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Fabrication of Silver Nanoparticles from Silver Salt Aqueous Solution at Water-Glass

Interface by Visible CW Laser Irradiation without Reducing Reagents

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*Supplementary data is available

Graphical abstract 4×8 cm



Silver nanoparticles can be directly fabricated on a glass substrate through a unique photochemical reaction at a water-glass interface.

ABSTRACT

We have investigated the excitation wavelength and intensity dependencies of fabrication of silver nanoparticles (Ag NPs) on a glass substrate through the laser-induced photoreduction of silver ions in aqueous solution. It was found that the nucleation of Ag NPs could occur not in an aqueous solution of silver nitrate but at a water-glass interface without any reducing reagents. The nucleation could be triggered by photoexcitation at visible to Near-IR wavelength regions where the silver nitrate solution has no absorption band. From the excitation wavelength dependence using five CW lasers at 325, 442, 532, 690, and 1064 nm, it has been presumed that one-photon absorption of unique surface chemical species such as silver oxide (Ag₂O) on the glass substrate is responsible for the reaction leading to the nucleation. Numerical simulation of a single Ag NP and a Ag@Ag₂O core-shell NP on the basis of Mie theory revealed the photoproducts consists of Ag, but not Ag₂O.

KEYWORDS: Silver nanoparticles; Localized surface plasmon; Photoreduction; Photooxidation; Water-glass interface.

1. INTRODUCTION

Controlled fabrication of noble metal nanoparticles with well-defined sizes and shapes is quite important for applications of these materials into photochemistry and nanophotonics. For this purpose, chemical processes have been widely employed as fabrication methods; spherical nanoparticles are produced by Turkevich method using citrate to reduce metal ions in an aqueous solution[1–4] and silver nanorods and nanowires are prepared by adding polyvinylpyrrolidone (PVP) into an ethylene glycol solution of silver nitrate[5,6] to induce the anisotropic propagation. In contrast to the above chemical processes, laser-induced reduction of silver ions has been proposed to confine the reaction within a small space. Abid *et al.* have demonstrated that irradiation of an aqueous solution of silver nanoparticles (Ag NPs) without a reducing agent such as citrate.[7] Fabrication of three-dimensional electronic/photonic microstructures on a glass substrate have been also achieved by irradiating silver ion solutions with focused 800-nm femtosecond laser pulses.[8–10]

For these laser-induced reduction processes, it has been reported that plasmonic enhancement of the excitation light[11,12] as well as local temperature elevation by photothermal effect[13,14] contribute to the growth of the nanoparticles. On the other hand, reactions leading to the initial process of the nucleation have been not yet clearly elucidated although some nonlinear processes have been suggested. Tanaka *et al.* employed focused 800nm femtosecond laser pulses for the fabrication of 3D silver microstructures and reported that the fluence for the fabrication in solution was twice larger than that at the water-glass interface.[9] Although similar results on the higher reactivity of photoreduction on the glass surface were found in other systems[13], clear mechanism on the preference of the formation of Ag NPs on the surface has not yet been clarified.

Not only the pulsed laser excitation but also CW laser irradiation was found to induce

the formation of Ag NPs on the glass surface. Bjerneld *et al.* demonstrated the fabrication of Ag NPs on a glass substrate by irradiating an aqueous solution of silver nitrate containing a small amount of citrate under the 514- or 647-nm CW laser irradiation[15,16] and they found that the formation of Ag NPs was observed only at the water-glass interface. Under the visible CW laser irradiation, photodecomposition of water by the multiphoton excitation has quite small probability to take place and chemical reactions leading to the reduction of silver ions by citrate are not so effective at room temperature.[15] Accordingly, it was suggested that the preformed Ag clusters with broad absorption in the visible wavelength region might play a primary role in the nucleation reaction of Ag NPs.

With an aim to elucidate the mechanism on the preferential formation of Ag NPs on the glass surface, we have investigated the wavelength and intensity dependencies under the CW laser irradiation of an aqueous solution of silver nitrate in the absence reducing agent. Although the aqueous solution of silver nitrate has no absorption in the wavelength region > 350 nm, the laser-induced formation of Ag NPs on the glass surface was observed at all excitation wavelengths of 325, 442, 532, 690, and 1064 nm. By introducing the efficiency of photoreduction dependent on the excitation wavelength and the characterization of NPs by atomic force microscopy (AFM), scanning electron microscopy (SEM), and energy dispersed X-ray spectroscopy (EDX), we will discuss the mechanism of the preferential formation of the Ag NP on the glass surface.

2. EXPERIMENTAL

2.1. Sample Preparation

Silver nitrate (99.8 %, Kishida) was used as received. An aqueous solution of silver nitrate at the concentration of 0.2 M was prepared using ultrapure water (Direct-Q UV, Millipore). Coverslips (borosilicate glass, $24 \times 32 \times 0.17$ mm, Matsunami) were cleaned in the following manner to prepare the sandwich-type sample chamber as schematically shown in Fig. 1a. First, coverslips were immersed into acetone and sonicated for 30 min and they were put in 5 wt % aqueous solution of sodium hydrate for 30 min to purify the surface. After rinsing with ultrapure water for several times, the coverslips were dried with a nitrogen gun. Finally, the sample chamber, which consists of two coverslips sandwiching a silicone rubber spacer of 0.3 mm in thickness, was filled with 80 μ L of the aqueous solution of silver nitrate. The absorption spectrum of silver nitrate in aqueous solution is shown in Figure 1b. As noted in the introductory section, no remarkable absorption was found in the wavelength region > 350 nm.

2.2. Optical Measurements

The sample was placed on an *x-y* scanning stage (BIOS-150T, Sigma) equipped with an inverted optical microscope (IX-71, Olympus). A schematic illustration of the optical setup to irradiate the sample with CW laser light is shown in Figure S1 in Supplementary data. Specifications of CW lasers at 325, 442, 532, 690, and 1064 nm employed in the experiment are also summarized in Table S1 in Supplementary data. For all optical measurements, a microscope objective (UPlanFl, 40X, NA = 0.75, Olympus) was used. All of CW lasers were focused to diffraction-limited spots at the water-glass interface using the microscope objective and a pair of plano-convex lenses installed in the optical path. The sample was illuminated with a dark-field condenser (U-DCD (NA = 0.8 - 0.92), Olympus) and a bright-field condenser (IX2-LWUCD, Olympus). Optical transmission and scattering images of the sample were acquired using a color CCD camera (K-TC202-USB-AT, Sigma) and a monochromatic CCD

camera (Infinity 3-1 URM, Lumenera). To evaluate optical responses of Ag NPs arising from localized surface plasmon resonance (LSPR), light-scattering spectra of the photoproducts were measured with a fiber-coupled spectrometer (SD-2000, Ocean Optics). Morphological information of the photoproducts was monitored by AFM (SPM-9700, Shimadzu) operated in tapping mode. SEM imaging and EDX analysis were performed with a scanning electron microscope (JSM-6060, JEOL). All measurements were performed at 22 ± 1 °C

3. RESULTS AND DISCUSSION

3.1. Excitation wavelength dependence of the photoreduction as detected by static optical imaging

Formation of NPs induced by the CW laser irradiation at the water-glass interface was monitored by dark-field imaging. Figure 2a - e show the scattering images of the focused spot under the CW laser irradiation, indicating that NPs were produced under all the irradiation conditions with 325-, 442-, 532-, 690-, and 1064-nm CW lasers. Irradiation period of the CW lasers was 30 s except for the 1064-nm laser. On the other hand, irradiation period of 300 s was needed for the formation of NPs with the CW laser at 1064 nm (Fig. 2e). Excitation intensities for the formation of detectable NPs were in the range of 10^2 to 10^5 W cm⁻², which were dependent on the excitation wavelength; in principle, higher excitation intensities were needed with an increase in the excitation wavelength. As will be shown in later, these NPs are safely attributed to the aggregates of Ag atoms by an EDX analysis. This indicates that the irradiation of the AgNO₃ aqueous solution in the visible to near-IR (NIR) wavelength region led to the formation of Ag NPs on the glass surface, while no remarkable absorption exists in the wavelength range of the irradiation. In addition, even under the irradiation at 325 nm, the formation of Ag NPs is interesting because of the absence of reducing agent. This result implies that the reaction pathway of CW-laser-induced photoreduction is different from that induced by the pulsed laser excitation [7] where the photodecomposition of water takes place through the multiphoton absorption of water.

To obtain deeper insight into the photoreduction process, laser intensity dependence was examined for the formation of Ag NPs under the excitation at 325, 442, 532 and 690 nm. In the case of the 1064-nm excitation, the sampling points sufficient to analyze were hardly obtained owing to the long irradiation period. Hence, we concentrate our discussion on the four excitation wavelengths. For the quantitative evaluation of the size of the photoproducts around the laser beam spot, brightness profiles of the static optical images were analyzed by fitting with a Gauss function. The peak intensity and FWHM (full width half maximum) correspond to the amount and the size of the NPs. Figure 2f and -g respectively show the excitation intensity dependence of the peak intensity and the FWHM of the spot at each excitation wavelength. Figure 2f indicates that the FWHM value slightly increases with an increase in the peak power density under the irradiation at 442, 532 and 690 nm. On the other hand, the spot size in the 325-nm irradiation is larger than other cases. While the photoproducts were confined in the laser beam spot by the irradiation at 442, 532, and 690 nm, a different behavior was observed by the excitation at 325 nm. As was shown in Fig. 2a, although the photoproducts were mainly formed in the beam spot of the 325-nm laser, weak scattering signals were observed within 20 µm in the radial distance from the center of the laser spot under large excitation intensities (details are shown in Figure S2 in Supplementary data). Production of small NPs around the laser beam spot may be due to the diffraction pattern of the excitation light by a circular aperture (Airy disk). Similar result was obtained under bright-field illumination at all the irradiation wavelengths, indicating the dense formation of Ag NPs in the laser spot (S3 in Supplementary data).

Consequently, the above experimental results indicate that the NP is produced mainly at the irradiated area of the CW laser, because the FWHM values, ranging from $1 - 2 \mu m$, are similar to diameters of the laser beam spots (Table S1 in Supplementary data). In contrast, the peak intensities noticeably increased with peak power density at all the excitation wavelengths as shown in Figure 2g. The increases in the peak intensity can be ascribed mainly to the increase the number of Ag NPs in the irradiation spot. These results indicate that the total amount of photoproducts increases with increasing peak power density at all the excitation wavelengths. Because the reaction area is confined in the laser spot at each excitation wavelength, a relative efficiency of photoreduction as a function of peak power density can be determined from Fig.

2g under the assumption that the peak intensity of the scattering signal is linearly in proportion with the peak power density. The normalized gradients of the linear relationships, which can be regarded as the rate of the formation of the Ag NP, were summarized in Table 1. The differences in Table 1 will be discussed in the following section to uncover the photoabsorber which plays a primary role for photoproduction.

Table 1. Relative rates of the photoproduction at each irradiation wavelength

λ _{ex} [nm]	325 nm	442 nm	532 nm	690 nm
Normalized gradient [W ⁻¹ cm ²]	100	19	0.8	0.2

3.2. Dynamics on the formation of Ag NPs

To elucidate the mechanism of the photoreduction, time evolution of the formation of Ag NPs under the CW laser irradiation was monitored by dark-field imaging with a monochromatic CCD camera. Figure 3 shows a series of snapshots displaying the time evolution of Ag NPs under the 442-nm CW laser irradiation. At the time origin of the irradiation (t = 0 s), no scattering signal was observed as shown in Figure 3a. With an increase in the irradiation time, weak scattering signals appeared at the center of the picture at the irradiation time of 30 s (Fig. 3b) and the scattering intensity in the laser beam spot noticeably increased with further increasing irradiation time (Fig. 3c- f).

To more quantitatively obtain the information on the dynamics of the formation of Ag NPs, a time course of peak scattering intensity in the laser beam spot was plotted in Fig. 3g, where results with other excitation wavelength are also shown (details are shown in S4 in Supplementary data). The scattering intensity under the irradiation at 442 nm (blue filled circles) increases within a few seconds after the time origin of the exposure, followed by the

significant increase with increasing irradiation time. At and after ca. 100 s, a clear saturating behavior is observed. A similar time profile of the scattering intensity was observed at lower excitation intensity, 1.0×10^3 W cm⁻² (Figure S4b in Supplementary data). This excitation intensity effect of the time evolution suggests that dynamics of the formation of Ag NPs under the CW laser irradiation does not depend on the excitation intensity. Similar time profile was observed by the irradiation at 532 nm (green filled triangles), suggesting that the primary process of the nucleation and the growth process of the NP are same for the cases of 442- and 532-nm irradiation.

In contrast, dynamics under the 690-nm irradiation (red filled squares) was markedly different from those by 442- and 532-nm irradiation. The detectable scattering signal appears after 10 s, and it rapidly increases in the time range of a few tens of seconds. Continuous irradiation at 690-nm over 30 s resulted in the ablation and a bubble formation around the laser spot (see S5 in Supplementary data). Reproducibility of ablation and the bubble formation within ca. 100 s was almost 100 % in the case where the excitation intensity was $> 10^6$ W cm⁻ ². Under the 1064-nm irradiation (red open circles), several tens of seconds were required for the initial rise in the scattering intensity. The time evolution of the scattering intensity was similar to that under the 690-nm irradiation although the time scale is slightly different from each other. That is, ablation and the bubble formation were also observed under continuous illumination over 200 s. The significant evolution in the scattering intensity and the bubble formation can be attributed to photothermal effects arising from the photoabsorption through LSPR. It has been reported that excitation intensities ranging from $10^5 - 10^6$ W cm⁻² results in local temperature increases up to 10^3 Kelvin, [17] which accelerates the growth of NPs. Although the photothermal effect contributes to the growth of the nuclei, formation of nucleus under the irradiation at 690 and 1064 nm cannot be explained only by the photothermal effect. Note that, even if the pre-formed small Ag NPs with diameters of a few nanometers existed in the laser spot before irradiation, the maximum local temperature increase can be estimated to be less than a few Kelvin on the basis of a simple heat conduction model developed in our previous work (see S6 in Supplementary data).[17,18]

3.3 Photochemical reactions leading to the reduction of silver ions.

As was mentioned in the introductory part, it was reported that the efficiency of the Ag NP formation at the water-glass interface under the photo-irradiation was much higher than that in the solution.[9,13,15,16] This result strongly suggests that the photochemical reaction takes place on the surface and/or in the vicinity of the interface. In order to clearly confirm the contribution of the surface, we monitored the formation of Ag NPs by changing the focal position of the 442-nm laser along z-axis as depicted in Fig. 4a. In other words, the area size of the laser spot on the glass surface was expanded compared to the experimental condition in previous sections where the focal spot was placed on the surface. In this experiment, we first irradiated the solution with a focused 442-nm CW laser for 30 seconds at z-distances of 25 and 50 µm under bright-field illumination. During this exposure, we observed no detectable formation of Ag NPs in the solution phase. After shutting off the 442-nm CW laser, the focal position of the objective was placed on the water-glass interface. Fig. 4b and c show transmission images thus obtained after 30-s exposures at 442 nm, indicating the formation of Ag NPs. Diameters of the circular region of Ag NPs on the glass surface were respectively ca. 20 µm and 50µm for the cases at the z-distances of 25 and 50 µm. Judging from the NA of the objective, these diameters are almost the same with the exposed area on the glass surface, indicating that the photoreduction can take place only on the glass surface exposed by the 442nm laser light. While monitoring transmission images during irradiation at each z-distance (typical time resolution: 30 ms), no Ag NPs exhibiting Brownian motion in the solution was observed. This result also ensures that the Ag NPs is produced not in the solution phase but on the surface.

To quantitatively elucidate the formation of Ag NPs on the surface, brightness profiles of the circular region were analyzed by the fitting with a Gauss function to determine the peak intensity and the width of the photoproducts (FWHM), as performed in Fig. 2. Figure 4d and e show FWHM and the peak transmittance as a function of z-distance. Fig. 4d shows the FWHM of the circular region being broadened with an increase in z-distance, together with relative transmittance increasing with z-distance as shown in Fig. 4e. Here, the relative transmittance is defined as a ratio of the transmittance of the background and the peak transmittance determined by the fitting with a Gauss function. These results indicate that the reaction area of the photoreduction is broadened and the density of Ag NPs decreases with increasing area size of the laser irradiation on the glass surface. In other words, FWHM in Fig. 4d and the relative transmittance in Fig. 4e respectively correspond to the unfocused laser beam spot size and excitation intensity at the water-glass interface. Hence, we have concluded that the photoreduction can occur at the water-glass interface even under the irradiation with a weak laser light and it does not take place in the solution irradiated even by the focused laser beam. In addition, it was proved that none of pre-formed Ag clusters or organic impurities contained in the solution affects to the photoreduction, because the reaction takes place only at the surface, but not in the solution.

To elucidate the chemical processes on the photoreduction without additional reducing agent, it is crucially important to clarify the species responsible for the light absorption and electron donors leading to the photoreduction of Ag at and/or in the vicinity of the glass surface. For the case of pulsed-laser-induced-reduction, it has been reported that the multiphoton-induced photodecomposition of water leading to the formation of hydrated electron is responsible for photoreduction of silver ions.[7,9] Because the ionization threshold of liquid water is reported to be 6.5 eV (190 nm),[19] two or higher order multiphoton absorption is necessary for the present excitation condition using the wavelength longer than 325 nm.

Compared with the photon density of a tightly focused femtosecond laser pulse, peak excitation intensities of the CW lasers employed in the present experiment were much smaller for the multiphoton absorption to take place. In addition, in the case where photodecomposition of water plays a major role in the photoreduction, formation of Ag NPs could be observed in the solution. However, the photoreduction could occur only at the water-glass interface, indicating that photodecomposition of water *via* multiphoton absorption can be clearly excluded as a candidate for the electron donor in the photoreduction on the glass surface under the CW laser irradiation.

For the one-photon absorption, water, Ag^+ , NO^{3-} , and borosilicate glass have no absorption in the wavelength region > 325 nm except for NO^{3-} . It is, however, strongly suggested that the excited state of NO^{3-} does not contribute to the photoreduction of Ag^+ under laser irradiation, because the formation of Ag NPs on the glass substrate was observed by the irradiation of an aqueous solution of silver perchlorate (AgClO₄) with no absorption at 325 nm (see S7-1 in Supplementary data).

Although the borosilicate glass has no remarkable absorption, it mainly consists of SiO_2 , B_2O_3 , Al_2O_3 , and Na_2O and can undergo several reactions in aqueous solution. It is known that the alkali oxides such as Na_2O dissociate from the glass substrate to water at interfacial region.[20] Accordingly, the formation of silver oxide (Ag₂O) could occur at room temperature because of the presence of OH⁻ through the following scheme:[21,22]

$Ag^+ + OH^-$	→ AgOH	(1)
2AgOH →	$Ag_20 + H_20$	(2)

Once Ag_2O is produced on the glass surface, the photodecomposition of Ag_2O could occur upon exposure to visible light due to its high photosensitivity.[23–25]

$$Ag_2 0 \rightarrow Ag0 + Ag$$
 (3)
 $Ag0 \rightarrow Ag + \frac{1}{2}O_2$ (4)

It has been reported that non-emissive Ag₂O nanoparticles were transformed into emissive Ag nanoclusters upon photoexcitation using continuous light sources.[25] Furthermore, Ag₂O has a broad absorption band ranging from UV to NIR wavelength region.[26] This kind of silver compounds which exists at the water-glass interface and has absorption band in the visible wavelength region can be a candidate of the species for the light absorption leading to the initiation of the reactions. On the other hand, impurities contained in the glass might be also responsible for the photoreduction. According to the previous reports on Na⁺/Ag⁺ ion exchange method in a glass matrix, Fe²⁺ could work as a reducing agent for silver ions at temperatures above 400 K.[27,28] However, it is considered in the present case that a minor contribution of Fe²⁺ is expected because the photoexcitation at the wavelength shorter than 300 nm is required for one-photon oxidation of Fe²⁺ in water.[29,30] Accordingly, we could presume that the formation of nucleation centers is attributed to the photoecomposition of pre-formed Ag₂O on the glass surface.

The growth of nuclei can be explained by a chain reaction of the photodecomposition and aggregation of small Ag clusters under CW laser irradiation. Once nuclei is produced, plasmonic enhancement of excitation light in near-field regime might assist the growth of them.[11,12] Results and discussion above strongly suggest Ag₂O at the water-glass interface play important roles both in the nucleation and growth. Moreover, saturation behavior of the formation of Ag NPs in Fig. 3g could be well accounted for by the local depletion of the reactant at the water-glass interface. To verify this hypothesis, we have conducted control experiments using quartz substrates at the excitation wavelengths of 325- and 442-nm. As a results, no formation of Ag NPs was observed by optical transmission imaging (see S7-2 in Supplementary data). This result indicates that silver oxide rarely forms at the interface between the quartz substrate without Na ion and the aqueous solution of silver nitrate.

3.4. Morphology of the photoproducts

In the case where the initiator of the photochemical reactions is Ag₂O, the photoproducts could be the aggregate of Ag₂O. In actuality, it was reported[25] for the photoactivation of Ag₂O nanoparticles that the emissive photoproducts could contain both Ag and Ag₂O. On the other hand, Grillet et al. have reported that the surface of Ag NP is easily oxidized upon exposure to visible light under the atmosphere with oxygen, resulting in the red-shifts and broadening of LSPR spectra.[31] In order to evaluate compositions of the photoproducts, we first measured AFM images for the NPs fabricated by 325-, 442-, 532-, and 690-nm irradiation. Because the sampling number of photoproducts was small for the 1064-nm irradiation.

Figure 5-a, -b, and –c show AFM images of photoproducts fabricated by 442-nm CW laser irradiation for 30 seconds at excitation intensities of 3.4×10^2 , 1.0×10^3 , and 3.4×10^3 W cm⁻². At the lowest excitation intensity, NPs with ca. 50-nm diameter were observed in the laser beam spot (Fig. 5a). As the excitation intensity increased to 1.0×10^3 W cm⁻², a nominal diameter and a number of NPs slightly increase (Fig. 5b). At the highest excitation intensity of 3.4×10^3 W cm⁻², NPs with diameters > 100 nm can be observed, together with an increase in the number of NPs (Fig. 5c). In addition, Fig 5 shows NPs smaller than 10 nm in diameter being spread out in the entire region of all AFM images. Increases in the diameter and the number of NPs are consistent with results obtained by optical micrographs shown in Fig. 2. In addition, the surface roughness of the glass surface increased with peak power density, reflecting the formation of smaller NPs around the laser spot (see Table S8 in Supplementary

data).

To obtain more quantitative information of the morphology of the photoproducts, AFM images were analyzed with a widely used freeware, Gwyddion (http://gwyddion.net/). While the information on height can be precisely obtained in AFM measurement, it is known that diameters of small objects such as NPs are roughly twice broadened. To compensate the broadened diameters of NPs, predefined functions in Gwyddion was used in the following manners. First, the circular regions were labeled as grains, and the peak heights in individual grains were determined. Second, the pixels higher than FWHM height in each grain were counted as the area of a NP. Although all NPs observed in AFM images were not exactly spherical, the obtained area for each NP was converted into a diameter by assuming a circle. Figure 5d, -e, and -f show the size distribution histograms of photoproducts at each excitation intensity. More than five AFM images were analyzed to obtain a histogram at each photoirradiation condition. NPs smaller than 20 nm in diameter were neglected in the histograms because their scattering signals are not detectable in our optical setup. At the excitation intensity of 3.4×10^2 W cm⁻², the median of the histogram is around 50 nm, and it shaped like a Gauss function (Fig. 5d). As the excitation intensity increased to 1.0×10^3 W cm⁻², a standard deviation of the histogram became slightly wider, but the median stayed around 50 nm (Fig. 5e). The photoexcitation at the highest intensity, 3.4×10^3 W cm⁻², promoted the widely-spread size distribution ranging from 20 to 120 nm (Fig. 5f). From the histograms shown in Fig. 5, it was demonstrated that the maximum diameter and the number of NPs increased with the excitation intensity. The height distribution histograms obtained in the same manner showed similar trends (see S8 in Supplementary data). Note that a correlation plot between diameter and height showed a liner relation with a slope of approximately 1.0 (see Figure S8d in Supplementary data). This result enables us to treat the photoproducts as spherical NPs. The AFM images of the photoproducts at the excitation wavelengths of 532 and 690 nm are exhibited in S9 in

Supplementary data, where spherical shapes were also observed. At the excitation wavelength of 325 nm (focused irradiation), we could not analyze AFM images because the entire region of the glass surface was covered by NPs smaller than 10 nm in diameter, as already mentioned.

3.5. Analyses of scattering spectra of the photoproducts with Mie calculation

Optical responses of the photoproducts in the laser beam spot were measured by means of scattering micro-spectroscopy, and analyzed on the basis of the Mie calculation[32] for spherical NPs. Figure 6a shows the scattering spectrum of photoproducts observed after the irradiation for 30 seconds with 442-nm CW-laser at the excitation intensity of 3.4×10^2 W cm⁻² (black solid line), indicating a clear peak around 530 nm. For comparison, we calculated scattering spectra of a single Ag NP with various diameters on a glass substrate and immersed in water on the basis of the Mie theory. An effective refractive index (n_{eff}) of 1.42 was employed for the surrounding matrix consisting of water (n_{water} = 1.33) and the glass substrate (n_{glass} = 1.52).[18] Note that the presence of Ag atoms in the photoproducts was proved by an EDX analysis (see S10 in Supplementary data). As the diameter of Ag NP increased, the peak wavelength shifted to longer wavelength region, together with an increase in the peak intensity and FWHM. The calculated spectra show the FWHM and the peak position comparable with those of the experimental results, of which results support that the optical responses of photoproducts are attributable to LSPR of Ag NPs.

To more precisely analyze the composition of the photoproduct, scattering spectra of the photoproducts fabricated at the excitation intensities ranging from $1.7 \times 10^3 - 1.7 \times 10^4$ W cm⁻² were measured. Figure 6b, -c, and –d show the peak intensity, peak wavelength, and FWHM as a function of peak power density. Fig. 6b shows the peak intensity monotonically increasing with peak power density. This result reflects increases in the diameter and/or the number of Ag NPs. The peak wavelength shifted from 525 to 570 nm as peak power density increased (Fig. 6c) and FWHM is in proportion with peak power density as shown in Fig. 6d.

These results can be ascribed to increases in the diameter of Ag NP in accordance with Mie calculation for a single NP. On the other hand, it is known that aggregation of plasmonic NPs results in redshift and broadening of LSPR band. As already mentioned in the previous section, a lot of NPs smaller than 50 nm in diameter were observed at higher excitation intensities. Summarizing above results and discussion, the excitation intensity dependence of the spectral changes in Figures 6b and 6c can be ascribed to increases in both diameters and the number of photoproducts.

Although the scattering spectrum attributable to the LSPR band was observed, the peak wavelength is largely different from that estimated by the Mie calculation. From the results obtained by AFM, the nominal diameter of the photoproducts was about 46 nm at the excitation intensity of 1.0×10^3 W cm⁻² and the peak wavelength of 526 nm was obtained at the similar excitation intensity of 1.7×10^3 W cm⁻², while the peak wavelength at 420 nm can be estimated for Ag NPs with a diameter of 46 nm by the Mie calculation. In addition to the difference in the peak wavelength, different FWHMs were observed in the experiment (ca. 6000 cm⁻¹) and the calculation (2700 cm⁻¹). These redshift and broadening in LSPR band can be generally attributed to three reasons: i) morphological anisotropy (e.g. nanorods or nanowires)[33], ii) interparticle coupling of LSPR induced by aggregation[34,35], and iii) photo-oxidation[31]. Morphological anisotropy can be excluded from the results obtained in the AFM measurement. On the other hand, it is known that the aggregation of plasmonic NPs results in the broadening of LSPR band[36]. On the possibility of the oxidation, it is worth noting that the excitation intensities employed in the present study were relatively high compared with that of the previous report on photo-oxidation of Ag NPs in a gas matrix[31]. Hence, silver NPs produced through the reaction pathway shown by eqs (1) - (4) might be followed by the photo-oxidation under the present CW laser irradiation.

3.6. Spectral evaluation of photo-oxidation with core-shell Mie calculation.

As discussed in the previous section, it was suggested that the surface of Ag NPs could be oxidized owing to rather high intensity of the laser light. It has been reported that the surface oxidation of Ag NP results in the pronounced redshift in LSPR band.[31] Consequently, the spectra of the photoproducts suggests the photo-oxidation. In addition, the aggregation and dense formation of Ag NPs also affect the spectrum of LSPR band. To clarify the contribution of these processes, we applied the Mie calculation modified for the spherical core-shell structure as depicted in Fig. 7a. This model consists of a Ag core having a radius of R_{core} [nm], Ag_xO shell layer with a thickness of t_{shell} [nm], and a homogeneous surrounding environment. In our previous work, this model was developed to calculate the extinction, absorption and scattering spectra of a single core-shell nanoparticle supported on a dielectric substrate and immersed in water.[17] For the core part, a dielectric constant of silver reported by Johnson was used.[37] For the shell layer, we employed experimentally obtained values for optical indices of thin films consisting of silver (I) oxide and silver (II) oxide.[38] It has been reported that the photo-oxidation-induced red-shifts in LSPR band of Ag nanocubes were reproduced well by FDTD simulation using thus optical indices of Ag_xO films ($1 \le x \le 2$).[31]

First, we estimated a proper ratio between t_{shell} and a radius of the core-shell NP (R_{NP} = $R_{core} + t_{shell}$) for the purpose of comparison with experimental results. Figure 7b shows the calculated scattering spectra of an 80-nm-diameter Ag@Ag_xO core-shell NP in the water / glass matrix at the ratios (t_{shell} / R_{NP}) of 0.05, 0.125, and 0.25 (Fig. 7b, break lines). A scattering spectrum of the Ag NP with 80-nm diameter is exhibited by the black solid line in Fig. 7b. While the spectrum of the Ag NP exhibited a sharp peak at a wavelength of 460 nm, a noticeable damping and red-shift in the LSPR spectrum were observed for Ag@Ag_xO NP at the ratio of 0.05 (blue dotted line in Fig. 7b). The damping and redshift in LSPR spectra were more pronounced with an increase in the ratio of the shell (break lines in Fig. 7b). To clarify the effect of photo-oxidation, the largest ratio of 0.25 was employed in the following calculation. To compare the calculated spectra with experimental results, all the spectra were fitted using a Gauss function to determine the peak wavelength and FWHM. Correlation between the peak wavelength and FWHM of Ag NP and Ag@Ag_xO NP between the calculated and experimental results are shown in Fig. 7c. The experimental result under the excitation at 442 nm is shown by the red plots with errors. In the case of Ag NP (black solid line), FWHM linearly increased with peak wavelength. This simple behavior based on Mie theory can be ascribed to the increase in diameter of the Ag NP. On the other hand, the correlation plot of a Ag@Ag_xO core-shell NP exhibited in the upper left region of the black solid line. This result indicates that the formation of Ag_xO shell results not only in redshifts of LSPR band but also in the drastic broadening of FWHM.

The experimental results show large difference from the calculated curves, although two points appeared in the upper left region of the calculated curve for a Ag nanoparticle in Figure 7c. FWHM of the experimental plots were always smaller than that of the Ag@Ag_xO core-shell NP: *i.e.*, the photoproducts had narrower spectra compared with that of the Ag@Ag_xO core-shell NP at the equivalent peak wavelength. This deviation in FWHM strongly suggests that the photoproduct contains fewer Ag_xO. Moreover, on the difference between the experimental plots and the calculated curve for a Ag NP, the peak wavelength exhibited small variations ranging from 520 to 570 nm, while FWHM markedly increased from 6000 cm⁻¹ to 9200 cm⁻¹. The most notable remark in the experimental results is that two points appeared in the lower right region of the calculated curve for a Ag NP, indicating that the peak of photoproducts is redshifted. Because the possibility of photo-oxidation is clearly excluded, the spectral redshift of the photoproducts can be assigned to the interparticle coupling of LSPR[36,39]. This assignment is consistent with the results obtained by AFM. Small variations in the peak wavelength can be attributed to the poly-dispersed size distribution of Ag NPs. In the previous reports on laser-induced reduction of silver ions under the optical microscope, the

composition of photoproducts was not discussed in detail.[9,13,15] In the present work, we have evaluated the photoproducts by means of light scattering micro-spectroscopy, SEM/EDX, and AFM. In addition, spectral simulation was performed using the core-shell model. As a result, it was concluded that the photoproducts are poly-dispersed Ag NP, but not Ag_xO NPs. For more detailed analyses of the composition of core-shell nanostructures, X-ray photoelectron spectroscopy (XPS) should be applied.[40] This finding could contribute to more precisely elucidate the reaction pathway of photoreduction at the water-glass interface.

4. CONCLUSIONS

Fabrication of Ag NPs at a water-glass interface was demonstrated by irradiating an aqueous solution of silver nitrate with various CW lasers. To elucidate the reaction pathway of photoreduction of silver ions in the absence of the reducing agent, excitation wavelength dependence was examined using CW lasers at 325, 442, 532, 690, and 1064 nm. From the excitation wavelength and intensity dependencies, it was presumed that pre-formed Ag₂O at the water-glass interface plays an important role for the formation of Ag NPs. The photoproducts were carefully analyzed by means of light scattering micro-spectroscopy, AFM, and SEM/EDX. Spectral analyses with modified Mie calculation revealed that the photoproducts consist of silver, but not silver oxide. These findings are consistent with the previous reports on the fabrication of Ag NPs at the water-glass interface, and might help precise fabrication of metallic nano/micro structures on a glass substrate.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version.

Figure 1



Figure 1. (a) Schematic illustration of fabrication of Ag NPs at a water-glass interface by CW laser irradiation. (b) Absorption spectrum of silver nitrate in aqueous solution (a concentration of 0.2 M), measured in a quartz cuvette with the 1-cm path length.





Figure 2. (a-e) Optical scattering images of the photoproducts at each excitation wavelength and excitation intensity. Note that the laser power [mW] in Fig. 2e is the measured value of the unfocused parallel beam at the backport of the inverted optical microscope, because the laser spot diameter of this wavelength was not measured. (f) The FWHM of the photoproducts as a function of peak power density at each excitation wavelength. (g) The scattering intensity of the photoproducts as a function of peak power density at each excitation wavelength.

Figure 3



Figure 3. (a-f) A time course of scattering images of the photoproducts upon the cw laser irradiation at 442 nm with the peak power density of 1.7×10^3 W cm⁻². (g) Time evolution of the normalized scattering intensity at each excitation wavelength. The peak power densities and the laser power at each excitation wavelength are as follows: 1.7×10^3 W cm⁻² (442 nm), 8.2×10^4 W cm⁻² (532 nm), 3.6×10^5 W cm⁻² (690 nm), 400 mW (1064 nm).





Figure 4. (a) Schematic representation of z-scan of a microscope objective from the glass surface to the solution under the 442-nm irradiation. (b) Optical transmission image of the photoproducts on the glass surface after the irradiation at z-distance of 25 μ m. (c) Optical transmission image of the photoproducts on the glass surface after the irradiation at z-distance of 50 μ m. (d) The FWHM of the photoproducts on the glass surface as a function of z-distance. (e) The relative transmittance of the photoproducts on the glass surface as a function of z-distance distance.





Figure 5. AFM images of the photoproducts fabricated by 442-nm CW laser irradiation at peak power densities of (a) 3.4×10^2 W cm⁻², (b) 1.0×10^3 W cm⁻², and (c) 3.4×10^3 W cm⁻². (d, e, f) Histograms of size distribution at each excitation intensity.





Figure 6. (a) Scattering spectrum of the photoproducts fabricated by 442-nm CW laser irradiation at a peak power density of 3.4×10^3 W cm⁻², and calculated scattering spectra of a Ag NP immersed in a homogeneous medium whose an effective refractive index (n_{eff}) of 1.42 at various diameters. (b) Scattering intensity of photoproducts as a function of peak power density. (c) Peak wavelength of photoproducts as a function of peak power density. (d) FWHM of photoproducts as a function of peak power density.





Figure 7. (a) Schematic illustration of a core-shell nanoparticle consisting of a Ag core, a Ag_xO shell, and a surrounding medium. (b) Calculated scattering spectra of an 80-nm-diameter Ag NP and a Ag@Ag_xO core-shell NP at various core-shell ratios. (c) Spectral correlations between FWHM and peak wavelength for the experimental results at 442-nm excitation and computational results.

References

- Z.S. Pillai, P. V. Kamat, What Factors Control the Size and Shape of Silver
 Nanoparticles in the Citrate Ion Reduction Method?, J. Phys. Chem. B. 108 (2004)
 945–951.
- J. Kimling, M. Maier, B. Okenve, V. Kotaidis, H. Ballot, A. Plech, Turkevich method for gold nanoparticle synthesis revisited., J. Phys. Chem. B. 110 (2006) 15700– 15707. .
- [3] D.D. Evanoff, G. Chumanov, Synthesis and optical properties of silver nanoparticles and arrays, ChemPhysChem. 6 (2005) 1221–1231.
- [4] M. Grzelczak, J. Perez-Juste, P. Mulvaney, L.M. Liz-Marzan, Shape control in gold nanoparticle synthesis, Chem Soc Rev. 37 (2008) 1783–1791.
- Y. Sun, B. Mayers, T. Herricks, Y. Xia, Polyol synthesis of uniform silver nanowires:
 A plausible growth mechanism and the supporting evidence, Nano Lett. 3 (2003) 955–960.
- [6] B. Wiley, Y. Sun, Y. Xia, Synthesis of silver nanostructures with controlled shapes and properties, Acc. Chem. Res. 40 (2007) 1067–1076.
- [7] J.P. Abid, A.W. Wark, P.F. Brevet, H.H. Girault, Preparation of silver nanoparticles in solution from a silver salt by laser irradiation, Chem. Commun. (2002) 792–793.

- [8] K. Kaneko, H.-B. Sun, X.-M. Duan, S. Kawata, Two-photon photoreduction of metallic nanoparticle gratings in a polymer matrix, Appl. Phys. Lett. 83 (2003) 1426.
- [9] T. Tanaka, A. Ishikawa, S. Kawata, Two-photon-induced reduction of metal ions for fabricating three-dimensional electrically conductive metallic microstructure, Appl.
 Phys. Lett. 88 (2006) 081107.
- [10] O. Wilson, G.J. Wilson, P. Mulvaney, Laser writing in polarized silver nanorod films, Adv. Mater. 14 (2002) 1000–1004.
- [11] B. Bin Xu, L. Wang, Z.C. Ma, R. Zhang, Q.D. Chen, C. Lv, B. Han, X.Z. Xiao, X.L. Zhang, Y.L. Zhang, K. Ueno, H. Misawa, H.B. Sun, Surface-plasmon-mediated programmable optical nanofabrication of an oriented silver nanoplate, ACS Nano. 8 (2014) 6682–6692.
- K.G. Stamplecoskie, J.C. Scaiano, Light emitting diode irradiation can control the morphology and optical properties of silver nanoparticles, J. Am. Chem. Soc. 132 (2010) 1825–1827.
- [13] A. Ishikawa, T. Tanaka, S. Kawata, Improvement in the reduction of silver ions in aqueous solution using two-photon sensitive dye, Appl. Phys. Lett. 89 (2006) 113102.
- [14] S. Hashimoto, D. Werner, T. Uwada, Studies on the interaction of pulsed lasers with plasmonic gold nanoparticles toward light manipulation, heat management, and

nanofabrication, J. Photochem. Photobiol. C Photochem. Rev. 13 (2012) 28-54.

- [15] E.J. Bjerneld, K.V.G.K. Murty, J. Prikulis, M. Käll, Laser-induced growth of Ag nanoparticles from aqueous solutions., ChemPhysChem. 3 (2002) 116–119.
- [16] E.J. Bjerneld, F. Svedberg, M. Käll, Laser-Induced Growth and Deposition of Noble-Metal Nanoparticles for Surface-Enhanced Raman Scattering, Nano Lett. 3 (2003) 593–596.
- [17] K. Setoura, D. Werner, S. Hashimoto, Optical scattering spectral thermometry and refractometry of a single gold nanoparticle under CW laser excitation, J. Phys. Chem.
 C. 116 (2012) 15458–15466.
- [18] K. Setoura, Y. Okada, D. Werner, S. Hashimoto, Observation of Nanoscale Cooling Effects by Substrates and the Surrounding Media for Single Gold Nanoparticles under CW-Laser Illumination., ACS Nano. 7 (2013) 7874–7885.
- [19] C.L. Thomsen, D. Madsen, S.R. Keiding, J. Tho/gersen, O. Christiansen, Two-photon dissociation and ionization of liquid water studied by femtosecond transient absorption spectroscopy, J. Chem. Phys. 110 (1999) 3453.
- [20] D.E. Carlson, K.W. Hang, G.F. Stockdale, Alkali-Containing Glasses, J. Am. Ceram. Soc. 55 (1972) 337–341.
- [21] A. Gannoruwa, B. Ariyasinghe, J. Bandara, The mechanism and material aspects of a

novel Ag ₂ O/TiO ₂ photocatalyst active in infrared radiation for water splitting, Catal. Sci. Technol. 6 (2016) 479–487.

- [22] H. Huo, H. Su, W. Jiang, T. Tan, Effect of trace Ag+ adsorption on degradation of organic dye wastes, Biochem. Eng. J. 43 (2009) 2–7.
- [23] B. Ohtani, S. Nishimoto, Photoactivation of silver loaded on titanium (IV)
 temperature decomposition of ozone oxide for room-, J. Photochem. Photobiol. A
 Chem. 71 (1993) 195–198.
- [24] X. Wang, S. Li, H. Yu, J. Yu, S. Liu, Ag20 as a new visible-light photocatalyst: Selfstability and high photocatalytic activity, Chem. Eur. J. 17 (2011) 7777–7780.
- [25] L.A. Peyser, A.E. Vinson, A.P. Bartko, R.M. Dickson, Photoactivated fluorescence from individual silver nanoclusters., Science. 291 (2001) 103–106.
- [26] A.J. Varkey, A.F. Fort, Some optical properties of silver peroxide (AgO) and silver oxide (Ag2O) films produced by chemical-bath deposition, Sol. Energy Mater. Sol. Cells. 29 (1993) 253–259.
- [27] M.H. Shaaban, K.R. Mahmoud, T. Sharshar, A.A. Ahmed, Positron annihilation lifetime study of Ag-ion exchanged and heat treated soda lime glass, Nucl. Instruments Methods Phys. Res. B. 258 (2007) 352–356.
- [28] A. Kipke, H. Hofmeister, Formation of silver nanoparticles in low-alkali borosilicate

glass via silver oxide intermediates, Mater. Chem. Phys. 111 (2008) 254-259.

- [29] A. Cairns-Smith, Precambrian solution photochemistry, inverse segregation, and banded iron formations, Nature. 276 (1978) 807–808.
- [30] M.C. P. Braterman, A. Cairns-Smith, R. Sloper, T. George Truscott, Photo-oxidation of Iron(II) in Water between pH 7.5 and 4.0, J. Chem. Soc. Dalt. Trans. (1984) 1441– 1445.
- [31] N. Grillet, D. Manchon, E. Cottancin, F. Bertorelle, C. Bonnet, M. Broyer, J. Lermé,
 M. Pellarin, Photo-Oxidation of Individual Silver Nanoparticles: A Real-Time
 Tracking of Optical and Morphological Changes, J. Phys. Chem. C. 117 (2013) 2274–
 2282.
- [32] K.L. Kelly, E. Coronado, L.L. Zhao, G.C. Schatz, The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment, J. Phys. Chem. B. 107 (2003) 668–677.
- [33] E. Hao, G.C. Schatz, Electromagnetic fields around silver nanoparticles and dimers, J. Chem. Phys. 120 (2004) 357–366.
- [34] A. Sujith, T. Itoh, H. Abe, A.A. Anas, K. Yoshida, V. Biju, M. Ishikawa, Surface enhanced Raman scattering analyses of individual silver nanoaggregates on living single yeast cell wall, Appl. Phys. Lett. 92 (2008) 103901.

- [35] Y. Tanaka, H. Yoshikawa, T. Itoh, M. Ishikawa, Laser-induced self-assembly of silver nanoparticles via plasmonic interactions., Opt. Express. 17 (2009) 18760.
- [36] X. Qian, X. Zhou, S. Nie, Surface-enhanced raman nanoparticle beacons based on bioconjugated gold nanocrystals and long range plasmonic coupling, J. Am. Chem. Soc. 130 (2008) 14934–14935.
- [37] P.B. Johnson, R.W. Christry, Optical Constants of the Noble Metals, Phys. Rev. B. 6 (1972) 4370–4379.
- [38] J. Qiu, P. Zhou, X. Gao, J. Yu, S. Wang, Ellipsometric study of the optical properties of silver oxide prepared by reactive magnetron sputtering, J. Korean Phys. Soc. 46 (2005) 269–275.
- [39] N.A. Mirin, K. Bao, P. Nordlander, Fano Resonances in plasmonic nanoparticle aggregates, J. Phys. Chem. A. 113 (2009) 4028–4034.
- [40] Y.S. Yamamoto, Y. Fujime, N. Takahashi, S. Nakanishi, T. Itoh, Formation mechanism of plasmonic silver nanohexagonal particles made by galvanic displacement reaction, RSC Adv. 6 (2016) 31454–31461.