# Room Temperature Space-selective Precipitation of Silver Nanoparticles inside Tb<sup>3+</sup>-doped Silica Xerogels using Femtosecond Laser

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Space-selective precipitation of silver nanoparticles inside transparent paramagnetic silica xerogels doped with  $Tb^{3+}$  and  $Ag^+$  ions was performed at room temperature by a one-step irradiation process of a femtosecond laser without subsequent heat treatment. Paramagnetic silica xerogels doped with  $Tb^{3+}$  ions were prepared via a sol-gel process using terbium nitrate with a drying process at temperature of 450 °C. The color change of the irradiated area and corresponding optical absorption peaks indicate the precipitation of Ag nanoparticles and localized surface plasmon resonance (LSPR) absorption. The  $Ag^+$  ions were reduced and Ag atoms aggregated to form Ag nanoparticles, suggesting that the light energy incident on the irradiated xerogel was directly spent to aggregate Ag atoms. The positive correlation between pulse energy and particle size is different from that observed in the two-step method that includes a post-annealing step. X-ray photoelectron spectroscopy analysis showed that Ag ions were actually reduced by fs laser irradiation. A larger absolute value of Faraday rotation angle was observed in the femtosecond laser-irradiated region compared to the non-irradiated region. The enhanced Faraday rotation is observed particularly in the refractive index change region, and the laser processing technique using this xerogel material is expected to be applied to the fabrication of waveguide-type Faraday devices in the future.

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# 1. Introduction

Noble-metal nanoparticles (NPs) exhibit localized surface plasmon resonances (LSPR), in which coherent oscillations of the electrons occur due to the resonance with incident visible light [1]. The resonant wavelength is critically dependent on the size, the shape and the dielectric environment of the NPs. Composite materials containing such plasmonic NPs exhibit enhancement of a variety of their optical properties, that is, Raman scattering [2], luminescence [3], and magnetooptical effect [4-6]. In addition, large third-order nonlinear susceptibility as well as ultrafast nonlinear response is also observed in such composites [7]. They are potentially applicable to integrated optoelectronics or ultrafast all-optical switching devices in the THz region [8]. To enhance the efficiency of these devices, a well-defined assembly of NPs should be developed and spatial distribution of NPs in materials should be strictly controlled. There have been considerable efforts on the fabrication and evaluation of glass materials doped with metal NPs [9-12]. For example, ion exchange or ion implantation process can realize space-selective precipitation of NPs. However, the size and spatial distribution are relatively broad and are not sufficiently controlled. In addition, some impurities are introduced due to a damaged glass matrix. In contrast, ultrashort pulsed laser processing is a powerful tool to make microscopic modifications to trans-

parent materials [13-17]. When focusing a laser beam in transparent materials, electric field intensity at a focal point reaches to as high as 100 TW/cm<sup>2</sup>, which is sufficient for inducing nonlinear optical effects, such as multiphoton absorption process. J. Qiu et al. have reported that the precipitation of Au NPs can be induced in three dimensions inside transparent silicate glasses by using focused femtosecond laser irradiation [18, 19]. This method is composed of two steps, that is, a femtosecond-laser irradiation process for noble metal ion-doped glasses and an annealing process of the irradiated glasses. In the first step, photo-reduction of the metallic ions gives rise to the metal atoms, and the subsequent annealing process causes the agglomeration of metal atoms into metallic NPs inside the irradiated area. If the annealing process is omitted, high throughput fabrication of NPs can be realized. A more recent work showed a one-step procedure without post annealing process to yield the space-selective growth of gold NPs inside a transparent silica matrix [20]. An aqueous solution of hydrogen tetrachloroaurate as a gold precursor was introduced into silica porous xerogels in the presence of sodium carbonate as an additive. Subsequent irradiation with a regenerative amplified Ti:sapphire laser induced precipitation of gold nanoparticles inside the silica matrix at room temperature. In our previous report, we also performed another type of single-step precipitation method of Ag NPs using a femtosecond-laser irradiation without additive agents. Ag NPs were space-selectively precipitated inside a silica xerogels doped with Ag<sup>+</sup> ions. In this paper, xerogels doped with Tb<sup>3+</sup> ions have been prepared and irradiated with femtosecond laser to precipitate Ag NPs inside the xerogels. Paramagnetic Tb<sup>3+</sup> ions exhibit relatively large Faraday rotation in a variety of glasses [21-24]. Tb<sup>3+</sup>-doped xerogels which are prepared via sol-gel reaction with a low processing temperature become promising materials for application of novel Faraday devices. The localized surface plasmon resonance due to Ag NPs can possibly enhance the rotation angles of the xerogels. In our previous paper, ZnFe<sub>2</sub>O<sub>4</sub> thin films and xerogels doped with ZnFe<sub>2</sub>O<sub>4</sub> NPs were irradiated with femtosecond laser [25, 26]. We have successfully induced a phase transition from a stable phase of ZnFe<sub>2</sub>O<sub>4</sub> with normal spinel structure to a metastable phase with random spinel structure. As a result, the magnetic properties were drastically changed and the room-temperature magnetizations were enhanced. The metastable phase of ZnFe<sub>2</sub>O<sub>4</sub> is a promising ferrimagnetic material [27] and may exhibit a large Faraday effect [28, 29], but its figure of merit is reduced due to the high content of Fe with strong d-d transition absorption. Tb<sup>3+</sup> ions selected for this study have no optical absorption in glasses and gels, and are expected to be a Faraday material with a high figure of merit over a wide range of wavelengths. Femtosecond laser irradiation may also precipitate Ag NPs and at the same time induce a refractive index change, resulting in an optical waveguide-type Faraday material that would be superior to our previous report [17].

# 2. Experimental

Transparent silica solid gels doped with Ag<sup>+</sup> and Tb<sup>3+</sup> ions were prepared using a conventional sol-gel technique. A mixture containing 6.25 g of tetraethoxysilane (TEOS) (Shin-etsu silicone 99%), 1.75 mL of ethanol (EtOH), 3.24 mL of pure water ( $H_2O$ ), 50µl of HNO<sub>3</sub> (an acid catalyst) and various amounts of Tb(NO<sub>3</sub>)<sub>3</sub> was stirred for 30 min. The molar ratio of reaction solution was  $TEOS/EtOH/H_2O/HNO_3 = 1:1:6:5.0x10^{-3}$ . The mole percent of  $Tb^{3+}$  ion to Si atom was changed from 0.25 to 1.0. Following that, an AgNO<sub>3</sub> aqueous solution was added to the solution and stirred for 1 h. The molar ratio of Ag<sup>+</sup>/Si was varied from 0.15 to 0.45. The reactant mixture was dropped into a polypropylene sample cell. Then, the solution was dried slowly at room temperature for two weeks to avoid cracking of dried gels. Finally, the obtained silica gels were dried in an electric furnace by raising the temperature to 200-600°C. The rate of temperature increase to each temperature was 20°C/min, and cooling to room temperature was started immediately after the temperature reached the maximum,. The xerogel sampels were irradiated with a regeneratively amplified Ti: Sapphire laser (Coherent, Legend) with a repetition rate of 1 kHz. The laser with a center wavelength of 780 nm and a pulse duration of 120 fs (full width at half maximum) was focused using an objective lens (Nikon, LU Plan Fluor, x20, NA = 0.45). The size of focal spot was about 2.2 µm. To irradiate a large area in a short time, 10-point irradiation was performed using a spatial light modulator (Hamahoto, SLM-OOO). The focal position was 200-µm beneath the surface of the

sample, and scanned horizontally on a PC-controlled *XYZ* translation stage.

Optical absorption spectra were measured for the asprepared, annealed, laser irradiated xerogel samples doped with  $Ag^+$  and  $Tb^{3+}$  ions using a spectrophotometer (JASCO, V-730) in the wavelength range from 350 to 1000 nm. The



**Fig. 1** Absorption spectra measured for (a) as-prepared xerogels doped with 0.5 mol% of  $Tb^{3+}$  ions and (b) as-prepared xerogels co-doped with 1 mol% of  $Tb^{3+}$  ions and 0.15 mol% of Ag<sup>+</sup> ions for different drying temperatures. The insets are photo images of xerogels. (c) Variation of the absorption coefficient of the as-prepared xerogels measured at 450 nm as a function of drying temperature.

change in valence state of Tb species in the sample before and after laser irradiation was investigated using an X-ray Photoelectron Spectrometer (Shimazu, Axis Ultra DLD). The magnetic field dependences of magnetization at room temperature were examined for each sample using a superconducting quantum interference device magnetometer (Quantum Design, MPMS-XL7).

External magnetic field dependence of Faraday rotaion angles were measured for Tb-doped xerogel samples using self-assembled measurement system. Xerogel samples were placed inside a magnet driven by bipolar power supply, which generates stable magnetic field ranging from -0.8  $\sim$ 0.8 T. A probing laser beam with a wavelength of 488 nm was polarized using a Glan-Taylor polarizer, transmitted through the samples, and then separated into two orthogonal components of polarization using polarizing beam splitter. The two beams were individually introduced into the auto-balanced photodetector. Faraday rotation angles as a function of external magnetic field were calculated using the log-output signals from the detector. High-sensitivity Faraday rotation angle measurement using a lock-in amplifier to detect minute changes for the femtosecond-laser irradiated area of xerogels. Microscopic Faraday effect for the irradiated area of xerogels was measured by focusing the laser beam with a long working distance objective lens (f = 4 mm, NA = 0.42).

## 3. Results and discussion

Optical absorption of Tb-doped xerogels prepared at different drying temperatures was investigated. Figure 1(a) shows the absorption spectra of xerogels with 0.5 mol% of Tb<sup>3+</sup> ions and no Ag<sup>+</sup> ions. Transparent samples with no absorption were obtained for the drying temperature of 200-450°C. These samples are suitable for laser irradiation without cracks or deformation, as shown in the photo images. All samples prepared with Tb<sup>3+</sup> concentrations from 0.25 to 3 mol% for a drying temperature of 450°C also resulted in transparent xerogels. The absorption spectra of xerogels co-doped with 1 mol% of Tb<sup>3+</sup> ions and 0.15 mol% of Ag<sup>+</sup> ions for different drying temperatures are displayed in Figure 1(b). The samples treated at 200 and 300°C showed a brownish color change and an obvious



Fig. 2 Absorption spectra measured at room temperature for xerogels doped with 1 mol% of  $Tb^{3+}$  ions and different concentration of  $A\sigma^+$  ions

absorption peak especially in the short wavelength region. This is presumably due to a strong absorption band in the Ag atoms formed as a result of the reduction of  $Ag^+$  ions, some of which precipitated as NPs. Figure 1(c) shows the variation of the absorption coefficient measured at 450 nm



Fig. 3 (a) Magnetic field dependences of Faraday rotation angles for xerogels prepared at different  $Tb^{3+}$  concentrations. (b) Variation of Faraday rotation angles at 8 kOe as a function of  $Tb^{3+}$  concentration. The plots were subtracted with the contribution of the xerogel matrix. (c) Magnetic field dependences of Faraday rotation angles for xerogels with different Ag<sup>+</sup> concentration.

as a function of drying temperature. It was found that the absorption coefficient was large at low drying temperatures, while transparent xerogel was obtained without coloration for drying temperatures higher than 450°C. It is considered that Ag reduction occurs at low temperatures below  $300^{\circ}$ C while Ag<sup>+</sup> ions can be dispersed in the xerogel in an oxidized state at drying temperatures higher than  $450^{\circ}$ C. Therefore, the optimal drying temperature was  $450^{\circ}$ C to obtain transparent xerogels.

Figure 2 shows the absorption spectra of xerogel samples in which the concentration of Tb<sup>3+</sup> ion was fixed at 1 mol% and that of  $Ag^+$  ion varied from 0.15 to 0.45 mol%. As the concentration of Ag<sup>+</sup> was increased, the absorption coefficient increased. In particular, an absorption peak was observed in the short wavelength region centered at 430 nm for the sample with 0.45 mol% of Ag<sup>+</sup>. This suggests that the reduction of Ag<sup>+</sup> ions is more likely to occur when the Ag<sup>+</sup> concentration is high. Since the aim of this study is to reduce Ag ions and precipitate Ag NPs by femtosecond laser irradiation, the xerogels doped with  $\mathrm{Ag}^{\scriptscriptstyle +}$  must remain in a transparent state before irradiation, where Ag is oxidized to Ag<sup>+</sup> ions. In our previous report on xerogels containing only Ag<sup>+</sup> ions, we found that the ions are partially reduced at the Ag<sup>+</sup> concentrations higher than 0.1 mol% after drying at 400°C. Although both cases are not identical, it is suggested that the addition of Tb<sup>3+</sup> ions makes the reduction of Ag<sup>+</sup> ions less likely to occur. The reason for this may be that the addition of Tb<sup>3+</sup> increases the number of non-bridged oxygen atoms, which increases the negative charge density at the oxygen atoms, thereby the Ag ions are



**Fig. 4** Photo images of the irradiated area of the xerogels doped with 1 mol% of  $Tb^{3+}$  and 0.3 mol% of  $Ag^+$  ions. Pulse energy was (a) 1.5, (b) 3.0, (c) 4.5 and (d) 6.0  $\mu$ J/pulse. (e) Micrograph of scanned line with refractive-index change.

relatively stabilized in the vicinity of non-bridged oxygen. However, the detailed mechanism is still open to discussions.

Figure 3(a) shows the magnetic field dependences of Faraday rotation angles for xerogels prepared at different  $Tb^{3+}$  concentrations from 0 to 3 mol%. The nondoped xerogel, in which the concentration is 0 mol%, exhibits positive slope corresponding to the diamagnetic behaviors. On the other hand, the slope gradually decreased with increasing Tb<sup>3+</sup> concentration, and the sign of the slope reversed to negative in the Tb<sup>3+</sup> concentration higher than 2.5 mol%. By subtracting the rotation angles for the xerogel with the concentration of 0 mol% from each sample, paramagnetic contributions of Tb<sup>3+</sup> ions on Faraday rotation can be estimated. Figure 3(b) plots the variation of Tbderived Faraday rotation angles (@8 kOe) as a function of  $Tb^{3+}$  concentration. It can be seen that the rotation angle increases approximately linearly with increasing the Tb<sup>3+</sup> concentration. From the experimental data for the sample with 1 mol% of Tb<sup>3+</sup> concentration, the Verdet constant was estimated to be 0.0174 deg./mm·kOe. Since this value is comparable to the Verdet constant (0.0203 deg./mm·kOe) reported for Tb<sup>3+</sup> doped in phosphate glass [21], the obtained Berde constant is considered reasonable. The inset of Fig. 3(a) shows the magnetic field dependences of the room-temperature magnetizations. In contrast to the magnetic field dependence of Faraday rotation angles, even the smallest amount of Tb<sup>3+</sup> ion (0.25 mol%) exhibits a paramagnetic magnetization curve with a positive slope. While a small amount of Tb<sup>3+</sup> ions can possess a paramagnetic magnetization that exceeds the diamagnetic magnetization of the xerogels, the diamagnetic Faraday rotation angle due to xerogels is dominant and can overcome the paramagnetic contribution of Tb<sup>3+</sup> ions.

The magnetic field dependences of Faraday rotation angles for xerogel samples with a  $Tb^{3+}$  concentration of 1 mol% and with a Ag<sup>+</sup> concentration of 0, 0.15, and 0.3 mol% are shown in Figure 3(c). All samples showed the same magnetic field dependent slope regardless of the Ag<sup>+</sup> concentration. As mentioned above, since these samples are almost transparent and have low absorption, enhancement



**Fig. 5** Optical absorption spectra for the irradiated area of the xerogels doped with 1 mol% of  $Tb^{3+}$  and 0.3 mol% of  $Ag^+$  ions. Pulse energy was (a) 1.5, (b) 3.0, (c) 4.5 and (d) 6.0  $\mu$ J/pulse.

of Faraday rotation due to LSPR does not occur. In the case of transparent xerogels, the Faraday rotation angles are directly determined by the concentration of  $Tb^{3+}$  ions.

A xerogel sample doped with 1 mol% of  $Tb^{3+}$  and 0.3 mol% of Ag<sup>+</sup> was irradiated with femtosecond laser. Pulse energy was varied from 1.5 to 6.0 µJ/pulse, and scanning speed was 100 µm/s. The irradiation was performed over the entire irradiated area of 1 mm square with 10 µm spacing between each scanning line. Microscopic images of the irradiated area of the sample are shown in Figure 4(a)-(d). The irradiated area turned brown for all pulse energies. As the increase in the pulse energy, the color changes become darker. A clear refractive index change could be observed from the typical image at high magnification (Figure 4(e)). The width of the refractive index change region increased with higher pulse energy. Since the refractive index changes were induced inside the xerogel over a length of 1 mm without interruption, xerogels are expected as a promising base material for optical waveguide-type devices.

The optical absorption spectra of the irradiated area for each pulse energy are shown in Figure 5. While no absorption peak was observed in the non-irradiated region, a clear absorption peak at around 430 nm was observed in the irradiated region for all pulse energies. This is considered to be due to the localized surface plasmon resonance absorption of Ag NPs precipitated by the reduction of Ag ions to form Ag atoms and at the same time agglomeration due to thermal effects. As increasing the pulse energy, the peak intensity increased significantly while the central wavelength of the peak shifted slightly toward the longer wavelength side. This indicates that the number density of Ag NPs of similar size can be controlled by the pulse energy. From the central wavelength of the peak, the size of the Ag NPs was estimated to be about 5-6 nm by calculating the scattering cross section based on Mie scattering theory. A slight increase in the particle size was observed at higher pulse energies. When glass materials are used as a matrix, reports



Fig. 6 Variation of Faraday rotation angles as a function of magnetic field measured at a wavelength of 488 nm using a lock-in amplifier for irradiation with the pulse energies of 1.5 to 6.0  $\mu$ J/pulse. These plots were subtracted with the contribution of the xerogel matrix.

of a two-process approach, i.e., laser irradiation followed by heat treatment, show a negative correlation between the pulse energy and the size of the precipitated particles in most cases. In other words, as the increase in the pulse energy, the particle size decreases. This tendency can be understood as follows. During the initial laser irradiation process, a greater number of metal ions are reduced in the higher pulse energy, resulting in more nucleation. Since many nuclei grow individually in the subsequent heat treatment process, the size of each particle is expected to be small compared with the case of the lower pulse energy. In contrast, a positive correlation between pulse energy and particle size was observed in the case of Ag NPs precipitated by a single process in this study. This suggests that the irradiated energy was spent for particle growth by aggregation and diffusion in addition to the photoreduction and nucleation processes. It is usually believed that ultrashort pulsed light has little thermal effect, and diffusion of atoms is unlikely to occur. The reason why NPs were precipitated contrary to this is thought to be the structure of xerogels used in this study. A xerogel, a precursor of glass, is amorphous with a composition similar to that of glass and has



Fig. 7 XPS spectra in Ag-3d electrons obtained from the nonirradiated and laser-irradiated regions. The raw data (green line) was fitted with the superposition of peaks attributed to the 3d5/2 and 3d3/2 contributions of Ag+ and Ag, respectively.

excellent transparency. However, the xerogel fabricated at low temperatures have a lower density and a lower refractive index than glass. Therefore, the phenomena induced by ultrashort pulsed light irradiation are likely to be different from those of glass. For example, unlike glass, which has a dense structure, xerogel with a small density has microscopic pores and a small amount of solvent such as water remaining inside. When laser irradiation is applied to the inside of such a xerogel, the reduced Ag atoms are more likely to diffuse into the porous structure and fluid medium than into the interior of the glass, and it is speculated that the formation of NPs by aggregation will occur. In addition, the vaporization of residual solvent by laser irradiation presumably creates a high-temperature and high-pressure condition in the surrounding area, which may exert an effect to promote the diffusion of Ag atoms.

Figure 6 shows the results of a high-sensitivity Faraday rotation angle measurement using a lock-in amplifier for a small area of laser irradiation. Unlike the magnetic field dependence measurement described above, an AC magnetic field was applied to the sample, and the rotation angle detected by the auto-balanced optical receiver was accurately measured by the lock-in amplifier. A probe laser beam focused by an objective lens was used for detection in a small irradiated area. The obtained rotation angles subtracted with the diamagnetic components of the xerogels are plotted as a straight line with a negative slope due to the paramagnetic Tb<sup>3+</sup> ions. The absolute values of the rotation angle in the laser-irradiated region were larger than those in the non-irradiated region. This suggests that the Faraday effect is enhanced by the LSPR of Ag NPs precipitated by laser irradiation. In addition, there was a clear increasing tendency for the rotation angles with increasing the pulse energy. This may be due to the stronger plasmon enhancement induced by the increase in the number of precipitated Ag NPs. This is consistent with the results in the absorption spectra, and the increase in the number density of Ag Ns at higher pulse energies is thought to be responsible for the enhancement of the rotation angles. For the irradiation region of 6 µJ, the enhancement ratio was estimated to be approximately 1.3 times greater, which is higher than that for core-shell Fe<sub>3</sub>O<sub>4</sub>/Ag composites [30].

X-ray photoelectron spectra for Ag-3d electrons obtained from the non-irradiated and laser-irradiated regions are shown in Figure 7. The peaks at 368.3 eV and 374.2 eV are attributable to Ag 3d5/2 and Ag 3d3/2, respectively. Meanwhile, the peaks ascribed to  $Ag_2O$ , that is  $Ag^+$ , can be observed at 367.7 eV and 373.5 eV for 3d5/2 and 3d3/2, respectively [30, 31]. Therefore, the obtained spectra were fitted with a superposition of these contributions from the 3d5/2 and 3d3/2 spectra for Ag+ and Ag, respectively. Fitted peaks are also shown in the figures. From the integrated values of these peaks, the ratio of the number of atomic state Ag to the total Ag atoms contained was estimated to be 0.383 and 0.564 for the non-irradiated and irradiated regions, respectively. This indicates that the number of zero-valent Ag atoms in the irradiated region is approximately 1.47 times as large as that in the non-irradiated region. Thus, it was demonstrated that Ag ions were actually reduced by femtosecond laser irradiation. In the irradiated region, the precipitation of Ag NPs is considered to have been induced by agglomeration.

### 4. Conclusions

We have achieved an enhancement of paramagnetic Faraday rotation due to Tb3+ ions for tetraethoxysilanebased transparent silica xerogels doped with Tb<sup>3+</sup> and Ag<sup>+</sup> ions prepared by conventional sol-gel method by irradiation with regenerative amplified femtosecond laser. A refractive index change was observed in the laser-irradiated region, suggesting that it may act as an optical waveguide. In addition, a color change was observed in the vicinity of the focal point, which is thought to be due to absorption by localized surface plasmon resonance as Ag<sup>+</sup> ions are reduced by laser irradiation and grow to form Ag NPs. The peak intensity increases with the increase in irradiation pulse energy, suggesting that the number density of Ag NPs in the laser irradiated area increased. The size of Ag NPs was estimated to be 4.97 to 5.93 nm from the absorption peak wavelength. The Faraday rotation angles in the irradiated area were larger than those in the non-irradiated area. The enhancement ratio estimated in the case of 6  $\mu$ J, where the largest change was observed, was calculated to be about 27%, which is higher than the enhancement ratio for coreshell type composites. XPS measurements of the laser irradiated and non-irradiated areas were performed to estimate the percentage of zero-valent Ag atoms in the total Ag atoms. The percentage of Ag atoms in the atomic state in the irradiated area was about 1.47 times higher than that in the unirradiated area, which is directly suggesting that the laser irradiation induces the reduction of Ag+ ions in the irradiated area.

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