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Scattering-based hole burning mediated by localized surface plasmon resonance in photoreactive random media containing Ag nanoparticles

Shunsuke Murai,^{1,a)} Yutaka Fujimoto,¹ Koji Iwata,¹ Koji Fujita,^{1,2} and Katsuhisa Tanaka¹

¹Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

²PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

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Photoreactive random media containing silver nanoparticles (Ag NPs) have been fabricated, and hole burning effects based on the interference of multiply scattered light have been investigated. Through the analysis of hole profiles, transport mean free path ℓ is estimated for the light with the wavelength of 585 nm. We find that ℓ in the samples embedded with Ag NPs is much shorter compared with that in a medium containing the same amount of titania (TiO₂) NPs, indicating that Ag NPs scatter 585 nm lightwaves much stronger than TiO₂ NPs because of their larger scattering cross sections due to the localized surface plasmon resonance. © 2011 American Institute of Physics. [doi:10.1063/1.3567929]

Random media refer to complex materials in which scatterers are randomly arranged on an optical length scale. Multiple scattering and interference in a random medium bring about interesting phenomena such as coherent backscattering (CBS),¹⁻³ random lasers,^{4,5} and scattering-based hole burning effect.⁶⁻⁸ Among them, scattering-based hole burning utilizes the high sensitivity of an interference pattern to small changes in the source frequency, polarization, and wave vector.^{9,10} Memories can be imprinted by irradiating a random medium containing photochromic species with a monochromatic laser that preferentially photobleaches the species located in the interference pattern.

Thus far, in many experimental studies on random media, nanoparticles (NPs) were adopted as the scatterers. Assuming that all the NPs in the medium are identical and every scattering event is independent of other scattering events, transport mean free path ℓ is expressed in terms of the transport cross section σ_{tra} of an NP and the number density of NPs ρ as $\ell = 1/\rho\sigma_{\text{tra}}$, where σ_{tra} can be expressed in terms of scattering (σ_{sca}) and absorption (σ_{abs}) cross sections and an asymmetric factor g : $(1-g)\sigma_{\text{sca}} + \sigma_{\text{abs}}$.¹¹ ℓ is related to the diffusion constant D as $D = v_E\ell/3$, where v_E is the energy velocity of light.¹² For fabricating a strongly-scattering medium, dielectric NPs having a high refractive index, such as titania (TiO₂), are commonly employed to attain a large σ_{sca} . Recently, the use of metal NPs as scatterers has been studied; metal NPs potentially possess excellent scattering properties due to the localized surface plasmon resonance (LSPR). σ_{sca} of a metal NP is much larger than that of a dielectric NP. For example, according to the Mie theory, a silver (Ag) NP (diameter=100 nm, dielectric constants were obtained from literature¹³) in a matrix with a refractive index of 1.49 exhibits LSPR at a wavelength of approximately 580 nm; σ_{sca} at this value is 4×10^{-14} m². σ_{sca} of a TiO₂ NP (refractive index=2.7) under the same conditions is 2×10^{-15} m², i.e., 1/20th of that of the Ag NP. Recent experimental reports stated that random lasers containing metal NPs exhibit a lower laser threshold than those

containing dielectric NPs,¹⁴⁻¹⁶ this observation suggests that metal NPs are a better choice.

In the present study, we have prepared photoreactive random media containing Ag NPs with a diameter of approximately 100 nm and examined the scattering-based hole burning effect. We calculate ℓ by analyzing the hole profile and compare ℓ with that obtained in the case of media embedded with TiO₂ NPs. The value of ℓ is smaller in the case of Ag-containing media, which points to a larger σ_{tra} of Ag NP.

Ag NPs were synthesized by a two-step seed-mediated growth method. First, a 0.188 M silver nitrate aqueous solution [AgNO₃ (aq), 3.0 ml] was added to water (8.0 ml) in the presence of poly(vinyl pyrrolidone) (molecular weight: 55 000; 1.41 g) and stirred for 24 h at 60 °C to obtain a seed solution. Next, ethylene glycol (EG, 4.0 ml) was added to the seed solution (1.5 ml) and it was heated for 20 h at 120 °C while being continuously stirred. Then, EG (2.0 ml) and 0.188 M AgNO₃ (aq) (2.0 ml) were added to the solution, and the mixture was stirred for 6 h at 120 °C to increase the size of the NPs up to 100 nm. The obtained NPs were coated with an anionic polymer, poly(4-styrenesulfonic acid) (PSS; molecular weight: 75 000), for obtaining better dispersion by mixing the suspension of Ag NPs (3.0 ml) with 20 ml of a 1 wt % PSS aqueous solution under sonication.

The photoreactive films were prepared by adding photochromic 1,3,3-trimethylindolino-6'-nitrobenzopyrrolospiran (SP1) and the solution of PSS-coated Ag NPs to a tetrahydrofuran solution of poly(methyl methacrylate) (PMMA; molecular weight: 120 000). The solvent evaporated slowly in air at 60 °C, forming films with a thickness of several hundred micrometers and containing 6.3×10^{-2} M SP1 in the PMMA matrix. We prepared various films having different Ag contents and named them as Ag- x ($x=0, 1, 3, 8, 12, 20$), where x was the relative value to ρ of Ag-1, for which $\rho = 7.4 \times 10^{16}$ m⁻³. For comparison, photoreactive media containing TiO₂ NPs (diameter=100 nm, PT-501A, Ishihara Sangyo) instead of Ag NPs were also prepared and named as TiO₂- y ($y=1, 3, 8, 12, 20, 50, 100, 200$). It should be noted here that TiO₂-1 and Ag-1 contain the same number of NPs.

^{a)}Electronic mail: murai@dipole7.kuic.kyoto-u.ac.jp.

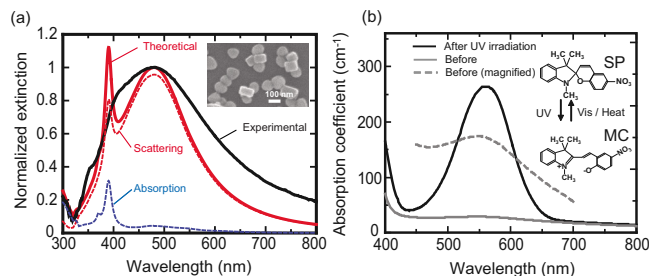


FIG. 1. (Color online) (a) Normalized extinction spectrum for Ag NPs dispersed in ethanol (solid curve). Also shown are the theoretical spectra for an Ag sphere in ethanol calculated using Mie theory. Theoretical extinction is represented by a solid curve, which consists of scattering and absorption components as indicated by dashed curves. The inset shows a SEM image for Ag NPs dispersed onto a silica glass substrate. (b) Optical absorption spectra for Ag-1 sample before (gray solid curve) and after (black) UV light irradiation ($\lambda = 365$ nm). For clarity, the spectrum before irradiation is magnified and shown as gray broken curve in a wavelength range of 450–700 nm. The inset illustrates two different forms of SP1; SP and MC.

The extinction spectrum of the Ag NPs dispersed in ethanol is shown in Fig. 1(a). The extinction peak at around 480 nm and the broad shoulder at around 390 nm can be ascribed to the dipole and quadrupole modes of the LSPR of the Ag NPs, respectively. Moreover, the figure shows a theoretical extinction spectrum calculated on the basis of the Mie theory for an Ag sphere in ethanol having a diameter of 96 nm. The theoretical peak position of the dipole mode is in good agreement with that of the experimental spectrum. The theoretical extinction curve consists of scattering and absorption components, as shown by the dashed curves. The scattering component is much larger than the absorption component. The broader experimental curve indicates a variation in the diameter and shape of the fabricated NPs. Moreover, the size of the Ag NPs is confirmed by scanning electron microscopy [inset of Fig. 1(a)].

Figure 1(b) shows the typical absorption spectra of the film (Ag-1). An as-prepared (before UV irradiation) film shows an absorption peak at around 550 nm because of the LSPR of the Ag NPs, while an additional intense absorption peak appears after irradiation with UV light ($\lambda = 365$ nm). The absorption occurs due to the open-ring merocyanine (MC) form of the dye; UV light transforms the structure of SP1 from closed-ring spiropyran (SP) to MC [inset in Fig. 1(b)].¹⁷ While the SP form of the dye hardly shows fluorescence, the MC form is fluorescent, with the maximum emission being observed at around 660 nm when excited by visible light; moreover, the MC form can be photobleached into SP form when the intensity of the visible light is high. From the data at a wavelength of 585 nm, the absorption length ℓ_a is estimated to be around 1000 μm for Ag-0 before the UV irradiation. This indicates that ℓ_a of TiO_2 - y before the UV irradiation (with dyes in SP form) is of the order of 1000 μm and that of Ag- x ($x \neq 0$) is smaller than 1000 μm due to the absorption by Ag NPs.

Scattering-based hole burning was evaluated by using a dye laser (rhodamine 6G) pumped by an Ar⁺ laser (Innova 300, Coherent, USA); the dye laser was used as both the writing and reading beams. First, the film was placed on a rotatable stage and irradiated with UV light for 15 min to convert the SP1 molecules to the MC form. Second, we illuminated the sample with a writing beam obtained from the cw dye laser (1 mW; wavelength $\lambda_w = 585$ nm; wave vector

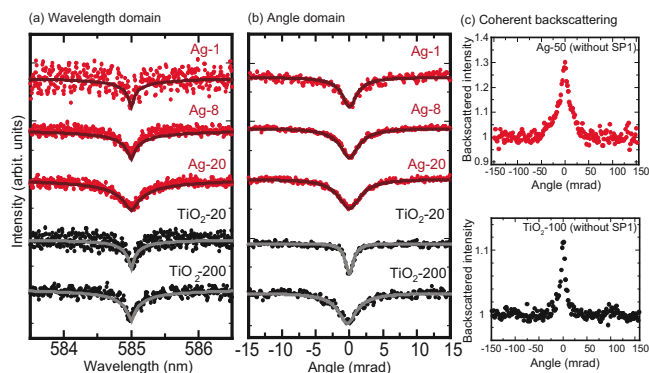


FIG. 2. (Color online) (a) Dependence of emission intensity on excitation wavelength of reading beam for representative samples. The holes were burned using a writing laser beam the wavelength of which was $\lambda_w = 585$ nm. (b) Dependence of emission intensity on incident angle of reading beam. The holes were burned at 0 rad under irradiation with a writing laser beam ($\lambda_w = 585$ nm). Closed circles denote experimental data and solid curves represent theoretical ones based on diffusion approximation [Eq. (1)]. (c) The backscattered intensities normalized to the diffuse background for Ag-50 without SP1 (top figure) and TiO_2 -100 without SP1 (bottom).

$k_w = 2\pi \sin \theta / \lambda$, where θ is the incident angle) for about 30 s. This illumination reconverts the MC forms to the SP forms in the interference pattern specific to λ_w (frequency ω_w) and k_w . In the reading process, the laser beam was attenuated by a factor of 200 (5 μW) and used as the reading beam to probe the hole without causing any additional photoreactions. The spot that was irradiated with the writing beam prior to reading was excited by a reading beam having wavelength λ_r (frequency ω_r) and wave vector k_r , and the emission intensity was plotted as a function of $\Delta\lambda = \lambda_r - \lambda_w$ ($\Delta\omega = \omega_r - \omega_w$) and $\Delta k (=k_r - k_w)$.

The representative hole profiles are shown in Fig. 2. All Ag- x films except Ag-0 exhibit holes in the wavelength and angle domains [Figs. 2(a) and 2(b)]. In contrast, for the TiO_2 - y films, no holes are observed in both domains unless y is more than 20, which indicates that ℓ is more than the film thickness when $y = 1, 3, 8$, and 12. This demonstrates that σ_{tra} is larger for Ag NPs than for TiO_2 NPs. To confirm the larger σ_{tra} of an Ag NP, we conducted a CBS measurement using the 514 nm line of the Ar⁺ laser¹⁸ [see Fig. 2(c)]. Ag (TiO_2)-containing films with thicknesses of around 300 μm and having the same number of NPs as Ag-50 (TiO_2 -100) were prepared without SP1, and they were used as samples. Ag-50 without SP1 (the top figure) shows a wider CBS cone than TiO_2 -100 without SP1 [the bottom], although the number of Ag NPs contained is half the number of TiO_2 NPs. Since a wider CBS cone means a smaller ℓ , this observation confirms the stronger scattering by Ag NPs. The enhancement in the CBS cones in the backscattering direction (1.3 and 1.1 for Ag-50 without SP1 and TiO_2 -100 without SP1, respectively) is much smaller than the theoretical value ($=2.0$). This is primarily due to the limited film thickness; the photons that take paths whose lengths are more than the thickness of the medium are transmitted and do not contribute to the CBS peak.¹⁹ In the case of the Ag-containing film, the absorption by Ag NPs is an additional reason for the low enhancement.^{19,20}

To estimate ℓ , the obtained hole profiles were analyzed using a theoretical curve based on the diffusion theory. The correlation between the intensities of the fluctuation patterns produced by the writing and reading beams at position r

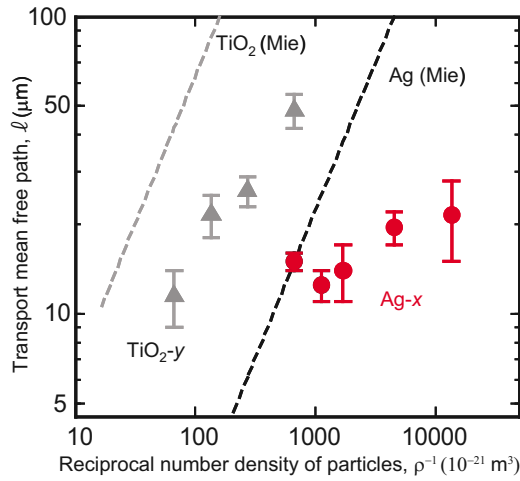


FIG. 3. (Color online) Transport mean free path estimated from the hole profiles as a function of reciprocal number density of NPs for Ag- x (closed circles, $x=1, 3, 8, 12$, and 20) and TiO₂- y (closed triangles, $y=20, 50, 100$, and 200). Broken lines denote the theoretical relations based on $\ell=1/\rho\sigma_{\text{tra}}$ for Ag- x (black) and TiO₂- y (gray).

inside the medium is described by an intensity correlation function $C(\Delta\omega, \Delta k, r)$,⁷ which essentially determines the shape of a hole. For a slab medium occupying a space $0 < z < L$, $C(\Delta\omega, \Delta k, z)$ can be represented as

$$C(\Delta\omega, \Delta k, z) = \frac{\cosh[2\gamma(L + 0.7\ell - z)] - \cos[2\delta(L + 0.7\ell - z)]}{\cosh[2\gamma(L + 1.4\ell)] - \cos[2\delta(L + 1.4\ell)]}. \quad (1)$$

Here $\gamma + i\delta = [\Delta k^2 + (c/\ell_a + i\Delta\omega)/D]^{1/2}$. For simplicity, we assumed $v_E = c/\langle n \rangle$, where $\langle n \rangle$ is the average refractive index of the medium and was assumed to be equal to that of the PMMA matrix ($=1.49$). We fitted the integration of Eq. (1) over z to the experimental hole profiles by considering ℓ_a (values in the range of 500 – $3000 \mu\text{m}$, expected from extinction spectra) and ℓ as fitting parameters. The results are superimposed on the experimental data in Figs. 2(a) and 2(b). The experimental hole profiles can be reproduced well by the theoretical curves.

The values of ℓ estimated from the fit are plotted in Fig. 3 as a function of the inverse number density of NPs, ρ^{-1} . The error bars reflect the variations in ℓ values caused by the various ℓ_a values used for the fit. The range of ℓ_a in which the hole profile can be reproduced is almost invariant with y for the TiO₂- y series, while the range for the Ag- x series tends to shift toward smaller ℓ_a values upon increasing x . For the TiO₂- y samples, ℓ decreases monotonically with increasing ρ . Compared to the TiO₂- y samples, the Ag- x series show smaller values of ℓ for smaller ρ . For example, the value of ℓ for Ag-1 (approximately $21 \mu\text{m}$) is comparable to that for TiO₂-100, suggesting that σ_{tra} of an Ag NP is 100 times larger than that of a TiO₂ NP. The theoretical value of ℓ estimated from the relation $\ell=1/\rho\sigma_{\text{tra}}$, in which σ_{tra} was

calculated for a sphere (diameter= 100 nm) using the Mie theory, is shown by broken lines. The absorption of SP1 was neglected in the calculation since the contribution of absorption estimated in the experiment ($\ell_a=500$ – $3000 \mu\text{m}$) was less significant than that of scattering, i.e., $\ell \ll \ell_a$. For both the Ag- x and TiO₂- y series, the calculated values are more than those estimated from the experimental data. This difference can be ascribed to the fact that NPs used in the experiment had distributions in size and shape. While the slope of the experimentally obtained curve between ℓ and ρ^{-1} is similar to the theoretical one for the TiO₂- y films, the slope for the Ag- x data does not match to the relation $\ell=1/\rho\sigma_{\text{tra}}$. A weaker dependence on ρ^{-1} could be due to the effect of multiple scattering. If the scattering is strong, the incident light is screened by other NPs and this results in a lower scattering strength of the system than that estimated when independent scattering is assumed.²¹

In summary, we have prepared photoreactive random media containing Ag NPs as scatterers and experimentally verified that σ_{tra} of Ag NPs is much larger than that of TiO₂ NPs on the basis of scattering-based hole burning effects. The result suggests that Ag NPs can be excellent scatterers with a large σ_{sca} and a reasonable σ_{abs} when their size is appropriate, as expected from the Mie theory.

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