Laser-induced Structural Conversions of Silver Nanoparticles in Pure Water —Influence of Laser Intensity—

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Laser irradiation onto silver colloidal nanoparticles dispersed in pure water was carried out at various laser intensities to modify structure of nanoparticles. At laser intensity higher than 150 mJ/cm^2, formation of wires and sheets, probably due to fusion of nanoparticles, were observed. On the other hand, at lower laser intensity (50–100 mJ/cm^2), it was found for the first time that particles with crystalline structures, nanoprisms and nanorods, were formed.

Nanosized metal particles concentrate much attention because of their unique properties differing from bulk state. Because the most of their optical and electronic properties strongly depend on their size and structure, it is important to control size and structure of metal particles in order to use them in various applications. Recently, laser irradiation (ablation) onto colloidal particle has been reported as an applicable method to modify particle size.[1–6] It has been reported that laser irradiation onto colloidal particles of noble metals resulted in size-reduction due to fragmentation[1,2] or size-growth due to fusion.[3,4]

Recently, we have carried out laser irradiation onto silver colloids dispersed in pure water which were prepared by using the laser ablation method, while colloids used in the former studies were chemically prepared and thus contained various reagents. We have found formation of colloidal particles with wire structure in addition to photoinduced fragmentation.[5] The lengths of the short and long axes of the wires were 10–100 nm and 200 > 1 μm, respectively. Mafuné et al. also reported preparation of gold and platinum nanowires using the similar procedure.[6] It was suggested that formation of the nanowires was due to fusion of particles. Fusion of colloidal particles must be efficiently promoted in colloids in pure water because protective reagents which prevent colloidal particles from contacting with each other were not contained. These findings suggest that the laser-irradiation method will be applicable not only for control of particle size but also for preparation of more complex nanosize structures. Thus, further investigation using more various laser irradiation conditions must be necessary. In this letter, we have investigated influences of intensity of laser irradiation on structural conversions of silver colloidal particles in pure water.

The experimental apparatus for preparation of silver colloids in pure water and laser irradiation onto prepared colloids were essentially the same as those reported elsewhere.[5] Briefly, the source silver colloids were prepared by using laser ablation of a piece of silver plate settled in pure water using the fundamental (1064 nm) of a Nd:YAG laser (Spectra Physics GCR-200). Laser ablation was carried out with focused laser light at 12 mJ/pulse for 10 min. After preparation of silver colloids, the silver plate was removed from the colloidal solution and laser irradiation onto the colloidal solution was carried out using the third harmonic (355 nm) of the Nd:YAG laser for 10 min. In this study, laser irradiation was carried out with nonfocused laser light, while focused laser light was used in our former study, in order to define intensity (fluence) of laser irradiation. Colloidal particles were analyzed by using a UV–vis spectrometer (Shimazu UV-2450) and a TEM (JEM-2000FX).

Figure 1 shows UV–vis spectra of silver colloidal solutions before and after laser irradiation at various intensities. At 25 mJ/cm^2, changes in the surface plasmon band of silver particles centered at 400 nm was small. On the other hand, at laser intensity higher than 50 mJ/cm^2, the intensity of the surface plasmon bands decreased with increase in laser intensity, suggesting that changes in size and structure of colloidal particles occurred. It must be noted that decrease in absorption intensity was also observed at the interband transitions around 250 nm, indicating that sedimentation of colloidal particles occurred at the high laser intensity.

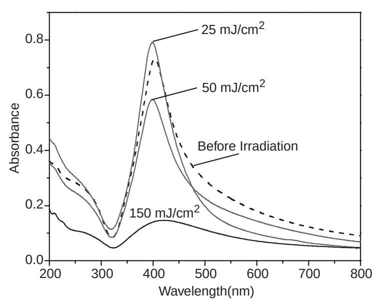


Figure 1. UV–vis spectra of silver colloidal solution before and after laser irradiation at various intensities.

Figure 2 shows TEM images of silver particles contained in the colloidal solutions before and after laser irradiation. Before laser irradiation (Figure 2a), spherical particles with average diameter of about 20 nm were observed. After laser irradiation at 25 mJ/cm^2, only slight decrease in size distribution was observed. On the other hand, drastic changes in both size and structure of colloidal particles were observed at laser intensity higher than 50 mJ/cm^2, consistent with the spectral change observed in the UV–vis spectra. First, photofragmentation of the silver colloids producing spherical particles less than 10 nm was observed. Second, structural conversions resulting in formation of nonspherical particles were observed, and laser-intensity dependence was observed for the structural conversion. At laser intensity from 50 to 100 mJ/cm^2, particles with prism- and rod-structures were observed (Figures 2b and 2c). The edge length of the nanoprisms was 100–300 nm. On the other hand, lengths of the short and long axes of the nanorods were 70–150 nm and 200–450 nm, respectively. These products have not been found in the previous studies. At laser intensity higher than 150 mJ/cm^2, colloidal particles with wire-structures were produced. In addition, it was found that sheet-structures were also formed (Figure 2d). The thickness of the sheets was estimated to be less than 20 nm from transparency of electron beam through the sheets in the TEM image.

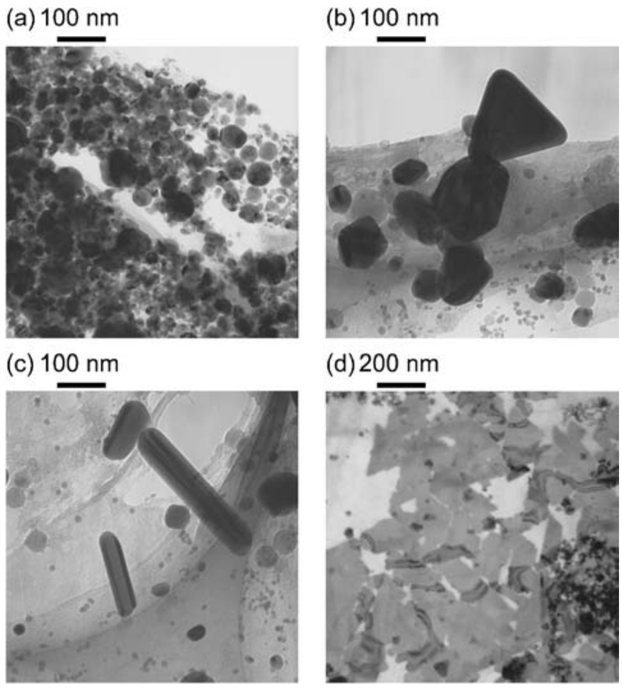
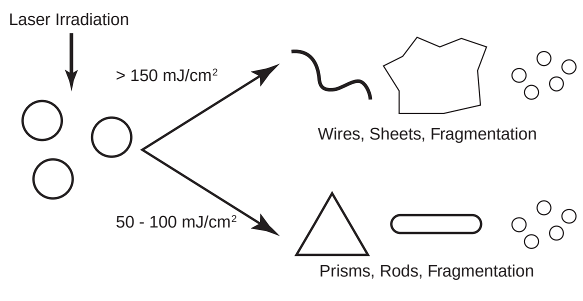


Figure 2. TEM images of silver colloidal particles. (a) Before laser irradiation. (b), (c) After laser irradiation at 50 mJ/cm^2. (d) After laser irradiation at 150 mJ/cm^2.



Scheme 1.

As summarized in Scheme 1, we have observed two types of structural conversion (formation of nonspherical particles) occurred by laser irradiation onto silver spherical particles dispersed in pure water. The first type is formation of the wires and sheets which occurred at laser intensity higher than 150 mJ/cm^2. As suggested in the previous reports, the wires must be formed via fusion of spherical particles. The fact that the wires were formed only at high laser intensity supports this assumption. The sheets must be also formed via fusion of spherical particles, because the sheets were observed with the wires. On the other hand, difference in formation process of the sheets from that of the wires, and mechanism of anisotropic fusion of particles resulting in formation of the wires and sheets must be investigated by further experiments.

The second type of structural conversion is the formation of the nanoprisms and nanorods which occurred at 50–100 mJ/cm^2. Differing from the wires and the sheets, such crystalline (ordered) structures cannot be formed via fusion of particles. Possibly, formation mechanism of the prisms and rods is crystal growth of silver, because these structures were effectively produced by using the chemical reduction methods.[7,8] Recently, Jin et al.[9] and Callegari et al.[10] reported that irradiation of fluorescent light onto chemically prepared silver spherical colloids resulted in formation of nanoprisms of which edge-lengths were from 20 to 150 nm. Jin et al. suggested that nanoprisms were formed via crystal growth of small (2–4 nm) clusters as precursor prepared by photofragmentation. Such clusters can be also formed by laser irradiation in our study. On the other hand, rods were also found in the present experiment, while only prisms were formed by fluorescent-light irradiation. Thus, further investigation of the formation mechanism of the laser-induced formation of the nanoprisms and nanorods from silver spherical particles in pure water must be carried out.

In conclusion, we have investigated influence of laser intensity on structural change of silver particles dispersed in pure water. It was found that in addition to nanowires, nanosheets were formed at laser intensity higher than 150 mJ/cm^2. On the other hand, it was found that nanoprisms and nanorods were formed at 50–100 mJ/cm^2. To clarify formation mechanisms of these structures, further investigations on more various irradiation conditions, such as irradiation time and colloid concentration, must be necessary. These studies are in progress.

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