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COMMUNICATION

Silver sputtering into liquid matrix containing mercaptans: the systematic size control of silver nanoparticles in single nanometer–orders

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We herein propose a novel methodology to synthesize silver nanoparticles with precisely controlled diameters in single nano–meter orders by a sputtering into liquid matrix (polyethylene glycol) containing mercaptans (11-mercaptopundecanoic acid) as an environmental friendly preparation without reductants.

Inorganic nanoparticles (NPs) such as metal NPs and quantum dots have recently attracted significant attention from materials science.^{1–6} These metal NPs exhibit unique physical characteristics that give rise to many potential applications for such as catalysis,⁷ electronics,⁸ luminescence,⁹ solar energy conversion,¹⁰ as well as biomedicine.¹¹ For these applications, size control of metal NPs is the most important, and many amines and mercaptans¹ have been used as stabilizing reagents due to their well coordination properties.

Typical approach for the preparation of metal NPs is a chemical reduction of the corresponding metal ions in a solution by employing external reducing agents such as NaBH₄, hydrazine, or citric acid, which may be associated with environmental and biological risks.¹ This method have been extensively developed, however, one limitation is the contamination and the formation of by-products and impurities. Since the purification and separation of products requires complicated purification procedure, simple processes for preparing NPs have been demonstrated. There are only a few reports on environmentally friendly methods for metal NP synthesis and their use.^{12–14}

In this view, we have developed a simple technique, matrix sputtering method,^{15,16} for a preparation of metal NPs without a formation of by-products (Figure 1). Sputtering is a well-known method and is basically used for syntheses of thin films onto solid substrates. In our matrix sputtering process, argon is ionized by high voltage and then attacks the target metal and ejects the target atoms or clusters in a vacuum chamber.¹⁷ Ejected atoms and clusters aggregate not only in a gas phase but also inside or interface of the capturing liquid matrix, and form NPs.

So far, several capturing matrices have been examined for a preparation of Au NPs by matrix sputtering method and they can be categorized to (i) 6-mercaptophexyltrimethylammoniumbromide (6-MTAB)¹⁵ and pentaerythritol tetrakis(3-mercaptopropionate) (PEMP)¹⁶, and (ii) propane-1,2,3-triol,¹⁸ polyethylene glycol

(PEG),^{17,19,20} ionic liquids,^{21,22} and pentaerythritol ethoxylate (PEEL).¹⁶ Group (i) depends on the affinity of mercaptan group and can form very small (~1.3 nm) fluorescent Au NPs, while group (ii) depends mainly on the viscosity of themselves and form rather large Au NPs (2–5 nm). The difference in their size can be explained by the coordination of mercapto groups that can prevent the aggregation and growth of Au NPs inside or interface of the capture media. From these results, it is expected that we can synthesize metal NPs with various sizes in single nanometer-order and thus can control the physical properties of NPs by matrix sputtering method.

While most results were for Au NPs due to its high stability and lots of previous studies, it is difficult to find other metal NPs such as silver by this matrix sputtering method except for a few reports.^{18,23} In this paper, we propose novel methodology to control the size of Ag NPs by matrix sputtering method. While previous approaches have used only capturing liquid matrix, our new approach in this study uses both capturing matrix and organic molecules with mercapto groups. The mercaptans can dissolve in capture media and prevent the aggregation and growth of Ag NPs inside or interface of the capturing matrix according to the concentration of mercaptans. As far as we know, this is the first example for the systematic size control of Ag NPs by sputtering techniques.

The capture media used here was polyethylene glycol (PEG) with average molecular weight of 600 g mol⁻¹ and the degree of polymerization is between 10 and 17. Since PEG does not have any functional groups stabilizing metal NPs, it has been reported that the viscosity affects the size of resultant NPs.¹⁷ Thus, in the current work the amount of PEG was constant under difference thiol concentrations. The thiol stabilizer used here was 11-mercaptopundecanoic acid (MUA). The experimental procedure is described below (Figure 1). At first, PEG and MUA were dried under vacuum (rotary oil pump) at 100 °C for 2 h to remove volatile substances including water in order to avoid boiling inside the vacuum sputtering chamber. 10 g of PEG and corresponding amount of MUA were put in a glass petri dish with a diameter of 6.5 cm and was horizontally set against the sputtering target. The amount of MUA in PEG was set at 0, 1, 5, 10, 100, 1000 mg (corresponding to 0, 5.2 × 10⁻⁴, 2.6 × 10⁻³, 5.2 × 10⁻³, 5.2 × 10⁻² and 5.2 × 10⁻¹ M, respectively) and MUA completely dissolved in PEG under all conditions. Ag was sputtered by a current of 30 mA under Ar at a pressure of 2.0 Pa. The distance between the surface of PEG and the

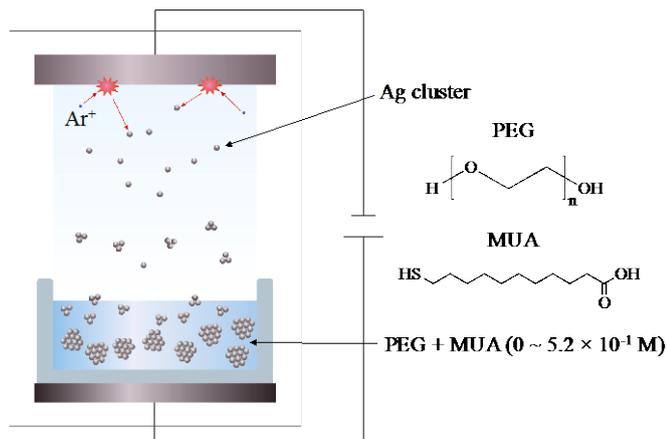


Figure 1. Schematic illustration of matrix sputtering method and the chemical structures of PEG and MUA.

surface of Ag target was set at 50 mm. Sputtering was carried out for 20 min at room temperature under stirring at 100 rpm. Further experimental details are described in Supporting Information.

Extinction spectra of Ag NP suspension in PEG were measured in a quartz cell with 1 mm optical path immediately after the sputtering preparation without further purification or dilution (Figure 2). Broad absorption peaks around 2.82 eV (440 nm), which correspond to the localized surface plasmon absorption of Ag NPs, were observed. The intensity of plasmon absorption decreased as the concentration of MUA increased, and it disappeared in Ag NPs prepared at 5.2×10^{-2} and 5.2×10^{-1} M of MUA. Moreover, new absorption shoulder was observed at 3.65 eV (340 nm) corresponding to the decrease of plasmon absorption. This absorption at 3.65 eV would be the absorption of very small Ag NPs. Similar absorption characteristic has been reported for glutathione stabilized Ag NPs²⁴ with *ca.* 2 nm of diameter (at 3.40 eV). Surface plasmon absorption is generated by the vibration of the group of free electrons in the surface region of NPs and they show the absorption

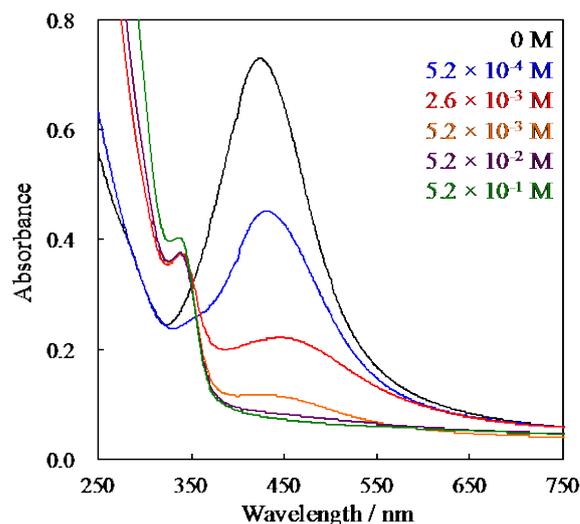


Figure 2. Extinction spectra of Ag NPs prepared at various concentration of MUA from 0 to 5.2×10^{-1} M.

peak corresponding to the vibration frequency. Therefore, the generation of plasmon absorption requires a certain particle size containing certain number of atoms.^{25,26} When the number of atoms in each particle decreases, the energy band gap becomes wider according to the quantum size effect and the particle becomes non-metallic. Then, plasmon absorption is not observable for such small particles. Judging from the absorption spectra in Figure 2, the size of Ag NPs would decrease by the increase of MUA concentration, and those prepared with 5.2×10^{-2} and 5.2×10^{-1} M of MUA should be very small and thus no plasmon absorption was observed. The differences in their absorptions thus should be understood by particle diameters by transmission electron microscopy (TEM).

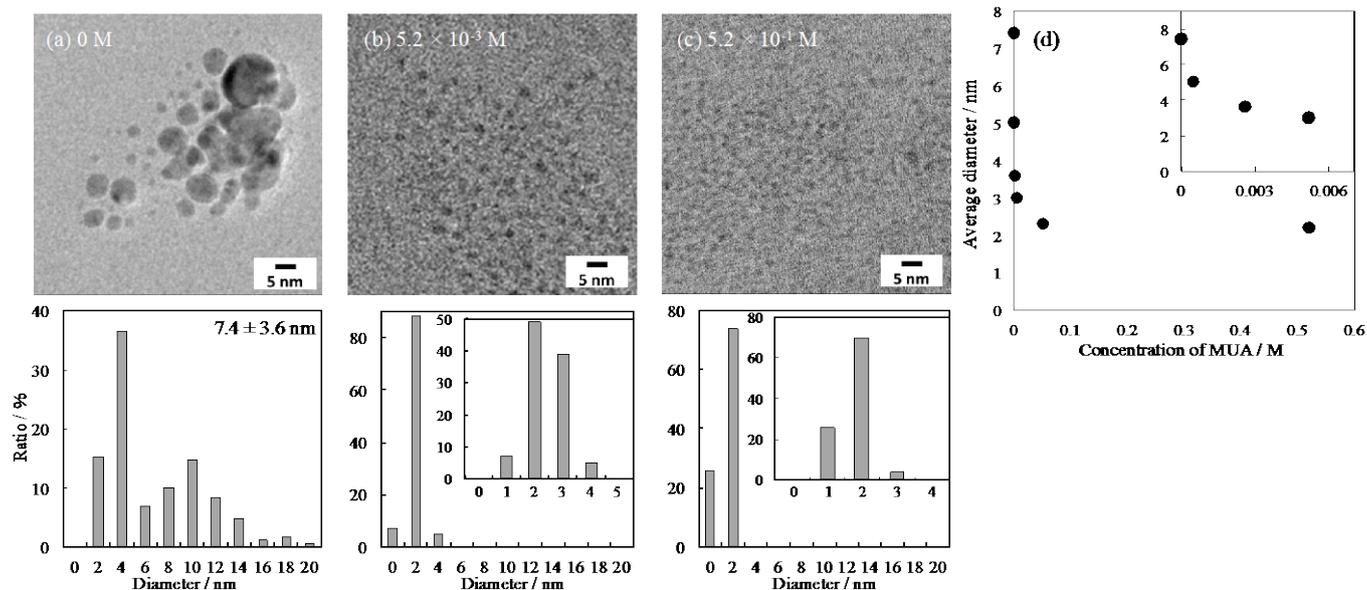


Figure 3. TEM images and size-distribution histograms of Ag NPs prepared at (a) 0, (b) 5.2×10^{-3} and (c) 5.2×10^{-1} M concentration of MUA in PEG. Inset shows the expansion of histograms. (d) Average diameter of Ag NPs prepared at various concentration of MUA from 0 to 5.2×10^{-1} M. Inset shows the expansion plots from 0 to 0.007 M.

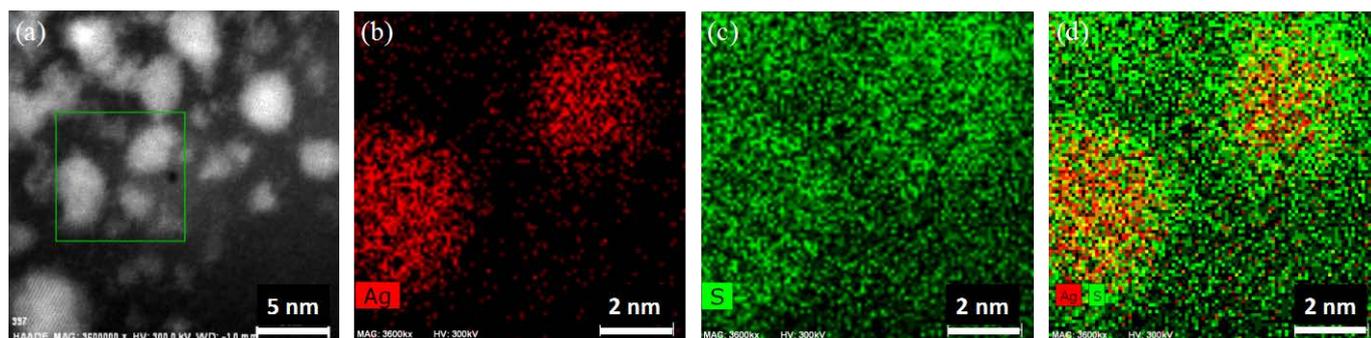


Figure 4. HAADF–STEM image of Ag NPs prepared under 5.2×10^{-1} M concentration of MUA in PEG (a), EDX mapping images of Ag (b) and S (c) and Ag + S (d). The green square in image (a) indicates the area for EDX mapping for (b)–(d).

Figure 3 shows representative TEM images and size-distribution histograms obtained from these images of Ag NPs prepared at (a) 0, (b) 5.2×10^{-3} and (c) 5.2×10^{-1} M concentration of MUA (see other samples in Figure S1). The TEM image of Ag NPs prepared without MUA (Figure 3a) showed poly-dispersed particles, and the shape of histogram is rather difference from the Gaussian distribution. Its average diameter is 7.4 ± 3.6 nm. Judging from this result, it is apparent that the preparation only by PEG without MUA cannot form the regularly ordered Ag NPs. Since the NP formation in PEG depends only on the viscosity of PEG, the aggregation of NPs in PEG solution is not suppressed. Thus, the induction of MUA, which can stabilize the Ag NPs by the coordination of its thiol group, is expected to control both the size and the distribution of Ag NPs in this method. With the induction of MUA, the average sizes are 3.0 ± 0.6 and 2.2 ± 0.5 nm for 5.2×10^{-3} and 5.2×10^{-1} M of MUA concentration, respectively. Most importantly, the size of Ag NPs drastically decreased and the distribution histogram became symmetrical, compared to that of Figure 3a.

The change of particle size as a function of MUA concentration is shown in Figure 3d. Judging from the results, it is obvious that higher MUA concentration makes smaller Ag NPs. This tendency can be simply explained by the collision probability of MUA to Ag NPs inside and interface of PEG. Hence, the decrease in their particle sizes reflects the decrease of plasmon absorption in Figure 2. It is known that UV-Vis spectroscopic method has been used as a quantitative means to measure the concentration of particles in one size. If the particle size changes, the peak position will shift, too. Thus, we consider that the decrease of plasmon absorption in the current experiment directly reflected the decrease of the number of particles that show plasmon absorption. As a result, the diameter reached to a “cluster region” and thus we observed a new absorption shoulder at around 3.40 eV that corresponds to Ag clusters. This result clearly suggests that the size of Ag NPs can be controlled by the concentration of thiol-stabilizer in the capture media, as we expected.

To clarify whether the MUA actually attaches to the surface of Ag NPs, HAADF–STEM and EDX mapping observation were carried out (see sample preparation method in SI). Figure 4 shows the HAADF–STEM image of purified Ag NPs (a), and EDX mapping images for Ag (b), S (c) and Ag + S (d) in the green square area in Figure 4a. As can be seen from the EDX mapping, the S atoms were obviously concentrated at the surface Ag NPs. These STEM images clearly indicate the stabilization of Ag NPs by MUA.

In conclusion, we proposed a novel and easy synthetic method for size-controlled silver nanoparticles (Ag NPs) by matrix sputtering method. While previous studies on sputtering method have used only capturing liquid matrix, our new approach in this study uses both capturing matrix (PEG) and

organic molecules with mercapto groups (MUA). The control of MUA concentration in PEG directly controlled the size of resulting Ag NPs from 2.2 to 7.4 nm in diameter. According to their size, the plasmon absorption was observed at 2.82 eV in larger NPs ($> 3.0 \pm 0.6$ nm) prepared at 0 to 5.2×10^{-3} M of MUA, however it was not observed and new absorption was detected at 3.65 eV for smaller NPs ($< 2.4 \pm 0.5$ nm). The stabilization of Ag NPs by MUA was clarified by STEM–EDX mapping. We believe the results presented in this paper will contribute as a novel and simple method for the preparation of functional metal NPs.

Experimental Section

Polyethylene glycol (PEG, Ave Mw = 600) was purchased from Wako. 11-Mercaptoundecanoic acid (MUA) was from Sigma-Aldrich. Ag target (5 mm ϕ , 99.9 %) was supplied by Tanaka Precious Metals (Japan). Ag was sputtered by a current of 30 mA under Ar at a pressure of 2.0 Pa. The distance between the surface of PEG and the surface of Ag target was set at 50 mm. Sputtering was carried out for 20 min at room temperature under stirring at 100 rpm.

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Notes and references

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