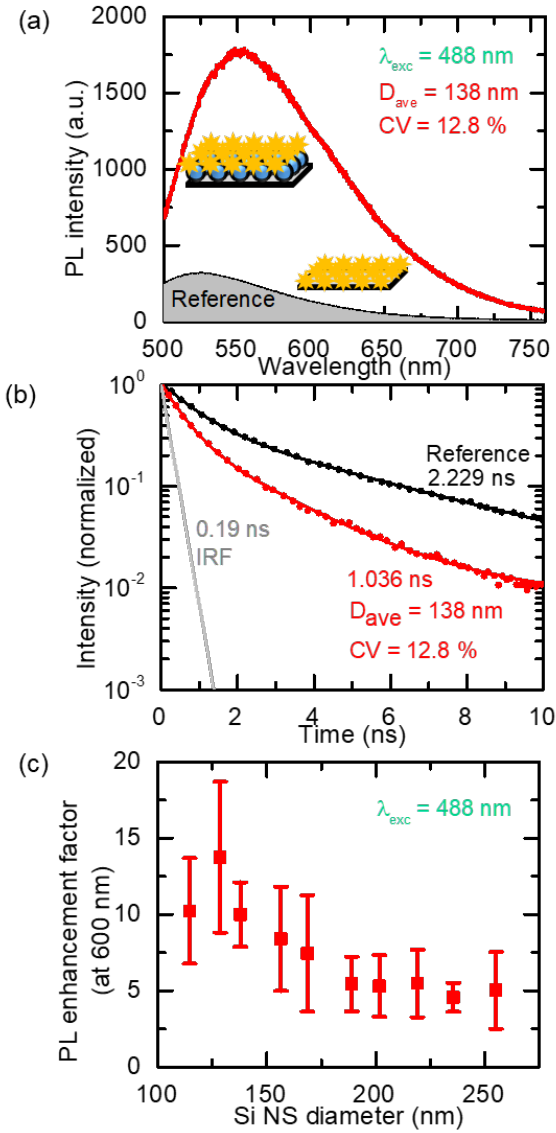


Figure 4. (a) PL spectrum of LY on a Si NS-immobilized substrate. The average diameter (D_{ave}) and the coefficient of variation of the size distribution (CV) of Si NSs are 138 nm and 12.8 %, respectively. The excitation wavelength is 488 nm. The PL spectrum LY on a flat SiO₂ substrate is also shown as a reference. (b) PL decay curves of LY on a Si NS-immobilized substrate (red dots) together with that on a SiO₂ substrate (black dots). Solid curves are the results of fittings by a double exponential function. The average lifetimes obtained from the fittings are shown in the Figure. The instrument response function (IRF) is shown in the grey curve. (c) PL enhancement factor detected at 600 nm as a function of Si NS diameter. The error bar represents maximum and minimum of the values obtained for 100 different points on a $1 \times 1 \text{ cm}^2$ size substrate.

In order to quantitatively understand the observed enhancement of the PL decay rate and the PL intensity, we calculate the enhancement factors in a model that an emitting dipole is placed at 5 nm from the surface of a Si NS, and there is no coupling between Mie modes of Si NSs. The model structure is shown in the inset of Figure 5a. The decay rate enhancement factor is defined as,

$$EF_{Decay}^{Cal} = \frac{\gamma_{rad} + \gamma_{nonrad} + \gamma_{nonrad}^0}{\gamma_{rad}^0 + \gamma_{nonrad}^0}, \quad (1)$$

where γ_{rad}^0 and γ_{nonrad}^0 are intrinsic radiative and nonradiative decay rates of a dipole, and γ_{rad} and γ_{nonrad} are the radiative and nonradiative decay rates near a nanoantenna. Considering the broad fluorescence spectrum of a molecule,²⁸

$$\gamma_{rad} = \gamma_{rad}^0 \int_0^\infty f_0(\omega) \frac{\Gamma_{rad}(\omega)}{\Gamma_0} d\omega, \quad (2)$$

and

$$\gamma_{nonrad} = \gamma_{rad}^0 \int_0^\infty f_0(\omega) \frac{\Gamma_{nonrad}(\omega)}{\Gamma_0} d\omega, \quad (3)$$

where $f_0(\omega)$ is the integral-normalized fluorescence spectrum of an isolated molecule, $\Gamma_0 = \gamma_{rad}^0 + \gamma_{nonrad}^0$, $\frac{\Gamma_{rad}(\omega)}{\Gamma_0}$ is the radiative decay rate enhancement factor, and $\frac{\Gamma_{nonrad}(\omega)}{\Gamma_0}$ is the nonradiative decay rate enhancement factor introduced by the nanoantenna normalized by Γ_0 .²⁸ In Figure 5a and b (black curves), $\frac{\Gamma_{rad}(\omega)}{\Gamma_0}$ and $\frac{\Gamma_{nonrad}(\omega)}{\Gamma_0}$, respectively, calculated for a Si NS 138 nm in diameter are shown. The data obtained for other size Si NSs are shown in Supporting Information (Figure S5). For the calculation, emitting dipoles both parallel (||) and perpendicular (⊥) to the surface of a Si NS are considered and averaged. The radiative rate is enhanced at the wavelengths of the MD and ED resonances, while the nonradiative rate is enhanced at those of the MD and MQ resonances.

In actual samples, Si NSs have size distributions as shown in Figure 1d. Therefore, we take into account the size distribution in the calculations by taking the weighted-average of $\frac{\Gamma_{rad}(\omega)}{\Gamma_0}$ and $\frac{\Gamma_{nonrad}(\omega)}{\Gamma_0}$ in the $\pm 3\sigma$ range of a Gaussian size distribution. The red curves in Figure 5a and b are the calculated results for $CV = 12.8\%$. The Mie resonance features are broadened and smeared by

the size distribution. However, strong radiative rate enhancement still remains. By using the data considering the size distribution, the decay rate enhancement factor is calculated to be 1.95 under the assumption that the intrinsic quantum yield of *LY* ($QY_0 = \frac{\gamma_{rad}^0}{\Gamma_0}$) is 0.21.²⁹ The estimated decay rate enhancement factor agrees well with the experimentally obtained one (2.15). Figure 5d shows calculated decay rate enhancement factors obtained for different size Si NSs. The decay rate enhancement factor is almost independent of the size, and is ~ 1.8 in the size range studied.

In general, the PL intensity enhancement factor of an emitter near a nanoantenna is defined as,

$$EF_{Intensity}^{Cal}(\omega) = \frac{|\mathbf{E}(\omega_\lambda)|^2}{|\mathbf{E}_0(\omega_\lambda)|^2} \times EF_{QY}$$

$$= \frac{|\mathbf{E}(\omega_\lambda)|^2}{|\mathbf{E}_0(\omega_\lambda)|^2} \times \frac{1}{QY_0} \frac{\frac{\Gamma_{rad}(\omega)}{\Gamma_0}}{\int_0^\infty f_0(\omega) \frac{\Gamma_{rad}(\omega)}{\Gamma_0} d\omega + \int_0^\infty f_0(\omega) \frac{\Gamma_{nonrad}(\omega)}{\Gamma_0} d\omega + \frac{1-QY_0}{QY_0}}, \quad (4)$$

where $|\mathbf{E}(\omega_\lambda)|^2$ is the electric field intensity at the position of an emitter, $|\mathbf{E}_0(\omega_\lambda)|^2$ is that without a Si NS at the excitation wavelength (ω_λ), $\frac{|\mathbf{E}(\omega_\lambda)|^2}{|\mathbf{E}_0(\omega_\lambda)|^2}$ is the enhancement factor at the excitation process and EF_{QY} is the enhancement factor at the emission process.²⁸ We calculate $\frac{|\mathbf{E}(\omega_\lambda)|^2}{|\mathbf{E}_0(\omega_\lambda)|^2}$ by integrating the electric field intensity at 5 nm from the surface of a Si NS under plane wave illumination. Figure 5c shows calculated $\frac{|\mathbf{E}(\omega_\lambda)|^2}{|\mathbf{E}_0(\omega_\lambda)|^2}$ for a 138 nm-diameter Si NS without size distribution (black) and with size distribution (red, $CV = 12.8\%$). The enhancement factor spectra are very similar to that of the radiative rate enhancement factor spectra in Figure 5a. In Supporting Information (Figure S4), $\frac{|\mathbf{E}(\omega_\lambda)|^2}{|\mathbf{E}_0(\omega_\lambda)|^2}$ spectra for different size Si NSs are shown. In Figure 5e, $\frac{|\mathbf{E}(\omega_\lambda)|^2}{|\mathbf{E}_0(\omega_\lambda)|^2}$ at 488 nm is plotted as a function of Si NS diameter. The size distributions shown in the table in Figure 1d are taken into account. The excitation efficiency has strong size dependence and is the largest (~ 4.5) when the diameter is around 130 nm.

In Eq. (4), the enhancement of emission collection efficiency by the existence of a Si NS is not considered. In order to roughly estimate the effect, we calculate it for an emitting dipole placed near a Si NS by assuming an experimental detection optics (N.A. = 0.8). In Supporting Information (Section 3), we show calculated enhancement factors of the emission collection efficiency for a dipole placed on top and on the side of a Si NS. The size distribution is considered. The data

indicate that the collection efficiency is not strongly modified by the presence of a Si NS compared to other factors.

Figure 5f shows the calculated PL intensity enhancement factor at the emission wavelength of 600 nm. The largest enhancement factor is obtained at $D_{ave} = 138$ nm; the enhancement factor reaches 10.5-fold. The enhancement factor value as well as the size dependence agree relatively well with the experimental ones in Figure 4c. Note that the enhancement factor depends on QY_0 of a molecule, and a larger enhancement factor is expected at smaller QY_0 (Figure S9 in Supporting Information). In a Si NS, a factor that limits the PL enhancement factor is the non-zero Γ_{nonrad} . In order to estimate the effect of the absorption loss, we calculate the PL enhancement factor for a loss-less Si NS (Figure S6 in Supporting Information). The enhancement factor for a $D_{ave} = 138$ nm NS increases about 30 % in the loss-less case.

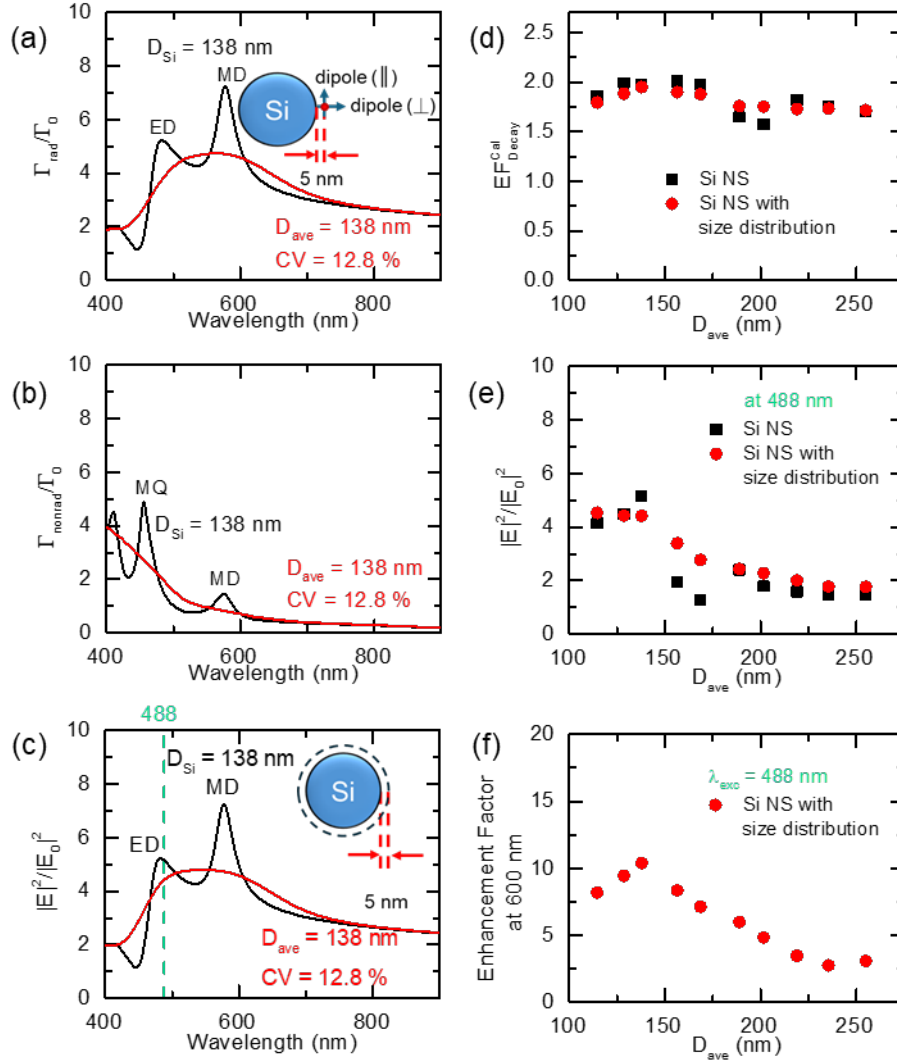


Figure 5. (a, b) Calculated (a) radiative and (b) nonradiative decay rate enhancement factors of a Si NS with $D_{ave} = 138$ nm (black curves). Results obtained by taking into account the size distribution ($CV = 12.8\%$) are shown in red curves. (c) Electric field intensity enhancement factor at 5 nm from the surface of a Si NS under plane wave illumination for a Si NS with $D_{ave} = 138$ nm (black curve). The electric field intensity is integrated over the whole surface. The red curve is the data obtained by taking into account the size distribution ($CV = 12.8\%$). (d) Calculated decay rate enhancement factor as a function of D_{ave} . (e) Calculated electric field intensity enhancement factor at 488 nm as a function of D_{ave} . (f) Calculated total PL enhancement factor at 600 nm as a function of D_{ave} .

3. Conclusion

A process to immobilize Mie resonant Si NSs on a large area substrate was developed, and a monolayer of Si NSs was formed on a $1 \times 1 \text{ cm}^2$ size SiO_2 substrate. The developed substrates exhibited clear Mie resonant color which can be controlled by the size of Si NSs. The reflectance of the monolayers reached over 40 %. To study the capability of the developed substrate as a SEF substrate, we placed LY dye molecules directly on a Si NS monolayer and studied the PL enhancement properties. The PL intensity was enhanced about 14-fold on a substrate on which Si NSs 129 nm in average diameters were immobilized. Theoretical calculations by taking into account the size distribution of Si NSs explained the observed size dependence of the enhancement factor very well. Because of the simple fabrication process, the high PL enhancement factor, and the wide tunability of the resonance wavelength, the fabricated Si NS-immobilized large area substrates can be a new platform for fluorescence-enhanced biosensors.

4. Experimental Section

Preparation of colloidal suspension of Si NS

SiO lump powder (several mm in size, 99%, FUJIFILM Wako) was annealed at 1500°C for 30 min in a N_2 gas atmosphere for the disproportionation into Si NSs and SiO_2 matrices. Si NSs were extracted from the matrices by etching out SiO_2 matrices in a hydrofluoric acid (HF, 46 wt%) solution for 1 hour, washed several times with methanol, and finally dispersed in a methanol solution.

The colloidal suspension of Si NSs was separated by size by a density-gradient centrifugation process.^{26,27} A 15 mL centrifugal tube was filled with 2.2 mL of a sucrose solution at six distinct concentrations (55–42.5, 2.5 wt% increments) in order to create a sucrose density gradient solution, and 1.8 mL of Si NS suspension was added from the top. Centrifugation of the tube at 5500 rpm for 60 min resulted in layers of size-separated Si NSs. Size-separated Si NSs were then carefully collected by a micropipette. The suspensions of size-separated Si NSs were washed several times with deionized water and then stored in methanol. The average diameter and the size distribution were obtained from the extinction spectra by the procedure shown in Supporting Information.³⁰

Fabrication of Si NS-immobilized substrate

Size-separated Si NSs were functionalized with (3-glycidoxypyl) trimethoxysilane (GOPTS, >97%, TCI) by the following process. Si NSs were dried to remove methanol, and then dispersed in N, N dimethylformamide (DMF) super hydrate (FUJIFILM Wako) with the concentration of 0.04 wt%. GOPTS was added to the solution and the mixture was sonicated for 2 hours at 50 °C. The amount of GOPTS was set to be 500 molecules per Si NS surface of 1 nm². Finally, Si NSs were washed several times with methanol by centrifugation.³¹

The surface of a SiO₂ substrate (1 × 1 cm²) was functionalized with an amino group by using 3-Aminopropyltriethoxylane (APTES, >98%, TCI) by the following procedure.^{31,32} A SiO₂ substrate was cleaned and hydroxylated by a UV-ozone treatment for 20 min at 110 °C, immediately immersed in 1 wt% APTES in DMF, incubated for 2 hours at 50 °C, rinsed by methanol, and baked for 20 min at 110 °C to cross-link APTES on the surface.

To prepare Si NS-immobilized substrate, 10 μL of ethanol suspension of GOPTS-functionalized Si NSs was dropped on the amino-functionalized SiO₂ substrate. The amount of Si NSs in the suspension was set to be equivalent to cover 60 % of the surface of the substrate. After evaporation of ethanol, the Si NS-immobilized substrate was washed by IPA and dried in N₂ gas to remove unbonded Si NSs.

Optical spectroscopy

Reflectance spectra: A double-beam spectrophotometer (UV-3101PC, Shimadzu) with incident and detection angles of 5° was used for the measurement of the specular reflectance spectra. A double-beam spectrophotometer equipped with an integrating sphere (Spectrapro 3700, Shimadzu) was used to measure the diffuse reflectance spectra with the incident angle of 0°. The reflectance of the area of 6 × 10 mm² within a 1 × 1 cm² size substrate was measured. In both measurements, the incident light was not polarized. The total reflectance spectra were obtained by adding the specular and diffuse reflectance spectra.

PL spectra and PL decay curves: PL spectra and PL decay curves of LY on a Si NS-immobilized substrates were measured by a custom-built inverted optical microscope. A substrate was placed facedown onto the stage and excited through a dark-field objective lens (50×, N.A. = 0.8). The emitted light was collected by the same objective lens and transferred to the entrance slit of a monochromator (Kymera 328i, Andor) and then detected using a cooled CCD (Newton, Andor). The excitation wavelength was 488 nm. For the measurement of PL decay curves, the emission

was brought to another port of the same optical microscope and detected using a time-correlated single photon counting module (PicoQuant, TimeHarp200) with an avalanche photodiode (PD-100-CTE, MPD). The excitation wavelength was 480 nm (76 ps pulse width, 40 MHz repetition, 6.3 nm bandwidth). The average PL lifetime (τ) was obtained by fitting the measured decay curves with a double exponential function, $I = A_1 \exp\left(\frac{-t}{\tau_1}\right) + A_2 \exp\left(\frac{-t}{\tau_2}\right)$, and calculating $\tau = \frac{A_1\tau_1 + A_2\tau_2}{A_1 + A_2}$.¹⁷

Calculation of electric field enhancement factor, radiative and nonradiative decay rate enhancement factors

The electric field enhancement factor and radiative and nonradiative decay rate enhancement factors were analytically calculated using MATLAB codes given in Refs [21] and [33]. For the calculations, we assumed isolated Si NSs and did not consider interaction between Si NSs. For the calculation of decay rate enhancement factors, power dissipation of a dipole placed 5 nm from Si NS surface was considered; power dissipations of a dipole parallel ($\Gamma_{\parallel}$) and perpendicular ($\Gamma_{\perp}$) to Si NS surface was calculated and averaged ($\Gamma_{\text{ave}} = 1/3\Gamma_{\perp} + 2/3\Gamma_{\parallel}$). The calculations were performed for up to 50th multipoles. The enhancement factor of the excitation efficiency was calculated by averaging the electric field intensity at 5 nm from the surface of a Si NS under plane wave illumination.

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