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

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

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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 \( \ell \) is estimated for the light with the wavelength of 585 nm. We find that \( \ell \) in the samples embedded with Ag NPs is much shorter compared with that in a medium containing the same amount of titania (TiO\(_2\)) NPs, indicating that Ag NPs scatter 585 nm lightwaves much stronger than TiO\(_2\) NPs because of their larger scattering cross sections due to the localized surface plasmon resonance.


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), multiple scattering and interference in a random medium bring about interesting phenomena such as coherent backscattering (CBS), random lasers, and scattering-based hole burning effect. 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. 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 \( \ell \) is expressed in terms of the transport cross section \( \sigma_{\text{tra}} \) of an NP and the number density of NPs \( n \) as \( \ell = 1 / n \sigma_{\text{tra}} \), where \( \sigma_{\text{tra}} \) can be expressed in terms of \( (\sigma_{\text{sca}}) \) and \( (\sigma_{\text{abs}}) \) cross sections and an asymmetric factor \( g = (1 - g) \sigma_{\text{sca}} + \sigma_{\text{abs}} \). \( \ell \) is related to the diffusion constant \( D \) as \( D = v_g \ell / 3 \), where \( v_g \) is the energy velocity of light. For fabricating a strongly-scattering medium, dielectric NPs having a high refractive index, such as titania (TiO\(_2\)), are commonly employed to attain a large \( \sigma_{\text{sca}} \). Recently, the use of metal NPs as scatterers has been studied; metal NPs potentially possess excel lent scattering properties due to the localized surface plasmon resonance (LSPR). \( \sigma_{\text{sca}} \) 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 literature) in a matrix with a refractive index of 1.49 exhibits LSPPR at a wavelength of approximately 580 nm; \( \sigma_{\text{sca}} \) at this value is \( 4 \times 10^{-14} \) m\(^2\). \( \sigma_{\text{sca}} \) of a TiO\(_2\) NP (refractive index=2.7) under the same conditions is \( 2 \times 10^{-15} \) m\(^2\), i.e., \( \ell \) of the Ag NP. Recent experimental reports stated that random lasers containing metal NPs exhibit a lower laser threshold than those containing dielectric NPs; 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 \( \ell \) by analyzing the hole profile and compare \( \ell \) with that obtained in the case of media embedded with TiO\(_2\) NPs. The value of \( \ell \) is smaller in the case of Ag-containing media, which points to a larger \( \sigma_{\text{sca}} \) of Ag NP.

Ag NPs were synthesized by a two-step seed-mediated growth method. First, a 0.188 M silver nitrate aqueous solution [AgNO\(_3\) (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 AgNO\(_3\) (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 sonicaton.

The photoreactive films were prepared by adding photochromic 1,3,3-trimethylindolino-6'-nitrobenzopyrylospiran (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 \( \rho \) of Ag-1, for which \( \rho = 1 \times 10^{16} \) m\(^{-3}\). For comparison, photoreactive media containing TiO\(_2\) NPs (diameter=100 nm, PT-501A, Ishihara Sangyo) instead of Ag NPs were also prepared and named as TiO\(_2\)-y (y=1,3,8,12,20,50,100,200). It should be noted here that TiO\(_2\)-1 and Ag-1 contain the same number of NPs.

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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 assigned 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 (λ = 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)]. 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 ℓₐ is estimated to be around 1000 μm for Ag-0 before the UV irradiation. This indicates that ℓₐ of TiO₂-γ before the UV irradiation (with dyes in SP form) is of the order of 1000 μm and that of Ag-x (x ≠ 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 λₘ = 585 nm; wave vector kₗ = 2π sin θ/λ, 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 λₗ (frequency ωₗ) and kₗ. 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 λₗ (frequency ωₗ) and wave vector kₗ, and the emission intensity was plotted as a function of Δλ = λₗ − λₑ (Δω = ωₗ − ωₑ) and Δk = kₗ − kₑ. 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 TiO₂-γ films, no holes are observed in both domains unless γ is more than 20, which indicates that ℓ is more than the film thickness when γ = 1, 3, 8, and 12. This demonstrates that σₑ₂ₙ for Ag NPs is larger than TiO₂-γ NPs. To confirm the larger σₑ₂ₙ of an Ag NP, we conducted a CBS measurement using the 514 nm line of the Ar⁺ laser [see Fig. 2(c)]. Ag (TiO₂)-containing films with thicknesses of around 300 μm and having the same number of NPs as Ag-50 (TiO₂-100) were prepared without SP1, and they were used as samples. Ag-50 without SP1 (the top figure) shows a wider CBS cone than TiO₂-100 without SP1 [the bottom], although the number of Ag NPs contained is half the number of TiO₂ 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 TiO₂-100 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.

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
inside the medium is described by an intensity correlation function $C(\Delta \omega, \Delta k, z)^3$, 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

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

Here $\gamma = [\Delta k^2 + (c/\ell_a i \Delta \omega)/D]^{1/2}$. 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 $\ell_a$ (values in the range of 500–3000 nm, expected from extinction spectra) and $\ell$ 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 $\ell$ estimated from the fit are plotted in Fig. 3 as a function of the inverse number density of NPs, $\rho^{-1}$. The error bars reflect the variations in $\ell$ values caused by the various $\ell_a$ values used for the fit. The range of $\ell_a$ in which the hole profile can be reproduced is almost invariant with $y$ for the TiO$_2$-y series, while the range for the Ag-x series tends to shift toward smaller $\ell_a$ values upon increasing $x$. For the TiO$_2$-y samples, $\ell$ decreases monotonically with increasing $\rho$. Compared to the TiO$_2$-y samples, the Ag-x series show smaller values of $\ell$ for smaller $\rho$. For example, the value of $\ell$ for Ag-1 (approximately 21 nm) is comparable to that for TiO$_2$-100, suggesting that $\sigma_{\text{tra}}$ of an Ag NP is 100 times larger than that of a TiO$_2$ NP. The theoretical value of $\ell$ estimated from the relation $\ell = 1/\rho \sigma_{\text{tra}}$, in which $\sigma_{\text{tra}}$ 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 ($\epsilon_a=500–3000$ nm) was less significant than that of scattering, i.e., $\ell \ll \ell_a$. For both the Ag-x and TiO$_2$-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 $\ell$ and $\rho^{-1}$ is similar to the theoretical one for the TiO$_2$-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 $\rho^{-1}$ could be due to the effect of multiple scattering. If the scattering is strong, the incident light is scattered 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 photoactive random media containing Ag NPs as scatterers and experimentally verified that $\sigma_{\text{tra}}$ of Ag NPs is much larger than that of TiO$_2$ NPs on the basis of scattering-based hole burning effects. The result suggests that Ag NPs can be excellent scatterers with a large $\sigma_{\text{scat}}$ and a reasonable $\sigma_{\text{abs}}$ when their size is appropriate, as expected from the Mie theory.

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