Multi-shaped Gold Nanoparticles Synthesized Using an Amino-terminated Poly(ethylene oxide)–Poly(propylene oxide) Block Copolymer in Aqueous Solutions

Toshio Sakai,*[1,2] Mai Ishigaki,[2] Tomohiko Okada,[2] and Shozi Mishima[2]

[1]*International Young Researchers Empowerment Center, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553*

[2]*Department of Chemistry and Material Engineering, Faculty of Engineering, Shinshu University,*
*4-17-1 Wakasato, Nagano 380-8553*

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Multi-shaped gold nanoparticles such as mushroom-like particles, dendritic particles, starlike particles, elongated particles, and spherical particles were synthesized through the reduction of tetrachloroaurate(III) ions ($[AuCl_4]^-$) by an amino-terminated poly(ethylene oxide)–poly(propylene oxide) block copolymer (SURFONAMINE L-207; $CH_3[OCH_2CH_2]_{33}[OCH_2CH(CH_3)]_{10}NH_2$) in aqueous solutions.

Nanometer-scale metal particles (metal nanoparticles) have generated new concepts and technologies in various fields such as nano-, bio-, and medical-science and -technology due to their unique properties (e.g., optical, magnetic, electronic, and catalytic properties) distinct from bulk materials.[1] Such physical and chemical properties of metal nanoparticles are affected by the size and shape of the particles. Therefore, controllable synthesis of metal nanoparticles with different sizes and shapes is still an important and challenging issue to be addressed.

The size and shape of metal nanoparticles synthesized through the metal ion reduction in solutions are typically controlled by the combination of capping agents (e.g., alkyl-thiols, surfactants, and polymers) and reducing agents (e.g., $NaBH_4$, hydrazine, and ascorbic acid). On the other hand, recently, the synthesis of metal nanoparticles using block copolymers such as poly(ethylene oxide)–poly(propylene oxide) block copolymers,[2] poly(ethylene oxide)–poly(styrene oxide) block copolymers,[3] amino-X-shaped poly(ethylene oxide)–poly-(propylene oxide) block copolymers,[4] 3-heptadecafluorooctyl-sulfonylaminopropyltrimethylammonium iodide,[5] polymeric amines,[6] a hyperbranched poly(ethylene imine)–(hydrophobic alkyl groups)–hydrophilic monomethyl poly(ethylene oxide),[7] and diology(ethylene glycol)-chained phenylenediamine[8] have attracted attention because these block copolymers have achieved the one-pot synthesis of metal nanoparticles and tuning the size and shape of the nanoparticles in solutions due to the dual functions of the block copolymers: reducing and capping functions. For further development of the synthesis using block copolymers, we should obtain better insight on the block polymers with reducing and capping functions for metal nanoparticle synthesis in solutions.

In the present work, we examine gold nanoparticle synthesis through the reduction of tetrachloroaurate(III) ions ($[AuCl_4]^-$) in aqueous solutions using an amino-terminated poly(ethylene oxide)–poly(propylene oxide) (PEO–PPO–NH_2) block copolymer (SURFONAMINE L-207, $CH_3[OCH_2CH_2]_{33}[OCH_2CH-(CH_3)]_{10}NH_2$; HUNTSMAN) (SURFONAMINE L-207 was gifted from Mitsui Fine Chemicals, Inc.). Gold nanoparticles were prepared by mixing of a 10×10^{-3} mol L^{-1} aqueous hydrogen tetrachloroaurate(III) hydrate ($HAuCl_4 \cdot 3H_2O$, 99.9+ %;
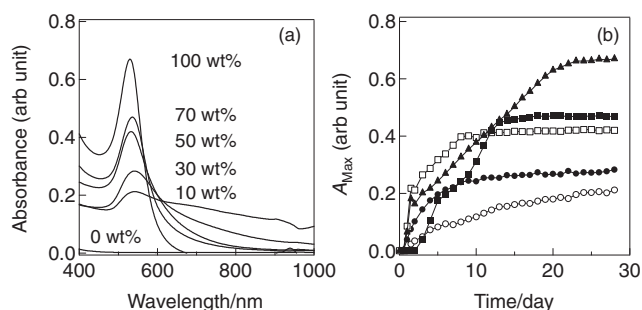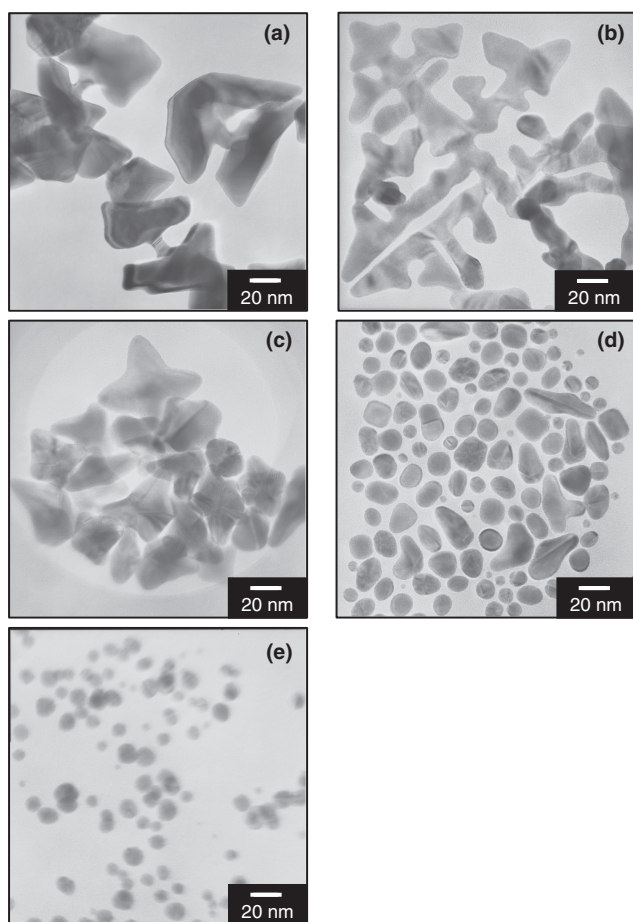

Figure 1. (a) Absorption spectra originating from SPR of gold nanoparticles recorded at 28 days after the reaction initiation in aqueous SURFONAMINE L-207 solutions with different SURFONAMINE L-207 concentrations (0, 10, 30, 50, and 70 wt %) and stock solution (100 wt %) at 25 °C. (b) Maximum absorbances (A_{Max}) originated from SPR of gold nanoparticles formed in 10 (○), 30 (●), 50 (□), and 70 wt % (■) aqueous SURFONAMINE L-207 solutions and 100 wt % (▲) SURFONAMINE L-207 stock solution, plotted as a function of the elapsed time.

Wako) solution with an aqueous SURFONAMINE L-207 solution at 25 °C. Following agitation by vortex mixer for ca. 10 s, the solutions were left standing at 25 °C for the reaction to proceed. Concentration of $[AuCl_4]^-$ in the solutions was 0.2×10^{-3} mol L^{-1} at the reaction initiation. Ultrapure water (18.2 MΩ cm at 25 °C, Millipore-filtered water) was used in all experiments.

Formation of gold nanoparticles was confirmed by monitoring changes in the absorption spectra peaked at ca. 540 nm originating from surface plasmon resonance (SPR) of the gold nanoparticles[9] using a UV–visible spectrophotometer (U-1900, HITACHI) (Figure 1a). The SPR bands were observed in the concentration range of 1–90 wt % SURFONAMINE L-207 in the aqueous solutions and SURFONAMINE L-207 stock solution (100%) (Figure 1a). The SPR band became more significant and shaper with increase of SURFONAMINE L-207 concentration (Figure 1a). Note here that no SPR band was observed in a 0.2×10^{-3} mol L^{-1} aqueous $[AuCl_4]^-$ solution (no polymer solution) at 25 °C for 28 days (4 weeks) that we monitored (Figure 1a). This obviously indicates that SURFONAMINE L-207 acts as a reducing agent for $[AuCl_4]^-$. The maximum absorbance (A_{Max}) of the SPR band originating from gold nanoparticles typically increased with the elapsed time and reached a plateau (Figure 1b).

Morphology of the gold nanoparticles thus formed was determined by transmission electron microscopy (TEM) (JEM-2010, JEOL Ltd.) in conventional transmission mode using 200 kV (Figure 2). The TEM observation revealed the formation

Figure 2. TEM images of gold nanoparticles synthesized in aqueous SURFONAMINE L-207 solutions with different concentrations: (a) 10, (b) 30, (c) 50, and (d) 70 wt % aqueous SURFONAMINE L-207 solutions, and (e) 100 wt % SURFONAMINE L-207 stock solution at 25 °C. The images were observed at 28 days after the reaction initiation.

of ca. 60 nm mushroom-like particles in 10 wt % aqueous SURFONAMINE L-207 solution (Figure 2a), dendritic particles with the trunk length of 100–200 nm and the branch length of ca. 50 nm in 30 wt % aqueous SURFONAMINE L-207 solution (Figure 2b), starlike particles with the length of ca. 40 nm in 50 wt % aqueous SURFONAMINE L-207 solution (Figure 2c) and elongated particles in the diameter range of 5–35 nm (the average diameter of 14.1 nm and standard deviation of 6.3 nm) in 70 wt % aqueous SURFONAMINE L-207 solution (Figure 2d). In the stock solution (100 wt %), spherical particles in the diameter range of 5–20 nm (the average diameter of 9.3 nm and standard deviation of 2.7 nm) formed (Figure 2e). So we realized that the shape of gold nanoparticles was remarkably affected by SURFONAMINE L-207 concentration. In addition, SURFONAMINE L-207 seems to direct the anisotropic growth of gold nanoparticles in aqueous solutions.

On the other hand, a PEO–PPO block copolymer (Pluronic L44, $H[OCH_2CH_2]_{10}[OCH_2CH(CH_3)]_{23}[OCH_2CH_2]_{10}OH$; BASF Corp.) did not affect significantly the particle shape in the same concentration range with aqueous SURFONAMINE L-207 solutions (see Supporting Information, Figure S1).[10] For exam-

ple, polyhedral particles and elongated particles with the diameter range of 5–140 nm (the average diameter of 41.6 nm and standard deviation of 24.6 nm) formed in the 10 wt % aqueous Pluronic L44 solution (Figure S1a[10]). In the case of the 30 wt % aqueous Pluronic L44 solution, polyhedral particles with the diameter range of 10–80 nm (the average diameter of 29.5 nm and standard deviation of 16.1 nm) were observed (Figure S1b[10]). Polyhedral particles with the diameter range of 10–60 nm (the average diameter of 33.4 nm and standard deviation of 11.0 nm) and 20–50 nm (the average diameter of 32.9 nm and standard deviation of 8.3 nm) formed in the 50 and 70 wt % aqueous Pluronic L44 solutions, respectively (Figures S1c and S1d).[10] No particle was observed in Pluronic L44 stock solution (100 wt %).

These TEM images shown in Figures 2 and S1[10] indicate that SURFONAMINE L-207 promotes the anisotropic growth of gold nanoparticles in aqueous solutions while Pluronic L44 induces the isotropic growth of gold nanoparticles in aqueous solutions. This implies that an amino group in SURFONAMINE L-207 plays a critical role for the growth (in particular, one-dimensional (1D) growth and dendritic growth) of gold nanoparticles in aqueous solutions as we observed the dendritic growth of gold nanoparticles in the 30 wt % aqueous SURFONAMINE L-207 solution (Figure 2b). Several reports have described anisotropic growth (1D growth and dendritic growth) of metal nanoparticles, in which two distinct routes: crystal growth[11] and aggregation growth[5,12] were proposed. The dendritc particles that we obtained in the 30 wt % aqueous SURFONAMINE L-207 solution are most likely formed via aggregation[5,12] as attested by TEM images of the pearl chainlike aggregates and in the course of fusion of particles (Figure 3). A proposed mechanism is the following: spherical gold nanoparticles initially formed aggregate like a pearl chain with aging; further $[AuCl_4]^-$ reduction occurs among the gold nanoparticle aggregates due to the $[AuCl_4]^-$ reducing function of SURFONAMINE L-207, rendering the surface of the branches smooth. It should be noted that spherical gold nanoparticles seem crystalline (Figures 3a–3d) while tips and branches of dendritic particles seem noncrystalline (Figures 3e and 3f). Electron diffraction patterns of the dendritic gold nanoparticles did not show any particular spots.

Formation of the various-shaped gold nanoparticles in aqueous SURFONAMINE L-207 solutions with different SURFONAMINE L-207 concentrations is most likely attributed to the competition between the aggregating function induced by affinity of an amino group (NH_2) with gold surface and the capping (stabilizing) function of SURFONAMINE L-207. In aqueous solutions with low concentration of SURFONAMINE L-207, the aggregating function of SURFONAMINE L-207 would be more dominant than the capping (stabilizing) function of SURFONAMINE L-207. Namely, a small amount of SURFONAMINE L-207 could not sufficiently cap particles in aqueous solutions, and the insufficient capping of SURFONAMINE L-207 on the particles could not prevent the particle aggregation. Consequently, the particles would grow in any direction randomly in aqueous solutions through the particle aggregation (which would correspond to the formation of mushroom-like particles in the 10 wt % aqueous SURFONAMINE L-207 solution). With increase of SURFONAMINE L-207 concentration in aqueous solutions, the particle aggregation
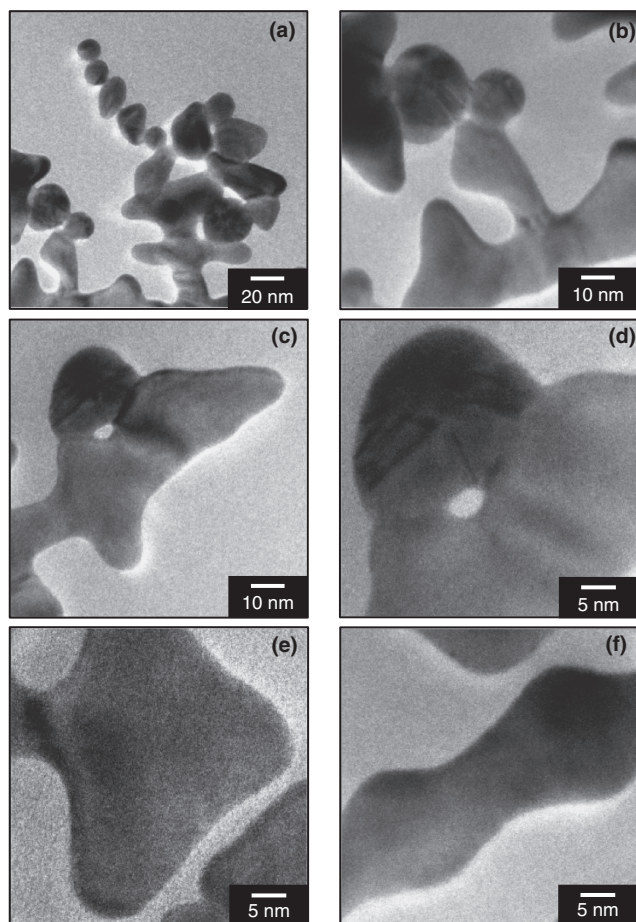
Figure 3. TEM images of dendritic gold nanoparticles synthesized in the 30 wt % aqueous SURFONAMINE L-207 solution. The images were observed at 28 days after the reaction initiation.

should be prevented and, at the same time, the direction of aggregation growth should be confined due to the capping (stabilizing) function of SURFONAMINE L-207. As a result, the particles would aggregate toward a certain direction (which would correspond to the formation of dendritic particles in the 30 wt % aqueous SURFONAMINE L-207 solution) (further investigation is required for full understanding of the mechanism on dendritic growth of gold nanoparticles). Further increase of SURFONAMINE L-207 concentration would enhance the particle stabilization more than particle aggregation due to the SURFONAMINE L-207 covering particles. Thus, the length of branches would be shorter, and the number of branches would decrease with increase of SURFONAMINE L-207 concentration such as starlike particles in the 50 wt % aqueous SURFONAMINE L-207 solution, elongated particles in the 70 wt % aqueous SURFONAMINE L-207 solution, and spherical particles in 100 wt % SURFONAMINE L-207 stock solution.

In summary, we revealed the formation of multi-shaped gold nanoparticles in aqueous solutions using an amino-terminated poly(ethylene oxide)–poly(propylene oxide) block copolymer (SURFONAMINE L-207) as a reducing and capping agent. In particular, SURFONAMINE L-207 seems to promote the anisotropic growth, in particular, 1D growth and dendritic growth of gold nanoparticles via aggregation in aqueous solutions. This is most likely attributed to the competition between the aggregating function of SURFONAMINE L-207 afforded by the affinity of an amino group (NH_2) with gold surface and the capping (stabilizing) function of SURFONAMINE L-207. These findings provide an insight that the morphology of metal nanoparticles could be tuned by nature of the block copolymer afforded by the segments such as PEO, PPO, and NH_2 segment. So we are currently exploring the effects of block copolymer segments on the reduction activity for metal ions and morphology of metal nanoparticles formed in aqueous solutions.

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