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Preparation of Silver Nanoparticles-Nafion Membrane Composite by Photoreduction Process

Takashi Hasegawa[a], Thomas Strunskus[b], Vladimir Zaporotjenko[b],
Franz Faupel[b], and Minoru Mizuhata[a]

[a] Department of Chemical Science and Engineering,
Graduate school of Engineering, Kobe University,
1-1 Rokkodai, Kobe 657-8501, Japan
[b] Institute for Materials Science, Faculty of Engineering,
Christian Albrecht University of Kiel,
Kaiserstraße 2, 24143 Kiel, Germany

Preparation method of silver nanoparticles (AgNPs) dispersed in Nafion 115 membrane using UV photoreduction process was established. The loading amount of AgNPs was controlled with UV irradiation time. AgNPs might exist in ionic cluster channel in Nafion membrane stably without any stabilizing reagent. The particle size was measured by transmission electron microscope (TEM). The mean particle size was ca. 13 nm in diameter. The obtained nanocomposite membrane has absorption bands due to local surface plasmon resonance (LSPR) at around 400 nm. The band position depends on the refractive index of suspension as expected by Mie theory. Furthermore very little amount of solvent affected the LSPR bands sensitively due to changing the highly localized refractive index.

Introduction

It is known that the perfluorosulfonic acid membrane such as Nafion can provide "nano scale cavities" and they play roles as for chemical reaction fields. The manufacturing which uses Nafion as a host matrix of the nanoparticles is widely investigated in the field of electrochemistry including PEFC and so on (1-3).

Nafion membrane is also known as the major cation exchange membranes with large exchange capacity and high chemical resistance. In the case of immersion in the liquid such as organic solvent, Nafion membrane is known to swelling and expands its size due to incorporating retention of these solvent. However, to obtain the silver nanoparticles (AgNPs) embedded in Nafion composite (Ag/Nafion) with well-dispersed AgNPs has less been reported anywhere. In the step of reduction of silver ion to AgNPs, they applied hydrogen gas or boron hydrate salts. Distributions of the silver particles are not homogeneous because diffusion of the silver ion within the membrane occurred in the reduction process. So we would like to suggest the photo reduction process to obtain the Ag/Nafion composites. N,N-dimethylformamide (DMF) penetrating into in that cavity (ionic channel) in the membrane reduced Ag^+ ion with irradiated light. Compared with other reduction process, e.g. hydrogen or boron hydrate salt (4), the photo reduction process can achieve the homogeneous reaction to Ag^0 by its energy transferring mechanism. Additionally this method can realize to prepare AgNPs without any

stabilization reagent and with bare surface which can interact directly to other species. Such environment of AgNPs is thought to be ideal for observing the shift of local surface plasmon resonance. The spectral position of the UV-vis absorbance is highly dependent on the local refractive index at the nanoparticle surface, which is widely investigated as the principle for the label-free chemical and biological sensing applications (LSPR sensor). LSPR sensors can be used as an alternative to surface plasmon resonance (SPR) sensors because the highly localized electromagnetic fields that occur at nanoparticle surfaces can improve the detection of nanoscale biological analytes. In other words, molecule at the vicinity of the nanoparticles changes the local refractive index, causing changes in the absorbance peak that are easily monitored using UV-vis spectroscopy. The spectral shifts on various refractive indices are necessary to investigate the potential of using LSPR as a sensing device.

The extinction function $\sigma_{ext}(\omega)$ of nanoparticles can be expressed by reduced Mie theory [1] (5, 6)

$$\sigma_{ext}(\omega) = \frac{9\omega}{c} \varepsilon_m^{3/2} V \frac{\varepsilon''(\omega)}{\left[\varepsilon'(\omega) + 2\varepsilon_m\right]^2 + \varepsilon''(\omega)^2} \qquad [1]$$

where ω is angular frequency of the exciting radiation, c is the speed of the light, $V = (\pi/6) d^3$, ε_m is the dielectric function of medium surrounding metal nanoparticles, and ε' and ε'' are the real and imaginary parts of dielectric function of metal nanoparticles respectively. Usually metal nanoparticles are prepared as the colloidal form in solution (7). Generally the colloidal particle should be embedded in fixed position or included in stable matrices due to difficult handling of dispersed nanoparticles in the liquid phase. In several studies, immobilization of metal nanoparticles onto glass substrate was tried using organic coupling agent for the LSPR sensor (8-10).

In this study, we developed the preparation process using ion exchanging process to Ag^+ form Nafion and DMF as reducing agent assisted with UV light irradiation for acceleration and controlling the reduction reaction. The correlation between refractive indices and spectral position was studied as a fundamental property of LSPR sensing application.

Experimental procedure

<u>Sample preparation</u>

To prepare the Ag/Nafion composite, Ag^+ form Nafion was prepared by ion exchanging process dipping H^+ form Nafion 115 into 0.1mol·dm^{-3}AgNO$_3$ (Nacalai Tesuque Inc 99%) aqueous solution for 24 h. After ion exchanging, Ag^+-form Nafion was immersed in N,N-dimethylformamide (DMF) and UV irradiation (SANEI Electric, Supercure203S 200W HgXe lamp) for various duration ranging 1 to 10 min for Ag reducing. Finally, obtained Ag/Nafion composite was washed by distilled water twice and immersed in 1.0 mol·dm^{-3} NaNO$_3$ (Nacalai Tesuque Inc 99%) aqueous solution to remove and exchange remained Ag^+ into Na^+ in Nafion membrane.

Evaluation techniques

Ag/Nafion was evaluated by several instrument techniques. Valence of Ag species was analyzed with X-ray photoelectron spectroscopy (XPS; JEOL JPS-9010MC) with monochrome AlKα as the X-ray source (1486.6 eV). Calibration for spectra was performed by taking the C 1s photoelectron peak (E_b = 285.0 eV) as internal reference. Distribution of AgNPs was observed by scanning electron microscope and energy dispersion X-ray spectra (FE-SEM; JEOL JEM-6335F, SEM-EDX JEOL). Quantification of AgNPs in Nafion was carried out using X-ray fluorescence spectra (XRF; Shimadzu XRF1800). The weight fraction was determined by the calibration curve method. The final weight fraction of Ag is adopted from the mean value of 5 samples for each UV irradiation time.

Investigation of LSPR property

1×1 cm^2 Ag/Nafion was put in the conventional quartz sample cell able to close system by lid. Absorbance spectra were measured in the 300 nm to 800 nm wavelength range by Jasco V-7200. Various refractive index media were prepared by dipping Ag/Nafion into various organic solvents. The refractive index of these solvents we studied were listed in TABLE I. These refractive indices were collected using Abbe refractometer of Atago 1T.

TABLE I. The list of the various solvent and its refractive index used in this study

Name of solvent	Refractive indices
methanol	1.3271
water	1.3333
water/ethanol mixture	1.3333-1.3625
ethanol	1.3583
iso-propanol	1.3753
1-hexanol	1.4154
DMF	1.428

In order to investigate the LSPR coupling wavelength dependence on the amount of loaded solvent, we measured the UV-vis absorbance spectra varying the value of solvent uptake as defined in equation [2]

$$\text{solvent uptake} / \% = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \qquad [2]$$

The solvent uptake of Ag/Nafion was controlled by exposing each vapor in the vials containing each liquid solvent. Then we confirmed that the weight of the membrane was hardly different between the before and after absorbance spectra measurements.

Mie theory with size effect

We compared the experimental LSPR coupling wavelength with the value expected by reduced Mie theory (5). The size effect was also considered for the dielectric function of silver ε_{Ag} explained by U. Kreibig [3] (6).

$$\varepsilon_{Ag} = \varepsilon_{bulk} + \omega_p^{\,2}\left(\frac{1}{\omega^2 + \gamma_\infty^{\,2}} - \frac{1}{\omega^2 + \gamma(R)^2}\right) + i\,\frac{\omega_p^{\,2}}{\omega^2}\left(\frac{\gamma(R)}{\omega^2 + \gamma(R)^2} - \frac{\gamma_\infty}{\omega^2 + \gamma_\infty^{\,2}}\right) \qquad [3]$$

where ε_{bulk} is the dielectric function obtained experimentally by P. B. Johnson and R. W. Christy[11], ω_p is the plasmon frequency of silver (1.39×10^4 THz), γ_∞ is the phenomenological damping constant of the bulk silver (2.42×10^{13}), the damping constant with size effect $\gamma(R)$ is illustrated by the equation[4]

$$\gamma(R) = \gamma_\infty + \frac{v_F}{R} \qquad\qquad\qquad [4]$$

where v_F is Fermi velocity (1.38×10^6 m s^{-1}), and R is radius of nanoparticles. We plotted the value of σ_{ext} as function of wavelength entering [3, 4] and each constant. The value of experimental ε_{bulk} by P. B. Johnson and R. W. Christy was used to draw the computational extinction spectra.

Result and discussion

Characterization of the reduction process

We propose the reaction scheme for the reduction of Ag$^+$ as shown in the equation [5]

$$2\text{ -SO}_3\text{Ag} + (CH_3)_2CHO + H_2O \rightarrow 2\text{-SO}_3H + Ag + (CH_3)_2NCOOH \qquad [5]$$
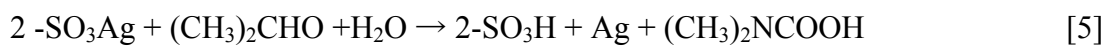
where -SO$_3$ represent the terminal sulfonyl group in Nafion. Silver metal formation could be observed in XPS spectra shown in Figure 1. The peak shift of Ag3d photoelectron peaks is noted. This chemical shift is due to the reduction of Ag$^+$ by reducing agent and UV irradiation. Therefore it is found that the Ag was stably reduced in Nafion membrane.
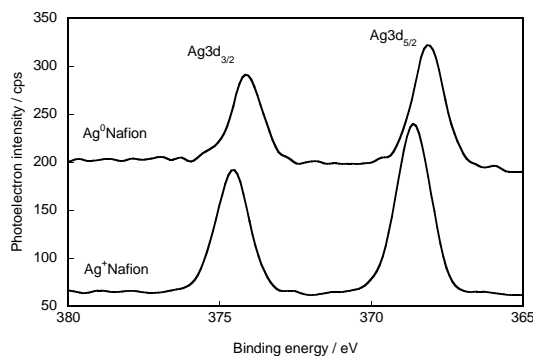

Figure 1. Variation of the XPS spectra on the process before/after UV irradiation for 10 min.

We carried out SEM-EDX analysis for the membrane cross section after UV irradiation for 10 min in order to investigate the distribution of Ag$^+$ shown in Figure 2. The mapping image of Ag indicate a uniform distribution of AgNPs thorough the Nafion membrane. Confirmation of Ag in the inner region of Nafion membrane indicates that the ion exchanged Ag$^+$ was converted to Ag^0.
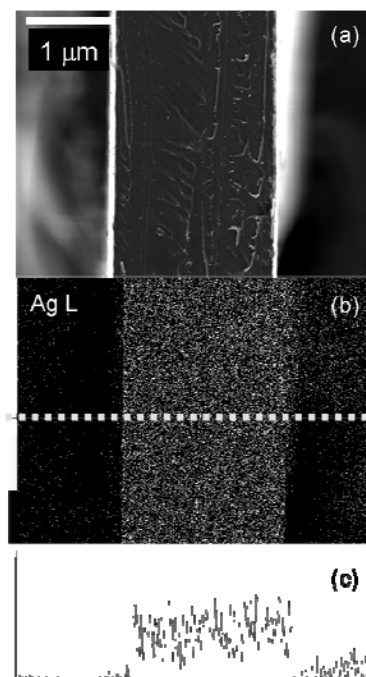
Figure 2. Cross sectional (a) SEM , (b) SEM-EDX images of AgL, and (c) line profile of Ag. The line profile of (c) was obtained from the dotted line indicated in (b).

Weight fractions of Ag in Nafion measured by XRF were plotted with irradiation time in Figure 3. Up to 5 min of irradiation, the weight fraction of AgNPs was slowly increased, while the Ag fraction after more than 7 min UV irradiation increased slightly and became saturated.
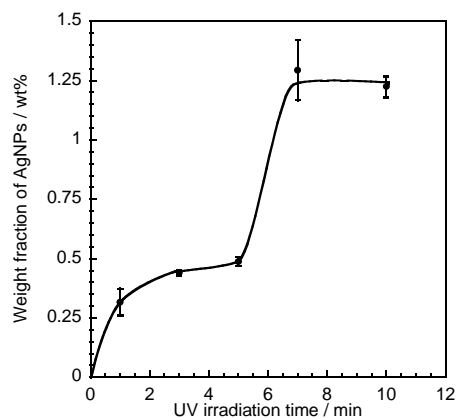

Figure 3. Variation of the weight fraction of silver in the Nafion membrane on UV irradiation time.

The behavior can be distinguished in absorbance spectra in visible region shown in Figure 4. The spectra indicated that 5 min UV irradiation caused aggregation of AgNPs with each other. Additionally we could confirm a visual color change from yellow transparent to dark brown.
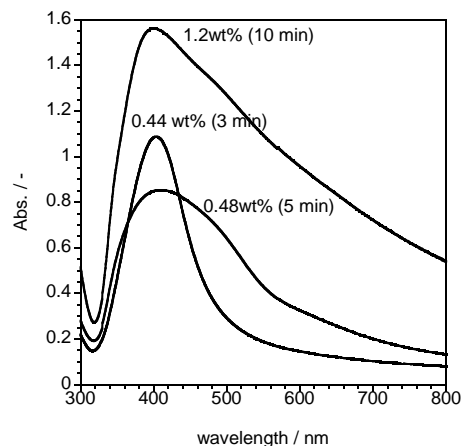
Figure 4. Variation of absorbance spectra on UV irradiation time. The numbers in the figure indicate the weight fraction of the AgNPs. These spectra of Ag/Nafion were obtained under water media.

For investigating the plasmon absorbance spectra, sharp absorbance spectra was suitable to observe the LSPR coupling wavelength and ideal to single particle calculation by Mie theory. In the cross sectional TEM images of the Ag/Nafion membrane prepared by UV irradiation for 10 min, the aggregation state was observed and the distance between each other aggregate is smaller than that of 3 min irradiation as shown in Figure 5.
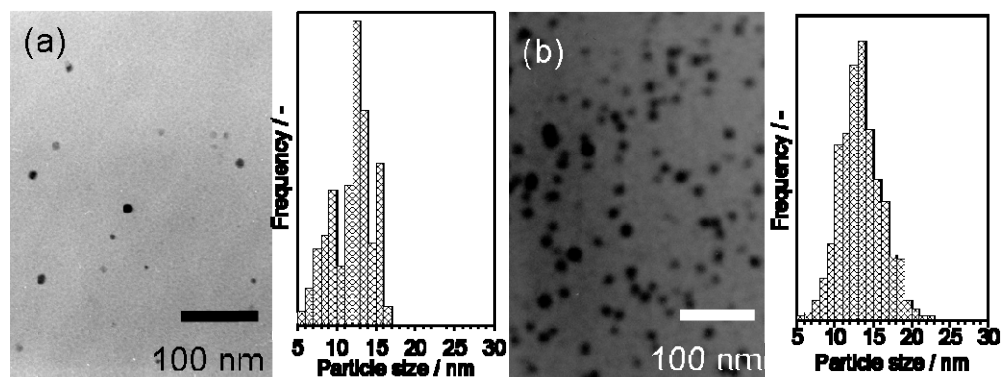

Figure 5. Cross sectional TEM images of Ag/Nafion membrane prepared by UV irradiation for (a) 3 min and (b) 10 min. The right sides of the pictures show the size distribution of AgNPs. Mean particle size was (a) 13.4 ± 2.8 nm, and (b) 12.5 ± 2.9 nm in diameter.

Investigation of LSPR spectral shift of Ag/Nafion

The dependence on the refractive index of the media surrounding AgNPs confined in Nafion membrane is investigated using UV-vis absorbance spectra. Surface plasmons, also known as surface plasmon polaritons, are surface electromagnetic waves which propagate at the metal NPs /dielectric interface. Since the wave is on the boundary of the metal and its media, these oscillations are very sensitive to any change of this boundary, such as the adsorption of molecules to the metal surface. LSPR represents collective electron charge oscillations in metallic nanoparticles that are excited by light. The coupling frequency (wavelength) was reflected as the peak top of the absorbance spectra. Consequently, the peak top value was important and sensitive to refractive index of media. The shift of the peak position in absorbance spectra of the Ag/Nafion on dipping media was confirmed as shown in Figure 6.
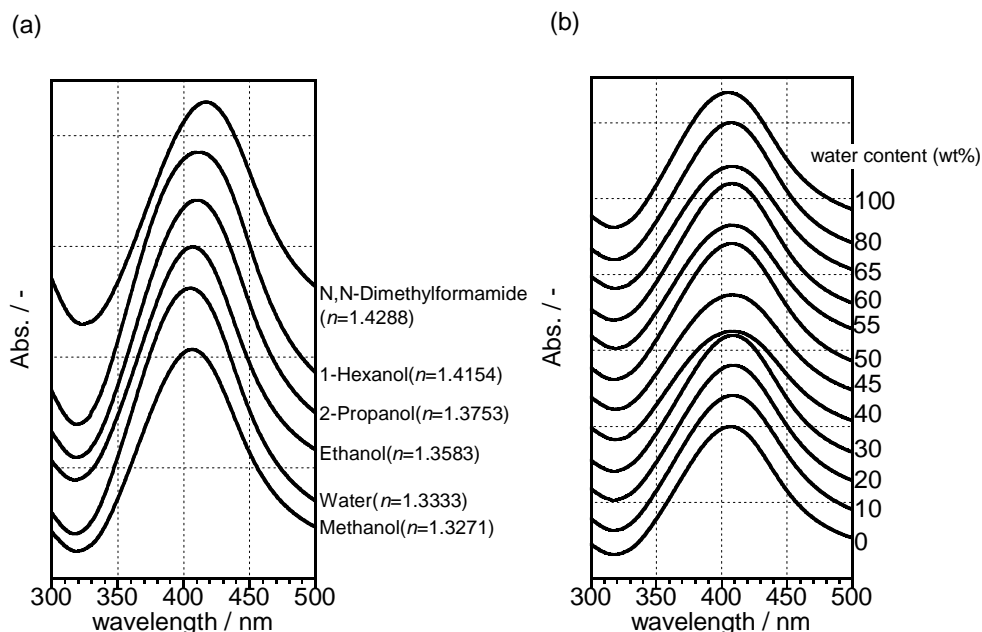

Figure 6. (a) Variation of the UV-vis absorbance spectra on refractive index of the dipping media; (b) Variation of the absorbance spectra on the water/ethanol mixture ratio in weight %.

The dependence of the absorbance spectra on the refractive index of medium surrounding AgNPs using Mie theory described in experimental section is studied. The computational extinction spectra using eq. [1, 3, 4] were shown in Figure 7(a). The model was defined as single particle embedded in various dielectric matrices. The calculated AgNPs particle size of 13 nm diameter corresponds to the experimental value. The correlation between refractive index and LSPR coupling wavelength is shown in Figure 7(b). It is found that the LSPR coupling wavelength of Ag/Nafion depends linearly on the refractive index of media surrounding the NPs. Such tendency is described also by other groups (6-8). This linear dependence can be utilized for the sensing application by detecting the difference of the refractive index of metal NPs environment.

The coupling wavelength mismatch between the experimental and computational values is due to the difference between the assumed model and the real sample: size,

shape, particle size dispersions, local refractive index affected by the ionic species and terminal groups in Nafion cluster and inter-particle separation dispersion play an important role. Nevertheless the model of single particle is able to qualitatively depict the system and reproduce the experimental features. The sensitivity in RIU (refractive index units) was introduced and determined by the slope of the linear dependence of LSPR coupling wavelength on refractive index (13). The computation method revealed the sensitivity of 106.3 nm /RIU which we consider the theoretical value for sensing application for AgNPs based LSPR sensor. On the other hand the value of the experimental performance was 102.01 nm / RIU. Since these two values are close to each other, the sensitivity indicates that Ag/Nafion has ideal condition for plasmonic sensing.
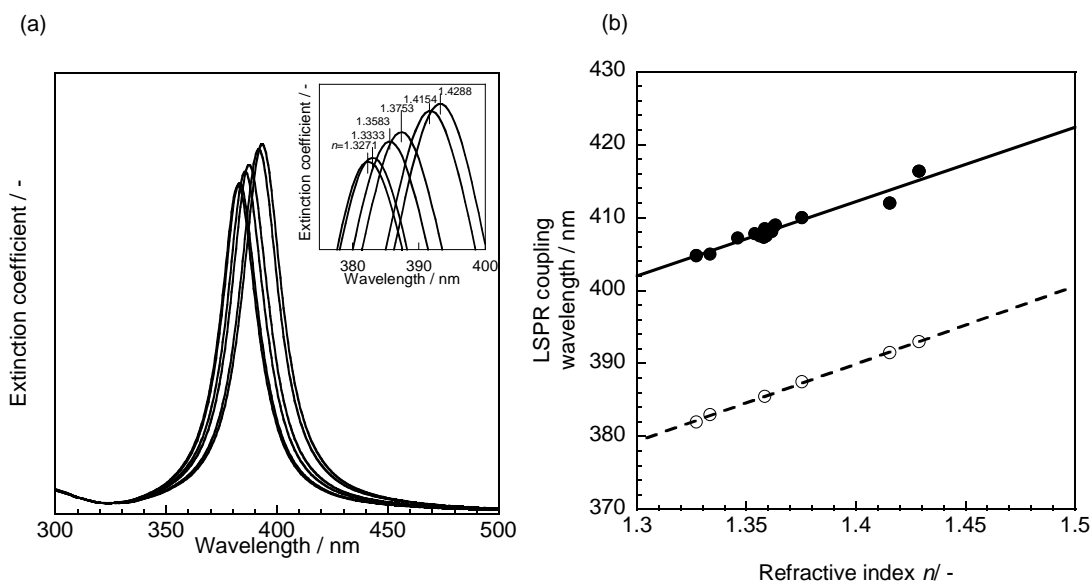

Figure 7. (a) Computational spectra between 300 – 500 nm in wavelength on refractive index of medium (n = 1.3271-1.4288). In the inset, each number corresponds to the refractive index of media. (b) LSPR shift (peak top) dependence on the refractive index; filled circles with solid line (-●-) represent experimental value, open circles with dotted line (-⊖-) represent computational value, respectively.

LSPR coupling wavelength for various solvent uptakes

LSPR exhibits enhanced near-field amplitude at the resonance wavelength. This field is highly localized at the nanoparticle and decays rapidly away from the nanoparticle/ dielectric media interface into the dielectric media. Light intensity enhancement is a very important aspect of LSPR and localization means that the LSPR has very high spatial resolution (subwavelength), limited only by the size of nanoparticles (6, 14). Dependence of loaded amount for each solvent on the LSPR coupling wavelength was evaluated using eq. [2] as shown in Figure 8.
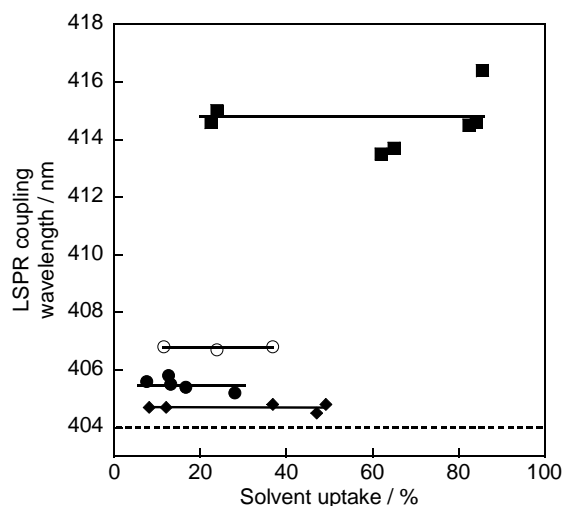
Figure 8. Variation of LSPR coupling wavelength on the solvent uptake. The symbols represent ■ DMF (n=1.4288), ○ Ethanol (n=1.3583), ● Water (n=1.3333), and ◆ Methanol (n=1.3271), respectively. The dashed line corresponds to the LSPR coupling wavelength of dried membrane.

The LSPR coupling wavelength does not depend on the solvent uptake. Even at the low solvent uptake, LSPR coupling wavelength was not different on dipping condition. However in case of DMF loading, the LSPR coupling wavelength was unstable. We think this is because the DMF itself swelled water in atmosphere resulting in the decreasing of refractive index.

Conclusion

Ag nanoparticles were dispersed into ionic channel in Nafion membrane by photo reduction reaction using DMF solution. The concentration of obtained AgNPs increased from ca. 0.25wt% to 1.2 wt% during UV irradiation for 1-10 min. Sharp LSPR coupling absorption bands was observed at ca. 400 nm for 0.44 wt% of AgNPs in Nafion. The shift of LSPR coupling wavelength could be expressed by Mie's theory. Experimental sensitivity in nm/RIU was close to the theoretical one. Even at the low solvent uptake, the peak shift of LSPR in Ag/Nafion could be detected.

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