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Influence of localized surface plasmon resonance on shape changes of nanostructures: Investigation using metal nanoblocks in halide solutions

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ABSTRACT

Photoinduced shape changes of metal nanostructures in halide solutions were investigated using gold and silver nanoblocks (NBs) patterned on a glass substrate, instead of nanoparticles dispersed in solution. It was found that size reduction of the NBs by halide etching was enhanced by photoirradiation. Furthermore, it was revealed that the halide etching efficiency corresponded to the intensity of the electric field induced by localized surface plasmon resonance (LSPR) of the NBs. The enhancement of halide etching by LSPR was explained on the basis of electron transfer reactions from metal NBs. Throughout this study, it was demonstrated that metal NBs fabricated on a substrate constitute a powerful system to investigate photoinduced shape changes of nanostructures, because of their defined shape, position, and configuration.

1. Introduction

Recently, photoinduced shape changes of metal nanostructures have attracted much attention as a shape control technique of nanostructures. A remarkable example is shape changes of colloidal silver nanoparticles (NPs) passivated by citrate [1–11]. As first reported by Jin et al. [1], irradiation of weak light for spherical silver NPs engenders the formation of nanoprisms. Furthermore, it has been demonstrated that the size of the resultant nanoprisms can be controlled by adjusting the wavelength of the irradiating light [2,3]. It has been suggested that localized surface plasmon resonance (LSPR) of a silver NP and citrates play critical roles in the shape changes of silver NPs. As the suggested mechanism, first, LSPR of silver NPs on which citrate molecules are absorbed will bring about electron transfer from the citrate molecules to the NPs [8,9,12–14]. Subsequently, the supplemental electrons injected into the silver NP will reduce silver ions around the silver NPs [8,9,14]. Here those silver ions are suggested to be formed by oxidative etching of the other silver NPs by oxygen dissolved in the solution [8,9]. As a result of these reactions, silver NPs subjected to LSPR can grow and NPs not subjected to LSPR will be reduced (those relations are determined by the size of NPs and the wavelength of irradiation light). Furthermore, when the heterogeneous electric field is induced on a NP, the above reactions will occur in a limited potion of a NP, resulting in the formation of the anisotropic shaped NPs (nanoprisms).

Alternatively, photoinduced shape changes of silver NPs are also observed in colloids containing no citrate. Our previous study showed that laser irradiation for colloids, which were prepared in pure water using laser ablation technique, formed various shaped well-faceted NPs such as nanoprisms and nanorods [15]. Moreover, the addition of a small amount of halide (NaCl, KCl, $MgCl_2$, NaI, and KI) into the colloidal solution enhanced the photoinduced shape conversions [16,17]. With halides, the shape changes were brought about by weak fluorescent tube and xenon lamp irradiation. It was revealed that the shape changes were brought about through the formation of oxidized silvers (AgI, $AgCl_2^-$) by halide etching.[1] On the other hand, the role of photoirradiation in the shape changes of silver NPs in halide solutions has not been clarified sufficiently. It was confirmed that well-faceted NPs were not formed by photoreduction of $AgCl_2^-$ because nanocrystals were formed by irradiation of light of which the wavelength (400–700 nm) is far from the absorption band of $AgCl_2^-$ (260 nm) [17].

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[1] In neat water, we now assume that silver ions must be generated via etching by oxygen or laser irradiation.

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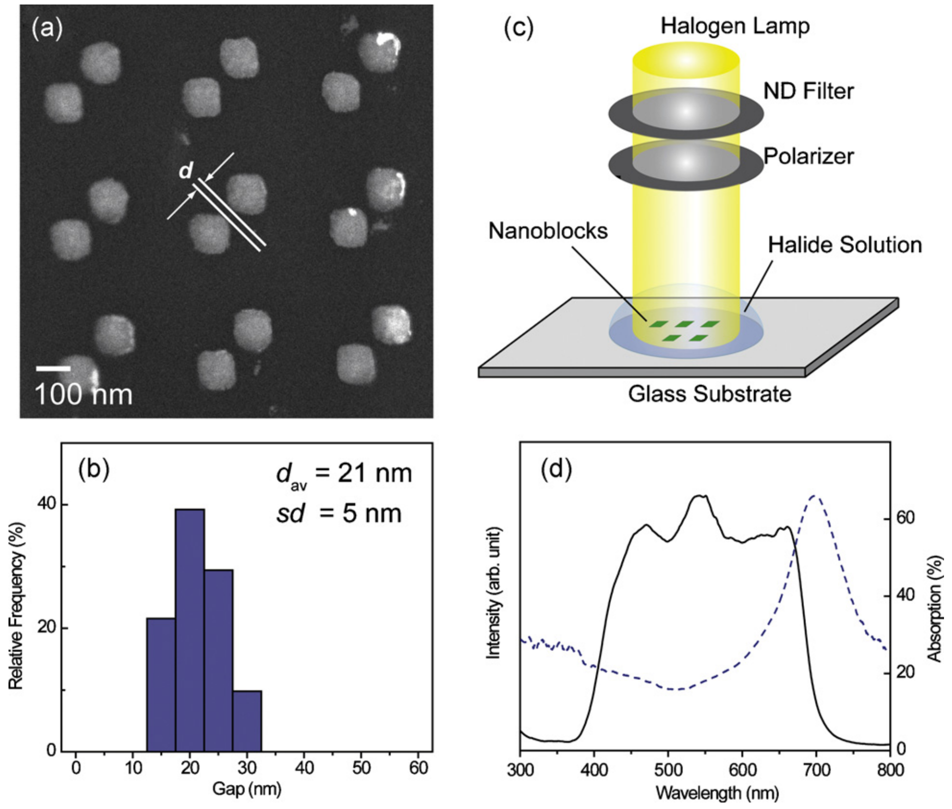

Fig. 1. The outline of the experimental setup. (a) SEM image of gold NB dimers patterned on a glass substrate. The "*d*" represents the gap separating two NBs in a dimer. (b) The size distribution [average (d_{av}), standard deviation (sd)] of the gap size, as obtained by counting 150 of the NB dimer in the SEM images. (c) The setup for photoirradiation for gold NBs set in a drop of halide solution. (d) Solid line: spectrum of the irradiation light of a xenon lamp. Dashed line: absorption spectrum of the gold NB dimers.

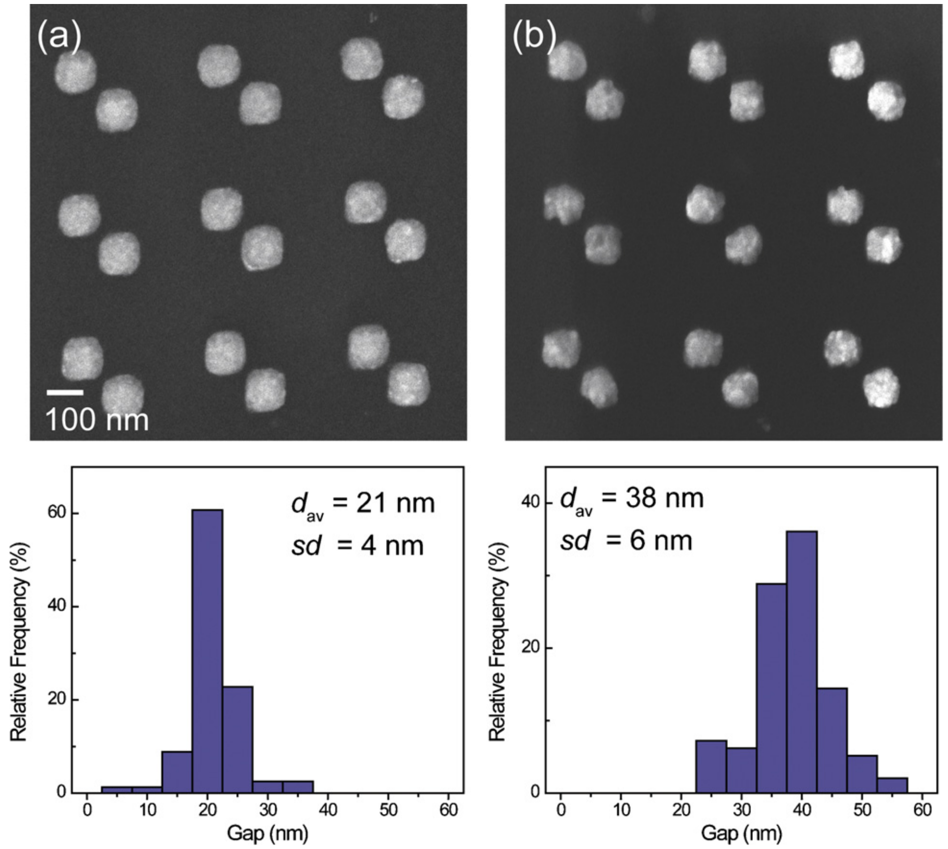

Fig. 2. SEM images of gold NBs after immersing in a drop of 100 mM NaI solution for 20 min: (a) without and (b) with photoirradiation. The distributions, averages (d_{av}), and standard deviations (sd) of the gap size of the NB dimers, as obtained by counting 150 of the NB dimers in the SEM images, are shown below each image.

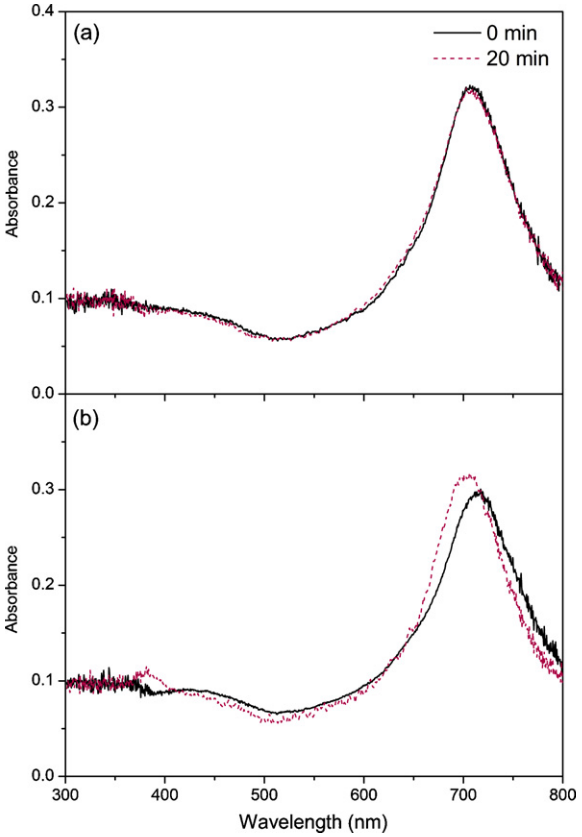

Fig. 3. UV–vis spectra of gold NB dimers set in a drop of 100 mM NaI solution for 20 min: (a) without and (b) with photoirradiation.

For the present study, we investigated the influences of photoirradiation on the shape changes of metal nanostructures in halide solutions. For the study, we introduce metal nanoblocks (NBs) fabricated on glass substrates [18] instead of NPs dispersed in solutions. Using the NBs, we can clarify the effects of photoirradiation more conveniently than using colloidal NPs, because (1) the shape of NBs can be controlled and NBs are fixed on a substrate; then trace of shape changes of NBs can be carried out more simply than that using colloids, and (2) the LSPR can be enhanced by a gap separating two NBs [19], which is useful when influences of LSPR are investigated. For example, it has been demonstrated that the photopolymerization reaction of a photoresist was enhanced in the gaps [20].

The photoinduced shape changes of metal NBs in halide solutions will be also important when NBs are used for SERS measurements. Maruyama et al. reported that SERS of dye molecules (R6G) obtained using silver NPs immobilized on a grass substrate were enhanced by halide ions [21]. They explained the mechanism of the enhancement in terms of the formation of Ag–halide–R6G complexes due to the strong interaction between silver and halides. In such studies, if shape of NBs or NPs will be changed by excitation light of SERS measurements, influences of the shape changes on SERS signal should be also taken into account.

2. Experimental

Gold and silver NBs on a glass substrate were fabricated using electron-beam lithography and lift-off techniques described in an earlier report [18]. Gold NBs with dimer configuration [Fig. 1(a)] were mainly used for the present study, because the silver NB was rather distorted and less stable as will described in the following part. The size of a NB was 100 nm × 100 nm × 40 nm. The average size of the gap in the gold NB dimers [represented as "*d*" in Fig. 1(a)] was 21 nm [Fig. 1(b)], which was obtained by counting 150 of the NB dimers in the SEM images. The experimental setup for photoirradiation is portrayed in Fig. 1(c). The NB dimers were set on the stage of an optical microscope (IX-71; Olympus Corp.). Then 0.5 mL of 100 mM NaI solution was dropped onto the substrate; irradiation of the halogen lamp of the optical microscope was applied through a condenser lens and ND filters to adjust the intensity of the incident light. To apply polarized light, a polarizer was set over the NBs. The irradiation spot size was 2 mm. The intensity of the irradiation light on the substrate was adjusted at 0.3 mW. The NB shape was observed using scanning electron microscopy (SEM, JEM-6700; JEOL). To measure absorption spectra of NBs, the transmitted light was corrected using an objective lens (UPLFLN40X; Olympus Corp.), and conducted into a UV–vis multichannel spectrometer (PMA-10; Hamamatsu Photonics KK). The spectrum of the irradiation light is presented in Fig. 1(d) with the absorption spectrum of the gold NB dimers. The band around 715 nm was assigned to the longitudinal SPR mode of the NB dimers [22].

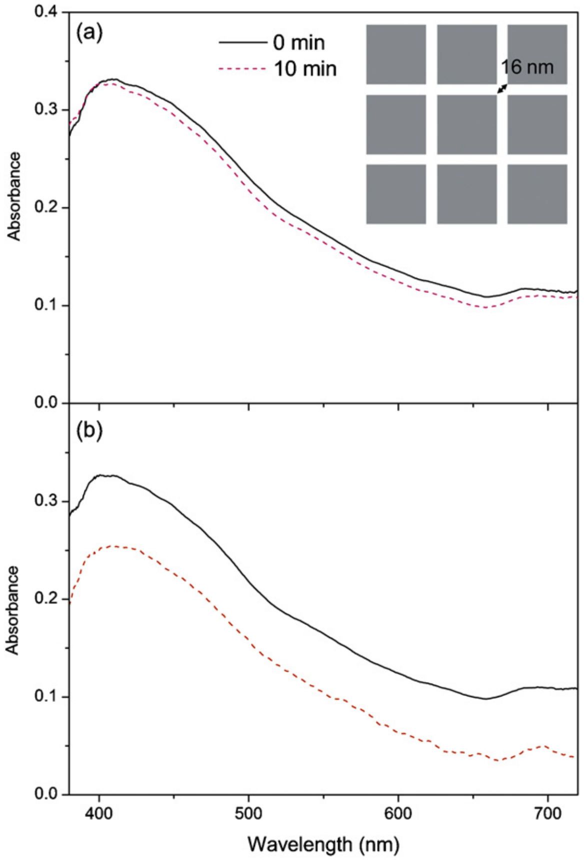

Fig. 4. UV–vis spectra of silver NBs (with a checker board configuration as illustrated in the figure) set in a drop of 100 mM NaI solution for 10 min: (a) without and (b) with photoirradiation.

3. Results and discussion

Fig. 2a and b portray SEM images of gold NB dimers immersed in a drop of 100 mM NaI solution without and with photoirradiation for 20 min. The distribution of the gap size for each condition was obtained by counting 150 of the NB dimers in the SEM images. The gap size distribution without photoirradiation was not changed significantly from that before setting in the halide solution. On the other hand, the average gap size of the NB dimers with photoirradiation was increased from 21 ± 5 to 38 ± 6 nm. The change in the

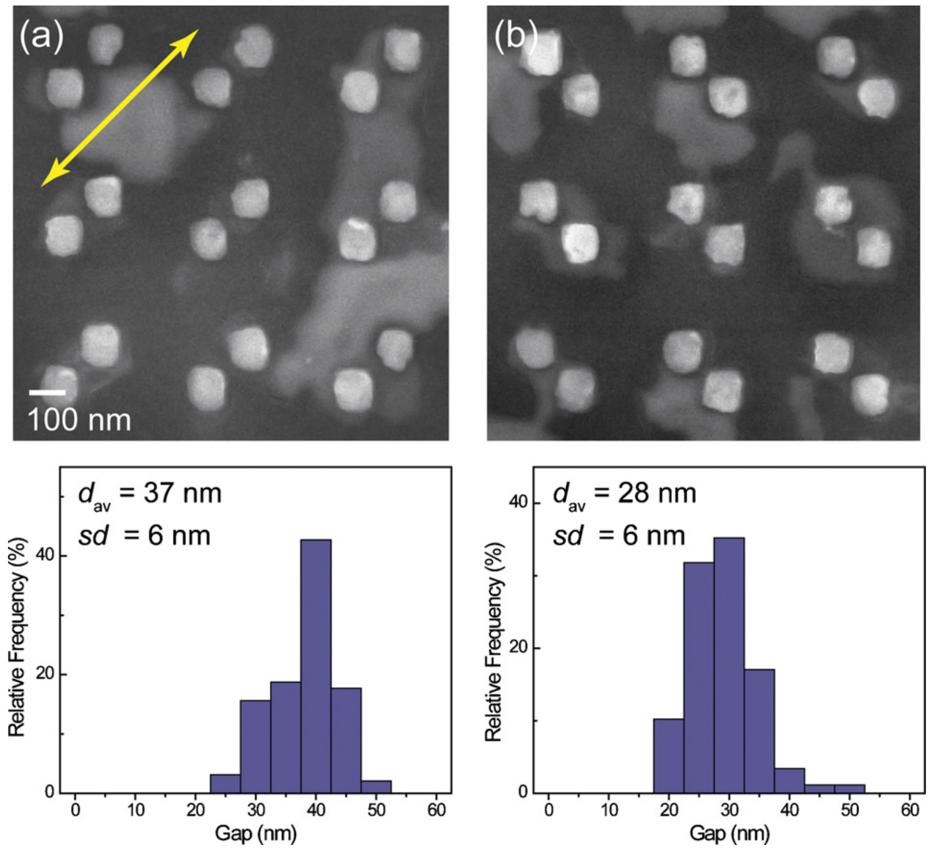

Fig. 5. SEM images of two sets of gold NB dimers with different orientation after photoirradiation in a drop of 100 mM NaI solution for 20 min. Those NBs were patterned in the same substrate to carry out photoirradiation simultaneously. The polarization plane of the incident light [indicated by the arrow in (a)] was set to be parallel and perpendicular to the longitudinal axis of the dimers in (a) and (b). The distributions, the averages (d_{av}), and the standard deviations (sd) of the gap size of the NB dimers are shown below respective images.

gap size was supported by the UV–vis spectra. As shown in Fig. 3, the band of the longitudinal SPR mode of the NB dimers around 715 nm was shifted to 705 nm under the light-irradiated conditions, although no remarkable change in the SPR band was observed for NBs without photoirradiation.

The similar results were observed for silver NBs. As shown in Fig. 4, the decrease in the absorption band of silver NBs in a drop of iodide solution, which implied that silver NBs were diminished, was enhanced by photoirradiation. For silver NBs, the change in the absorption band was more enhanced than that for gold NBs. The decrease in the absorption band was observed even in the dark conditions. Such diminishing of silver NBs is consistent with morphological changes of silver NPs in iodide solutions. The morphology of silver NPs in iodide solutions was deformed due to halide etching accompanying with the formation of AgI [17]. It had been confirmed that no changes in the absorption spectra were observed when silver and gold NBs were immersed in deionized water, indicating that the size reduction of gold and silver NBs was not due to thermal melting of the NBs. Therefore, the size reduction of gold and silver NBs in iodide solutions are due to halide etching, and the above results showed that photoirradiation enhanced halide etching of gold and silver NBs. It must be noted that silver NBs disappeared in the SEM images after photoirradiation in iodide solutions. Unfortunately, we could not find proper experimental conditions to observe the morphological changes of silver NBs by photo-enhanced halide etching.

Halide etching of gold and silver are electron transfer reactions from metal atoms to electron acceptors through a reaction with halide ions forming MX, MX_2^- or MX_4^- ions (M = metal; X = halogen) [23,24]. Actually, we detected $AgCl_2^-$ and AgI after addition of NaCl and NaI into silver colloids in neat water [17]. Maruyama and Futamata also reported that halide ions strongly adsorb on silver NPs on a glass substrate [21].

Typical reactions of gold and silver with iodide ions are

$$\mathrm{Au} + \mathrm{I}^- \rightleftharpoons \mathrm{AuI} + \mathrm{e}^- \quad -0.50\,\mathrm{V} \tag{1}$$

$$\mathrm{Ag} + \mathrm{I}^- \rightleftharpoons \mathrm{AgI} + \mathrm{e}^- \quad 0.15\,\mathrm{V} \tag{2}$$

In aqueous solutions in which oxygen is dissolved, it is suggested that oxygen would be the electron acceptors [25]. For example, the following reaction can be considered [23,24]:

$$\mathrm{O_2} + 2\mathrm{H_2O} + 4\mathrm{e}^- \rightleftharpoons 4\mathrm{OH}^- \quad 0.40\,\mathrm{V} \tag{3}$$

Due to the higher oxidation potential of gold (scheme 1), halide etching of gold hardly occurs in the normal conditions in contrast to silver, which is consistent with the difference in the stability between gold and silver NBs in the dark conditions. In the photoirradiated conditions, the etching of NBs was observed for both gold and silver. If we assume that scheme 3 is the major electron accepting reaction, then the change in the free energy of the electron transfer reaction from gold to oxygen:

$$4\mathrm{Au} + 4\mathrm{I}^- + \mathrm{O_2} + 2\mathrm{H_2O} \rightleftharpoons 4\mathrm{AuI} + 4\mathrm{OH}^- \tag{4}$$

is estimated to be 38 kJ/mol. This value leads that the ratio of Au:AuI is estimated to be 1:10^{-7} at 300 K and 1:10^{-5} at 400 K by assuming Boltzmann distribution. Ito et al. measured the temperature of dyes attaching on nano-aggregates of silver under photoirradiation by measuring anti-Stokes and Stokes surface enhanced Raman scattering [26]. They estimated the temperature of dyes to be ca. 350 K when photoirradiation at 0.3 W/cm^2 was carried

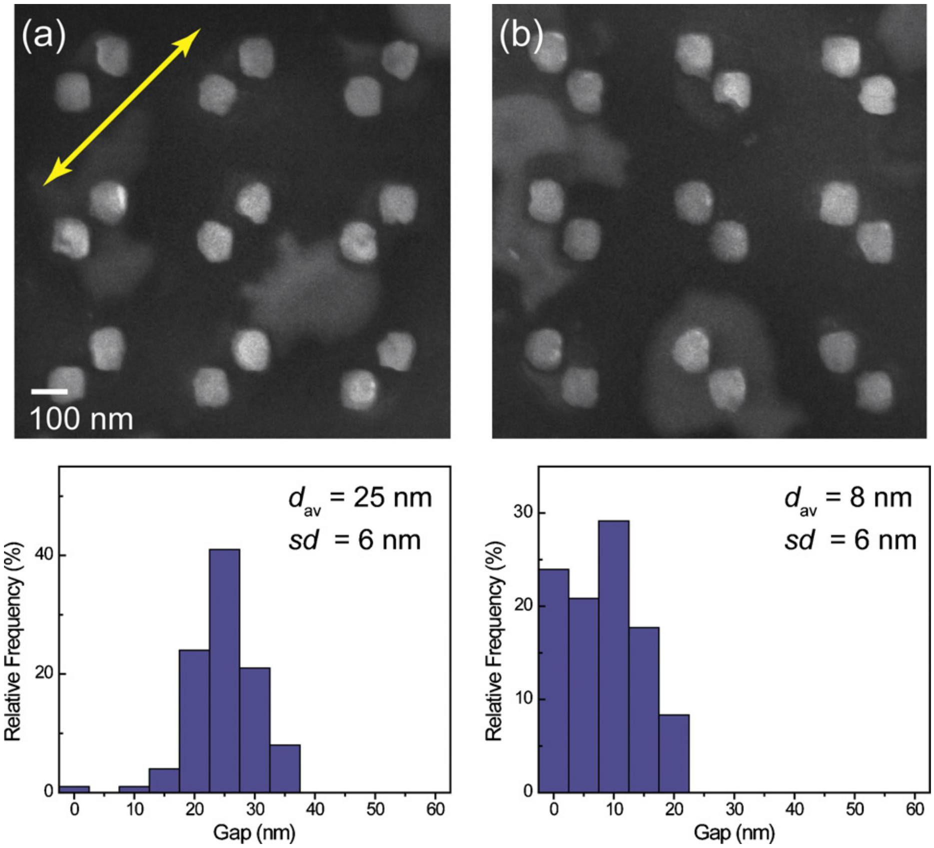

Fig. 6. SEM images of sets of gold NB dimers with the narrower gap size (4 nm before photoirradiation) after photoirradiation in a drop of 100 mM NaI solution for 20 min. The experimental conditions were identical to those presented for Fig. 3, except for the gap size. The longitudinal axis was (a) parallel and (b) perpendicular to the polarization plane of the incident light [indicated by the arrow in (a)]. Distributions of the NB dimers, the averages (d_{av}), and the standard deviations (sd) of the gap size are shown below respective images.

out. Therefore, it is reasonable that the enhancement of etching of gold and silver NBs by photoirradiation is not due to photo-thermal effect.

Another possible factor of the enhancement of halide etching is electronic effects induced by LSPR. To investigate effects of LSPR on halide etching, further experiments were carried out. Substrates on which two sets of gold NB dimers with different orientations were patterned were prepared. The longitudinal axes of the two sets of NB dimers were mutually perpendicular. Those sets of NB dimers were immersed in the same drop of halide solution (the distance between the sets was 60 μm); photoirradiation was conducted for both sets of NB dimers using polarized light. The polarization plane of the irradiation light was parallel to the longitudinal axis of one set of the NB dimers [Fig. 5(a)]. A strong electric field is induced on the gap of the NBs dimers when the longitudinal axis is parallel to the polarization plane of the irradiation light [19], although the temperature increase of the solution around both sets of NB dimers will be the same because they were set in the same drop of solution, and the numbers of photons absorbed by each set of NBs was not significantly different (parallel:perpendicular = 6:7, see Appendix A). Fig. 5(a) and (b) depict SEM images of gold NB dimers after 20 min photoirradiation in 100 mM NaI. The gaps in the NB dimers that were parallel to the incident light were increased more than those in the NB dimers that were perpendicular to the incident light. We also conducted the same experiments for gold NB dimers with a narrower gap (ca. 4 nm before photoirradiation). The result [Fig. 6(a) and (b)] reflects that the differences in the gap size between the parallel NB dimers and perpendicular NB dimers were increased. Because the intensity of the electric field induced by LSPR is increased concomitantly with decreasing gap size, it is strongly suggested that LSPR enhances the halide etching of the gold NBs, i.e., LSPR promotes the electron transfer from NBs.

While further investigation of mechanism of the enhancement of electron transfer by LSPR of NBs has not been conducted at present, an insight is provided from another system. Recently, Tatsuma and co-workers reported that photoirradiation of silver NPs supported by TiO_2 film induces dilution of the silver NPs [27–32]. From the results of analyses of photocurrent [28] and the influence of humidity [32], they concluded that LSPR of silver NPs excites electrons of silver NPs and promotes electron transfer from the silver NPs to TiO_2. As a result of the electron transfer, silver ions are dissolved from silver NPs into water on the surface of the TiO_2 film. They also reported that photoinduced electron transfer was observed for gold NPs on TiO_2 [33]. By analogy with the Au– and Ag–TiO_2 systems, it is suggested that LSPR of gold and silver NBs can excite electrons of NBs and promote electron transfer. It must be noted that etching of some of the NBs in Figs. 5(a) and 6(a) occurred isotopically, while the distribution of LSPR-induced electric field was anisotropic, i.e., the electric field in the vicinity of the gap was stronger than that in the other portion of the NBs. This inconsistency between the etching efficiency and the spatial distribution of electric field might be due to migration of excited electrons from portion in the vicinity of the gap to the other portion of the NBs. Such behavior of excited electrons, in addition to the mechanism of the LSPR enhancement of electron transfer, must be confirmed through future studies.

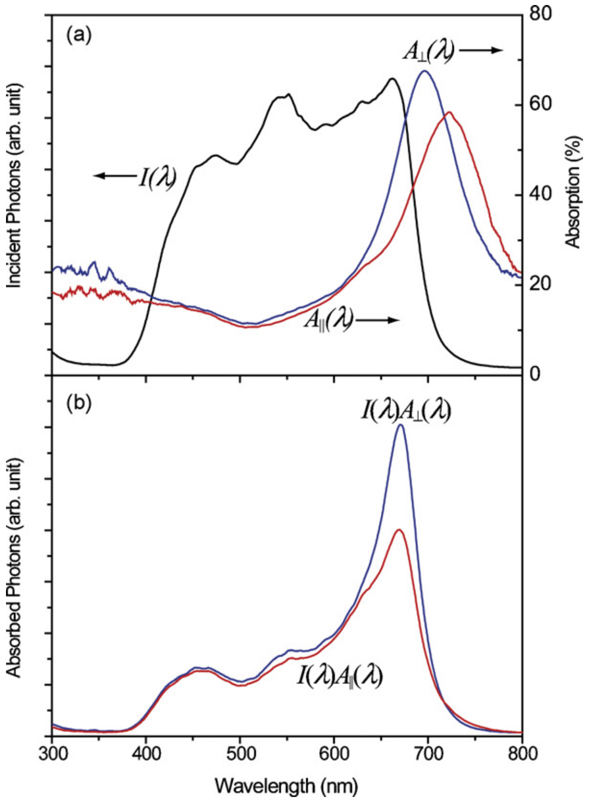

Fig. A. (a) Spectra of incident light (with a polarizer) [$I(\lambda)$] and absorption by gold NB dimers set to be parallel [$A_{||}(\lambda)$], and perpendicular [$A_{\perp}(\lambda)$] to the polarization plane of the incident light. (b) Relative numbers of photons absorbed by the two sets of gold NB dimers calculated from the $I(\lambda)$ and $A(\lambda)$.

Finally, we briefly comment on the mechanism of the evolution of well-faceted silver NPs in halide solutions [17]. The present results indicate that LSPR enhance the oxidation of silver atoms in NPs. These oxidized silver atoms can be reduced thermally and form new silver NPs or grow other NPs. This oxidation-reduction cycle is very similar to Ostwald ripening processes of metal NPs, in which unstable atoms in small NPs leave from the nanoparticles and move to other NPs with stable morphologies. As a result of repetition of the transportation of metal atoms, NPs with stable morphologies are formed. In fact, it was reported that well-faceted NPs of gold [34] and silver [35] are formed from NPs with diameters less than 5 nm via Ostwald ripening processes. Therefore, NPs with stable morphologies (well-faceted NPs) can be formed as a result of repetition of oxidation–reduction process of silver atoms in halide solutions. It must be noteworthy that LSPR will not participate in the evolution process of well-faceted NPs in halide solutions. Well-faceted NPs can be formed via spontaneous crystal growth as those observed in chemical synthesis processes. The role of LSPR is promotion of the atom transfer. This is a remarkable different point of the shape changes of silver NPs in halide solutions from those of citrate-passivated silver NPs.

4. Conclusion

Photoinduced shape changes of metal nanostructures in halide solutions were investigated using gold and silver nanoblocks (NBs) fabricated on a glass substrate using a lithograph technique, instead of nanoparticles dispersed in solution. It was found that halide etching of NBs was enhanced by photoirradiation. Furthermore, the halide etching efficiency corresponded to the intensity of electric field induced by LSPR. The enhancement of halide etching by LSPR was explained in terms of an electron transfer from NBs. This study demonstrates that metal NBs fabricated on a substrate constitute a powerful tool to investigate photoinduced shape changes of nanostructures, because of their defined shape, position, and configuration. Therefore, we will apply this system to investigate effect of LSPR on crystal growth reactions of silver and gold NPs.

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Appendix A.

The comparison of the numbers of absorbed photons between two sets of gold NB dimers shown in Fig. 5 was conducted as follows. The spectrum of the incident light and the absorption by each sets of gold NB dimers are shown in Fig. A(a). The numbers of photons absorbed by each set of gold NB dimmers were estimated by multiplying the spectrum of the incident light with the absorption of each sets of dimmers [$I(\lambda)A_{||}(\lambda)$ and $I(\lambda)A_{\perp}(\lambda)$ in Fig. A(b)]. The ratio of the area under $I(\lambda)A_{||}(\lambda)$ to that under $I(\lambda)A_{\perp}(\lambda)$ was 6:7.

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