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Preparation of Gold Nanoparticles by the Laser Ablation in Room-temperature Ionic Liquids

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Gold nanoparticles have been prepared by the laser ablation of a gold plate in imidazolium-based ionic liquids. The size and stability of gold nanoparticles were dependent on the wavelength of the laser light and the alkyl-chain length of the imidazolium-based cation.

In the past decade, nanometer-sized metal particles are of great interest, and a lot of researches have been done until now in order to prepare size-regulated metal nanoparticles.[1] Room-temperature ionic liquids (RTILs) have also been used as solvents to prepare nanometal materials by, e.g., electrochemical depositions.[2] Very recently, Torimoto et al. have reported that very fine gold (Au) nanoparticles were obtained by sputter deposition of gold onto ionic liquids.[3] They found that the simple sputter deposition onto 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIm][BF_4]) resulted in the formation of a solution containing highly dispersed Au nanoparticles whose average diameter (d_{av}) is 5.5 nm with a standard deviation (σ) of 0.86 nm. The prepared Au nanoparticles were stable without any additional stabilizing agents. Inspired by this finding, we tried to prepare Au nanoparticles by the laser ablation of a Au plate in RTILs. A number of researches have been performed for the preparation of Au nanoparticles in solutions by the laser ablation using fundamental (1064 nm) or second harmonic output (532 nm) of a nanosecond pulsed Nd:YAG laser. Typical diameters of the particles were less than 20 nm depending on the solvents, the concentration of surfactants, the excitation wavelength, and so on.[4–6] In this work, we tested three different imidazolium-based RTILs; 1-X-3-methylimidazolium tetrafluoroborate, where X = ethyl ([EMIm][BF_4]), butyl ([BMIm] [BF_4]), and octyl ([OMIm] [BF_4]). We have found that the particle size and stability were strongly dependent on the alkyl-chain length of imidazolium-based cation.

[EMIm][BF_4] and [BMIm][BF_4] were purchased from Kanto Kagaku, and [OMIm][BF_4] was purchased from Merck. Before the experiment, RTILs were evacuated by a vacuum line for more than 30 min. A nanosecond pulsed Nd:YAG laser (Continuum Surelite II, typically 5-ns pulse width, 10 Hz) was used for the laser ablation. A Au plate of 0.1-mm thickness (>99.99%) was pasted on a vertical wall inside a 1-cm glass cell which contained RTILs (ca. 0.5–1 cm^3). The laser pulse was horizontally introduced into the cell and focused on the plate by using a lens of 200-mm focal length. The spot size was estimated by a burning paper placed at the same position of the Au plate. During the laser irradiation, the solution was continuously stirred by a magnetic stirrer inside the cell. The absorption spectrum of the solution was measured by a UV–vis spectrometer (Shimadzu UV-3100), typically every 1 min for the case of the fundamental excitation (typically every 2 min for the case of the second harmonic excitation).

Since RTILs do not vaporize, a special technique is required to measure the transmission electron micrograph images of Au nanoparticles in RTILs with high resolution. We employed cryogenic transmission electron microscopy (cryo-TEM) in order to fix the Au nanoparticles in RTILs on TEM microgrid. A thin RTIL layer supported on the TEM microgrid was vitrified by plunge into liquid propane at −180 °C. The grid was transferred into a cryo-TEM (JEM-4000SFX, JEOL) operating at 400 kV and observed at the liquid helium temperature.[7]

Figure 1a shows the absorption spectra of the solutions just after the ablation by the 1064-nm pulse in RTILs. In all cases, a surface plasmon absorption band characteristic to Au nanoparticles appeared. However, the spectrum shape and the peak position were dependent on the solvent; the peak position shifted to the longer wavelength with decreasing the length of the alkyl-chain (540 nm in [OMIm][BF_4], 552 nm in [BMIm] [BF_4], and 562 nm [EMIm] [BF_4], respectively), suggesting that the average particle size of the nanoparticles became larger.[8] A similar trend was observed for the cases of the 532-nm ablation, although the peak position was blue-shifted relative to those by the 1064-nm ablation (519 nm in [OMIm][BF_4], 520 nm in [BMIm] [BF_4], and 552 nm [EMIm] [BF_4], respectively), and the absorption increased much more steeply to the UV region. It is to be noted here that nanoparticles produced by the ablation were not necessarily stable in RTILs. Especially in [EMIm][BF_4], the absorption spectra showed a gradual red shift

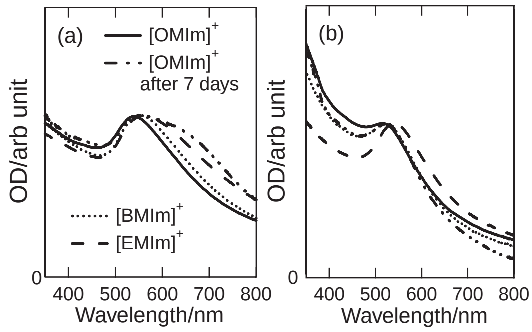

Figure 1. Absorption spectra just after the laser ablation of a Au plate by (a) 1064-nm pulses (6000 shots) and (b) 532-nm pulses (19200 shots except for [BMIm][BF_4] (18000 shots)). The spectra are scaled at the plasmon peak intensity. The average laser energy densities were (a) 150 mJ cm^{-2} and (b) 350 mJ cm^{-2} except for [EMIm][BF_4] (300 mJ cm^{-2}). The absorption spectra after 7 days in [OMIm][BF_4] are for samples after (a) 9600 shots and (b) 31200 shots ablation, respectively.

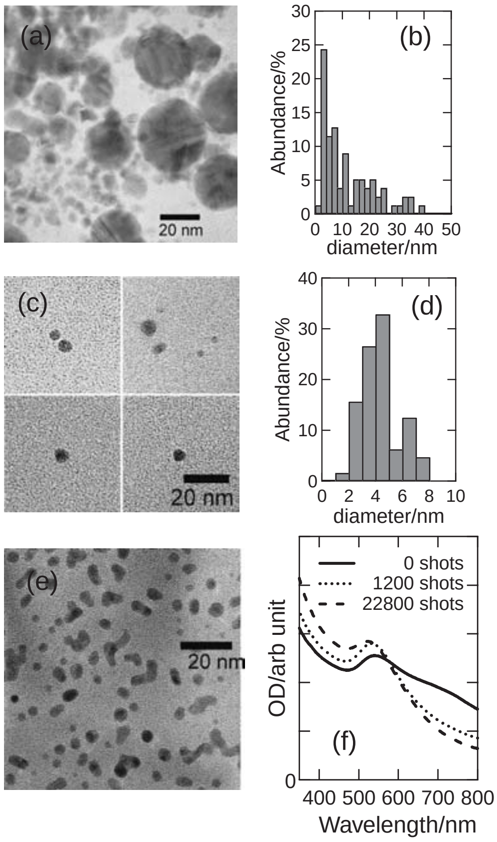

Figure 2. (a)–(e) TEM images of Au nanoparticles and its size distributions produced by laser ablation of a Au plate. (a), (b) 1064-nm ablation in [OMIm][BF_4] (the image is taken at 28 days after preparation). (c), (d) 532-nm ablation in [OMIm][BF_4] (the image is taken at 26 days after preparation). (Histograms are preliminary results of (b) 78 and (d) 64 particles in different areas.) (e) 532-nm ablation in [BMIm][BF_4] (27 days after the preparation). (f) The change of the absorption spectrum by the 532-nm excitation on the solution obtained by the 532-nm ablation in [BMIm][BF_4] (3 days after the ablation).

in a time scale of several minutes and became broad spectra centered around 680 nm within a few days irrespective of the ablation wavelength, and finally sedimentation of aggregated particle were observed. With lengthening the alkyl-chain of cations, the stability of nanoparticles increased. In [OMIm][BF_4], no sedimentation was observed more than two months and the color of the solutions were almost unchanged except for the variations observed for a few days (See Figure 1).

Figures 2a–2d show TEM images and histograms of particle size distributions produced by the ablations in [OMIm][BF_4]. As is expected from the absorption spectrum, nanoparticles produced by the 1064-nm ablation have a broad distribution of the diameter from a few nm to 50 nm ($d_{av} = 13$ nm, $\sigma = 10$ nm). On the other hand, nanoparticles produced by the 532-nm ablation have smaller diameters and distribution ($d_{av} = 4.2$ nm, $\sigma = 1.4$ nm), consistent with the blue shift of the plasmon peak position. The image for the solution obtained by the 532-nm ablation in [BMIm][BF_4] showed an interesting feature (Figure 2e); among almost spherical particles ($d_{av} = 3.6$ nm, $\sigma = 0.9$ nm), rod-like particles were observed. These particles may be one of the reasons for the broader absorption in the longer wavelength region.

The smaller particle size by the 532-nm ablation is probably due to the effect of fragmentation of nanoparticles by the absorption of the 532-nm pulse as is demonstrated by the cases of aqueous solutions.[4,5] In order to confirm this, we have irradiated the solution produced by the 532-nm ablation with the 532-nm laser pulses. The absorption spectra before and after the 532-nm irradiation are shown in Figure 2f. The initial broadened absorption spectrum became sharp and the peak position shifted to the blue, indicating the reduction of the particle size. After the laser excitation, the color of the solution turned to be light pink and kept unchanged for more than 4 months. The fragmentation was confirmed by the TEM observation (not shown) where the number of nonspherical particle was much reduced.

In our method, the size and stability of Au nanoparticles were strongly dependent on the cation species. The cation with the longer alkyl-chain may have a role as surfactants which stabilize nanoparticles by surrounding their surfaces, preventing the aggregation to form larger particles. The difference of the stability of the Au particles produced by the sputter deposition is another interesting issue. The nanoparticles produced by the sputter deposition method were stable in [EMIm][BF_4],[3] while the nanoparticles by the laser ablation were unstable. We consider that there may be a threshold size of particle with which RTILs can stabilize. As is demonstrated in the absorption spectra, the Au nanoparticles produced by the ablation in [EMIm][BF_4] had larger sizes and a larger size distribution compared with those by the sputter deposition. Further in the case of [BMIm][BF_4], the reduction of the particle size by the laser irradiation increased the stability of the nanoparticles. This point should be investigated further in the future.

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References and Notes

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