Preparation of gold microparticles using halide ions in bulk block copolymer phases via photoreduction

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ABSTRACT

Gold microparticles were prepared from the gold salt in the solid bulk phase of a poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) block copolymer via a photoreduction process in the presence of halide ions. The shapes and sizes of the gold microparticles were found to be dependent on the types and amount of halide ions as well as the types of cations used due to the combined effects of the adsorption power and oxidative dissolution ability of the additives on gold surfaces. Gold nanorods were obtained when poly(ethylene oxide) was used instead of the block copolymer. This suggests that the poly(propylene oxide) (PPO) parts in the block copolymer are essential for the formation of gold microparticles, even though the degree of the direct interaction between the PPO blocks and gold salt is not significant.

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1. Introduction

Over the past decade, there has been considerable interdisciplinary effort aimed at developing synthetic routes for monodisperse gold nanoparticles because of their potential applications in chemical sensing, biolabeling, catalysis, electronic and optical devices as well as the fundamental scientific interest in quantum physics [1–7]. The most popular method for preparing air-stable gold nanoparticles is the two-phase method reported by Brust et al., which involves the reduction of gold salts with sodium borohydride in the presence of a phase-transfer catalyst and a capping agent, such as alkanethiols [8]. In this method, the size of the gold nanoparticles can be controlled on the nanoscale by changing the initial gold salt to capping agent molar ratio [9–11]. In addition, there are many reports on the synthesis of gold nanocrystals with various shapes, such as rods, plates, tetrahedra, and octahedra [12–17]. Among them, the polyol process, which employs either liquid polyols or diols as solvents for both the metal precursors and reducing agents, has been used widely to synthesize gold polyhedral nanocrystals. For example, Yang et al. obtained gold nanocrystals using surface-regulating polymers, such as poly(vinyl pyrrolidone) (PVP) and ethylene glycol [18]. Gold nanoboxes were also synthesized using silver nanocubes as sacrificial templates [19]. However, there are relatively few reports on the synthesis of micrometer-sized gold crystals, even though these colloidal gold microparticles may have technological importance in a variety of areas, such as surface-enhanced Raman

spectroscopy (SERS), chemical and biological sensing, optics, and catalysis [16,20–22].

Recently, we reported a novel synthetic method for gold nanowires and nanosheets using the bulk phases of a poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO_{20}–PPO_{70}–PEO_{20}) block copolymer, Pluronic P123, as the reaction medium [23]. In this system, the block copolymer was found to be a capping agent and/or a template for the formation of gold nanocrystals. Moreover, both the structure of the bulk phase and reduction conditions were found to play an important role in determining the shape of the resulting gold nanocrystals. As part of our ongoing study about the controllable preparation of gold crystals with different shapes, we investigated herein the effect of halide ions on the shape of gold crystals using the previously reported polymeric bulk phase approach. Halide ions, such as Cl^-, Br^-, and I^-, have been known to have the ability to interact with a gold surface, which can lead to anisotropic crystal growth in the solution state [24]. However, the effect of halide ions on the crystal growth of gold in a polymeric bulk phase has not yet been demonstrated. In this study, micrometer-sized gold crystals with sizes ranging from 0.48 to 3.2 μm were prepared by introducing a small quantity of halide ions to a Pluronic P123 bulk phase containing gold salts.

2. Experimental section

2.1. Chemicals and materials

Hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4 \cdot 3H_2O$), potassium chloride (KCl), potassium bromide (KBr), potassium

iodide (KI), lithium bromide (LiBr), sodium bromide (NaBr), cetyltrimethylammonium bromide (CTAB), and poly(ethylene oxide) ($M_n = 750$) were purchased from Aldrich. Poly(ethylene oxide) ($M_n = 2,000$) was purchased from Fluka. Poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) block copolymer (PEO$_{20}$–PPO$_{70}$–PEO$_{20}$, Pluronic P123) was supplied by BASF. Tetrahydrofuran (THF) was dried by refluxing over sodium and benzophenone followed by distillation. All other reagents were used as received.

2.2. Preparation of gold microcrystals

The synthesis of gold crystals with different sizes and shapes is exemplified by the preparation of gold microparticles with an average size of $0.54 \pm 0.08\,\mu m$ with various shapes, such as octahedra, decahedra, and twinned polyhedra containing small amount of gold nanosheets. A THF solution (10 mL) containing the gold salt (HAuCl$_4 \cdot$3H$_2$O, 39.4 mg, 0.10 mmol) and Pluronic P123 (1.18 g, 0.20 mmol) was mixed with 1 mL of a 10^{-3} M aqueous KBr solution, where the molar ratio of KBr and the gold salt was 0.01. An Au^{3+} to ethylene oxide molar ratio, 1/80, was used in this study because gold nanowires and nanosheets with regular sizes and shapes have been prepared using the same molar ratio of Au^{3+} to ethylene oxide unit in Pluronic P123 [23]. THF and H$_2$O were removed using a rotary evaporator and the residue was vacuum dried at 30 °C for one day to produce a solvent free complex composed of Pluronic P123, HAuCl$_4$, and KBr. The complex was exposed to a glow lamp (tungsten-filament incandescent lamp, 200 W, 220 V) for six days to reduce the gold salt. The vial containing the complex was constantly rotated using a motor to allow uniform irradiation. The complex was then purified by centrifugation using THF, ethanol, and water to remove the polymer and any remaining salts, yielding the gold microparticles. Other gold crystals with different sizes and shapes were prepared
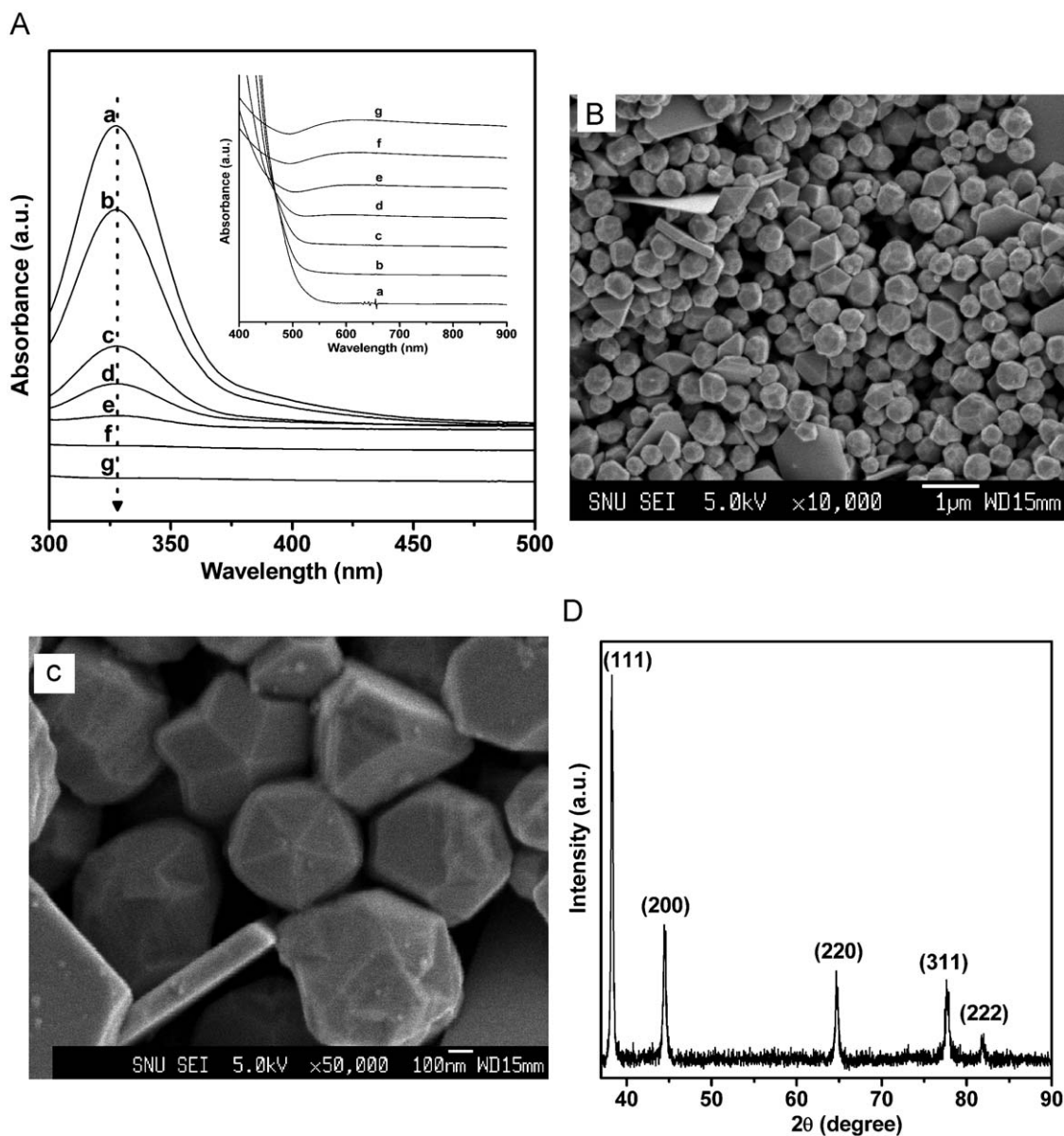

Fig. 1. (A) UV–Vis absorption spectra of the gold microparticles after glow lamp irradiation of gold complexes containing HAuCl$_4$, Pluronic P123, and KBr in a bulk phase, where the molar ratio of KBr to gold salts is 0.01, for (a) 0 day, (b) 1 day, (c) 2 days, (d) 3 days, (e) 4 days, (f) 5 days, and (g) 6 days. The inset shows the intensity of the peaks originating from the surface plasmon resonance (SPR) band of the gold microparticles. (B) Low and (C) high magnification SEM images and (D) representative powder XRD pattern of the gold microparticles obtained at a KBr to HAuCl$_4$ ratio of 0.01 after six days irradiation with the glow lamp.

using the same procedure but with the following differences: different gold salt to KBr molar ratios; different types of halide ions, such as LiBr, KCl, KI, or cetyltrimethylammonium bromide; and/or the use of poly(ethylene oxide) instead of Pluronic P123. In addition, a UV lamp (Black Ray longwave ultraviolet lamp model B100 AP, UVP Inc.) was used for the photoreduction process instead of a glow lamp.

2.3. Characterization

The sizes and shapes of the gold crystals were examined by JSM 6330-F scanning electron microscopy (SEM) and JEM 200 CX transmission electron microscopy (TEM). The UV–Vis spectra were obtained using an Agilent 8453E spectrometer. The X-ray scattering patterns were collected using Bruker D5005 X-ray diffractometer ($\lambda = 1.5406$, CuK) in the range of 2θ between 35° and 90° at room temperature.

3. Results and discussion

Fig. 1A shows the formation of gold crystals, as monitored by the time evolution of the UV–Vis spectra of the complex containing the gold salts, Pluronic P123, and KBr in the polymeric bulk phase, where the molar ratio of KBr to gold salt is 0.01. Before glow lamp irradiation, only one strong absorption band centered at ~330 nm originating from the $AuCl_4^-$ solution was observed [25]. The intensity of this band decreased gradually with increasing irradiation time of the glow lamp, indicating a decrease in the concentration of gold salt, which then disappeared over the six day period of irradiation. This decrease coincided with an increase in the intensity of a new broad band at around 590 nm, which is the surface plasmon resonance (SPR) band of gold crystals, suggesting that gold crystals had formed from the reduction of $AuCl_4^-$ through glow lamp irradiation [26,27]. From the broadness and red-shift of the SPR band compared to that of spherical gold nanoparticles, the gold crystals obtained in this experiment were either larger than typical gold nanoparticles or had an anisotropic morphology and/or sharp corners [28]. SEM images (Fig. 1B and C) and TEM images (see Supplementary materials) of the products formed after six days irradiation showed that the gold crystals obtained in the presence of halide ions, KBr in this case, are gold microparticles having an average size of $0.54 \pm 0.08\,\mu m$ and various shapes, such as octahedra, decahedra, and twinned polyhedra with a relatively small amount of gold nanosheets. The powder X-ray diffraction (XRD) pattern of the gold microparticles showed five peaks at 38.30°, 44.44°, 64.66°, 77.62°, and 81.98° which were complete agreement with diffractions from the (111), (200), (220), (311), and (222) planes of the face-centered cubic (fcc) structure of gold, respectively, indicating that the microparticles are fcc structured crystalline gold (Fig. 1D) [29]. The energy-dispersive X-ray spectroscopy (EDS) spectrum also revealed these gold microparticles to be pure metallic gold (see Supplementary materials).

The morphology, size, and yield of gold crystals were found to be affected by the amount of KBr in the complex through a photoreduction process. When the KBr:gold salt ratio was increased to 0.1, the yellowish color of the complex consisting of Pluronic P123, $HAuCl_4$, and KBr was still preserved after six days irradiation with the glow lamp, indicating that most of the gold salt had not been reduced. Therefore, a larger amount of KBr appears to retard the reduction process of the gold salt, as reported elsewhere [30]. The gold crystals obtained using larger amounts of KBr were mostly aggregates with an irregular size and shape (Fig. 2A). When the KBr:gold salt ratio was decreased to 0.005, all the gold salts were reduced to mixtures of gold nanosheets and gold microparticles with an average size of $1.07\,\mu m$ after six days irradiation with the glow lamp (Fig. 2B). Previously, single crystalline gold nanosheets with an average width and thickness of approximately 8 μm and 100 nm, respectively, were obtained when a similar complex containing only a gold salt and Pluronic P123 without KBr was irradiated with a glow lamp [31].

It has been known that halide ions, including bromide, chloride, and iodide have the ability to control the size and shape of gold crystals due to their chemisorptions on certain facets (mostly [111]) of the gold surface [24]. Others have also reported the oxidative dissolution ability of halide ions to suppress crystal growth and even the ability to fuse the metallic crystals [32,33]. In the present case, the very small amount of KBr (KBr:gold salt ratio = 0.005) in the gold salt and Pluronic P123 complex interfered with the formation gold nanosheets to some degree, leading to the formation of a large amount of gold microparticles together with gold nanosheets. It is possible that crystal growth in the [111] direction is inhibited by competition between the chemisorption ability of bromide ions on the gold surface and the original capping ability of Pluronic P123 to produce gold nanosheets. When a very large amount of KBr (KBr:gold salt ratio = 0.1) was added, the coexistence of both chemisorbed bromide ions and Pluronic P123 on the gold surface mostly prevented the anisotropic crystal growth of gold resulting in the production of gold aggregates. Moreover, a large amount of KBr
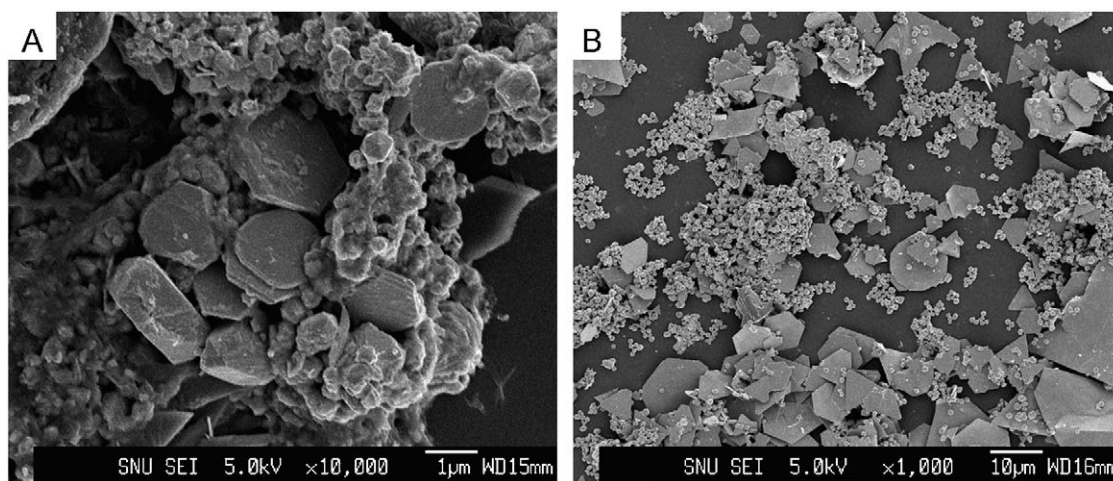

Fig. 2. SEM images of gold crystals obtained using a KBr to HAuCl₄ ratio of (A) 0.1 and (B) 0.005 after six days irradiation with the glow lamp.

even inhibits the reduction of gold salts due to the oxidative dissolution ability of bromide ions [34]. When the optimum amount of KBr (KBr:gold salt ratio = 0.01) was added, the bromide ions adsorbed on the top of the gold nanosheet interfered with the capping ability of Pluronic P123 to facilitate growth in the top direction. On the other hand, those adsorbed on the side of the gold nanosheet suppressed crystal growth through their oxidative dissolution ability, and then gold microparticles with quite regular sizes could be produced as shown in Fig. 1B.

KCl or KI were also used as additives instead of KBr to further understand the effect of the binding ability of halide ions on the formation of gold crystals. The adsorption and oxidative dissolution ability of halide ions onto a gold surface have been known to be in the order of iodide > bromide > chloride ions [35]. When KCl at a KCl to gold salt ratio of 0.01 was used instead of KBr, gold microparticles with various shapes (Fig. 3A) were observed although there was a higher fraction of gold nanosheets compared with the case of KBr. Intriguingly, the surface and edge of these gold microparticles were found to be quite rough. Similar gold microparticles with a rough surface and edge were obtained when the gold salts were reduced using cellulose as the reducing agent in an ionic liquid containing chloride ions [36]. Therefore, the cooperative effect of Cl^- ions with relatively weak binding and oxidative dissolution ability should produce gold crystals with a rough surface.

Interestingly, when a very small amount of KI was added to the polymeric bulk phase, we found that the size of gold nanosheets increased compared with that prepared in the absence of halide ions, as previously reported [31]. Fig. 3B shows gold nanosheets (larger than 20 μm in size) prepared at a KI to gold salt ratio of 0.001. Moreover, as the ratio of KI to gold salt increased to 0.01, the edge size of the gold nanosheets decreased to about 10 μm whereas there was a drastic increase in the proportion of randomly shaped gold microparticles (Fig. 3C). These observations are in sharp contrast to our expectations. Originally, the combined effect of the strongest adsorption power and oxidative dissolution ability of iodide ions to the gold surface are believed to lead the formation of smaller sized gold crystals compared with those prepared using other halide ions as additives, such as bromide and chloride ions. Therefore, it can be suggested that the addition of a very small amount of iodide ions in this system (KI:gold salt ratio = 0.001) limits crystal growth in the [111] direction more severely than the other facets, such as the [110] and [100] directions, due to the strong tendency to form a hexagonal packed adlayer on the Au(111) surface. The weak interaction of iodide ions with the other facets leads to anisotropic crystal growth of gold. Another phenomenon originated from iodide ions, i.e., the energetic-injection induced fusion of gold crystals, was observed simultaneously from the coalescence of the adjacent gold nanosheets. This fusion process, which is similar to Ostwald ripening where larger particles with lower surface energy are favorably formed at the expense of smaller particles, has been known to be enhanced by the addition of KI [37]. Then, it is believed that the formation of larger sized gold nanosheets is
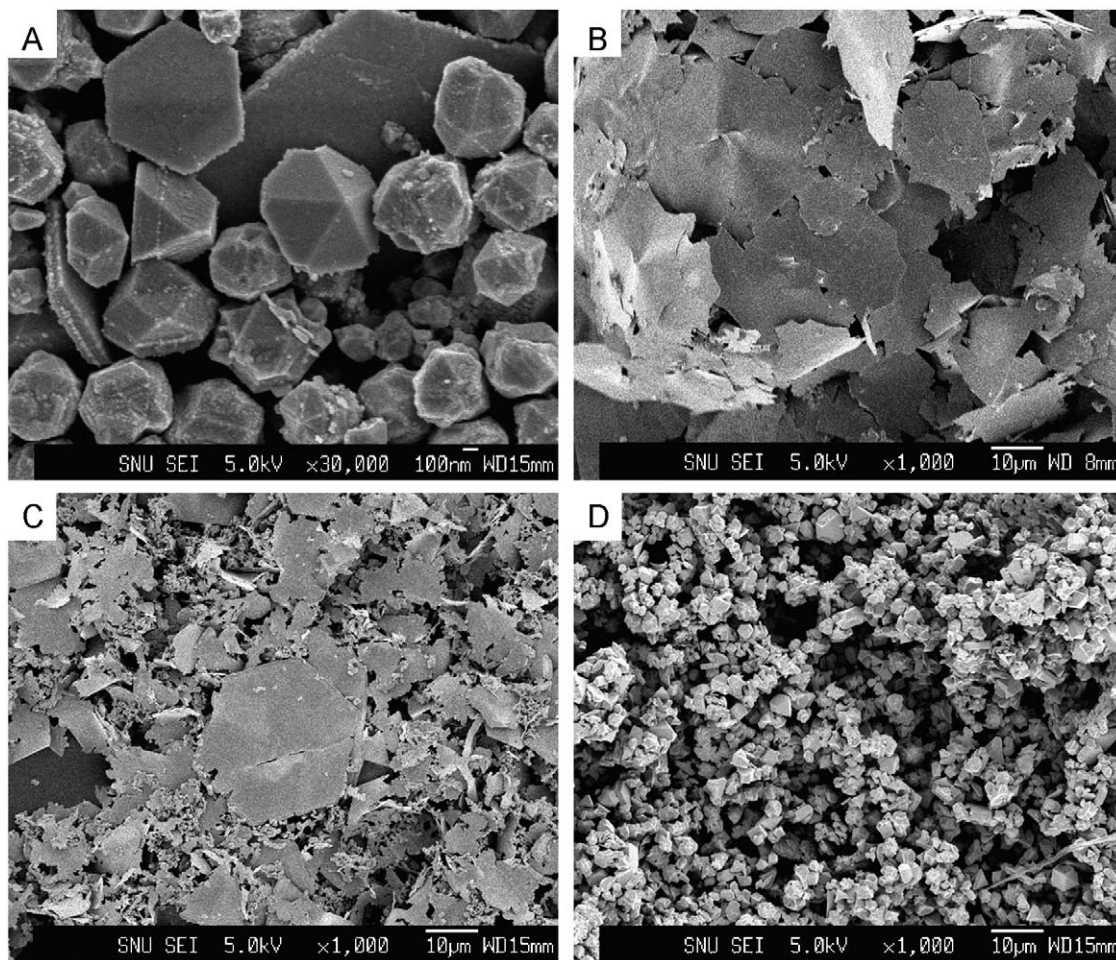

Fig. 3. SEM images of gold crystals after six days irradiation with the glow lamp at (A) $KCl/HAuCl_4$ of 0.01, (B) $KI/HAuCl_4$ of 0.001, (C) $KI/HAuCl_4$ of 0.01, and (D) $KI/HAuCl_4$ of 1.
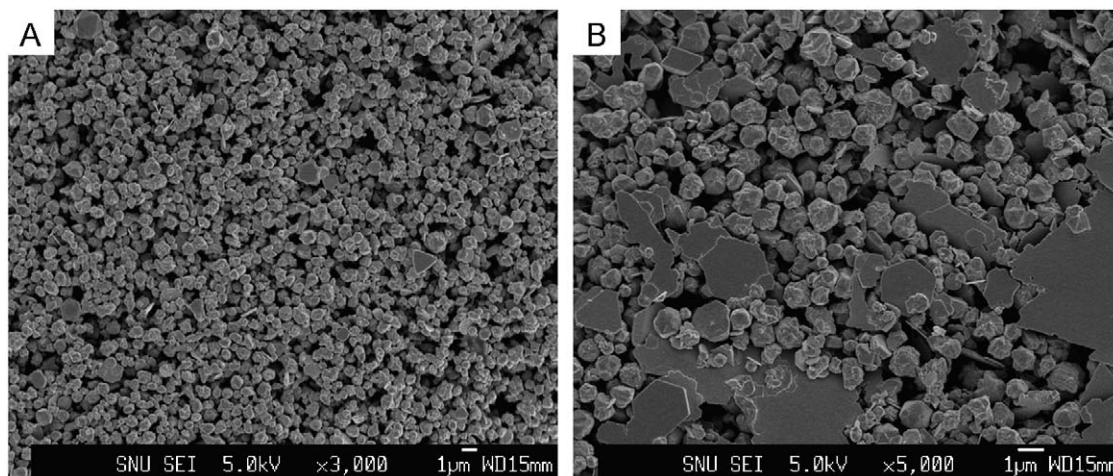
Fig. 4. SEM images of gold microparticles using (A) NaBr and (B) LiBr as additives instead of KBr. The additives to HAuCl$_4$ ratio was 0.01.

induced by both functions of iodide ions, i.e. the strong suppression of crystal growth along the [111] direction and fusion between the edge of the gold nanosheets at a KI to gold salt ratio of 0.001. On the other hand, the formation of randomly shaped gold microparticles and size reduction of the gold nanosheets at a KI to gold salt ratio of 0.01 means that the crystal growth of gold in the other directions is also inhibited. This suggests that adsorption on a Au(110) and/or Au(100) surface and/or the oxidative dissolution ability of iodide ions increases with increasing iodide concentration while the yield of gold crystals is low due to the retardation for the reduction of gold salts. The increased chemisorption ability of iodide ions to the whole surface of growing particles was further confirmed from the gold crystals (Fig. 3D) obtained at a KI to gold salt ratio to 1, where gold microparticles having twinned polyhedral gold crystals with mean size of 3.2 μm were mainly obtained.

The influence of the types of cations in the additives on the formation of gold crystals was also investigated. Fig. 4A and B show typical SEM images of gold microparticles obtained using NaBr and LiBr, respectively, where the ratio of additives to gold salt was 0.01 and the glow lamp irradiation time was six days. Predominantly, randomly shaped gold microparticles with an average size of 0.83 ± 0.13 μm were obtained using NaBr, and larger irregular-shaped gold microparticles (1.01 ± 0.20 μm in size) with gold nanosheets were obtained using LiBr. Since the size of the gold microparticles formed using KBr were about 0.54 ± 0.08 μm, the average size of the gold microparticles decreases with increasing cation size from Li$^+$ to K$^+$. This size dependence of the gold microparticles on the types of cations was confirmed from the corresponding UV–Vis spectra (see Supplementary materials). The spectra showed the blue-shifted SPR bands of the gold microparticles as the additive was changed from LiBr to KBr [38]. When an additive halide compound having even larger cation was used, such as cetyltrimethylammonium bromide, smaller randomly shaped gold microparticles with an average diameter of about 0.44 μm were obtained (see Supplementary materials). It is possible that the greater dissociation ability of the halide additive with a larger cation increases the relative concentration of halide ions in the polymeric complex [39], then the increased interaction between the halide ions and gold surfaces might prevent the growth of gold crystals, resulting in the formation of smaller-sized gold microparticles.

It has been known that the ethylene oxide units have the intrinsic ability to interact with the growing gold crystals as
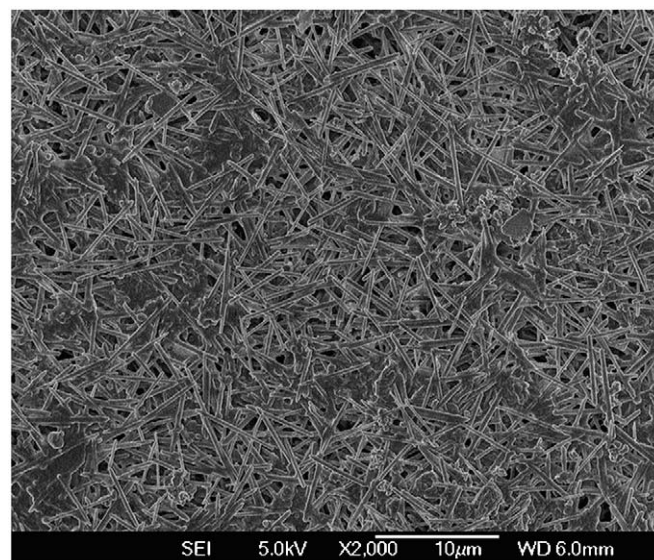

Fig. 5. SEM image of gold nanorods prepared from a complex consisting of HAuCl$_4$, KBr, and poly(ethylene oxide) homopolymers after glow lamp irradiation.

capping reagents, therefore, poly(ethylene oxide) (PEO) homopolymers were used instead of Pluronic P123 to prepare shape-controlled gold crystals [40]. Interestingly, gold nanorods with diameters and lengths of about 360 nm and 5.74 μm on average, respectively, were mainly obtained when a complex of PEO having M_n of 750, HAuCl$_4$, and KBr (ratio of KBr to gold salts is 0.01) was irradiated with a glow lamp for seven days as shown in Fig. 5. PEO with molecular weight of 750 was selected because the molecular weight of the PEO block of one-side chain end in Pluronic P123 is about 850. The formation of gold nanorods using bromide ions with low molecular weight organic compounds has been reported by others and it was ascribed to the cooperative capping ability of the bromide ion and the functional groups of organic compounds [30]. Competition of the capping ability of PEO and the other functions of bromide ions in this system might induce the 1-dimensional crystal growth of gold. On the other hand, aggregated gold crystals having irregular shapes were obtained at very low yield when PEO with a large molecular weight ($M_n = 2,000$) was used. PEO with a molecular weight of 2000 was used because the molecular weight of the total PEO block in Pluronic P123 is about 1800. It is believed that this is most likely due to the highly

crystalline structure of the large molecular weight PEO at room temperature [41], that is, the absorption ability of the halide ions and/or ethylene oxide units on the gold surface as well as the crystal growth rate determined by the mobility of the gold salts in the complex are expected to be low. Therefore, gold microparticles can be prepared with Pluronic P123 containing PPO blocks, and gold nanorods can be prepared using PEO with a molecular weight of 750. We do not have any clear explanation for this result, while PPO blocks have been known to control the interaction between the PEO blocks and gold salts [42], even though PPO blocks do not have any direct interaction with gold salts because of their immiscibility [43]. Gold crystals with various shapes and sizes have been prepared with block copolymers containing PPO blocks with different molecular weights [31,42,43]. In this case, the anisotropic crystal growth of gold was facilitated by PPO blocks in the polymeric bulk phase probably because the PPO blocks can enhance the capping ability of the polymers to some degree.

Finally, UV light was used instead of a glow lamp (mainly visible and infrared) for reduction to determine the effect of the reducing energy on the formation of gold crystals. When a complex composed of Pluronic P123, $HAuCl_4$, and KBr at a KBr to $HAuCl_4$ molar ratio of 0.01 was irradiated with UV ($> 350\,nm$) for 24 h, all the gold salts were reduced to smaller gold microparticles (average diameter about $0.48 \pm 0.09\,\mu m$) with an irregular shape and rough surface (Fig. 6). Therefore, UV light with a shorter wavelength (higher energy) reduces the reduction time and produces smaller microparticles, possibly due to the formation of a larger number of nucleation sites and subsequent rapid growth of gold crystals [44,45].

4. Conclusion

Herein, we have established a simple method for the preparation of gold microparticles using halide ions as additives in a poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) polymeric bulk phase by photoreduction. The shape and size of the gold microparticles are affected by both the types and amount of halide ions. The low dissociation energy of the additives and the strong power of the reduction source in photoreduction have a tendency to decrease the size of the gold microparticles. Although the PPO block does not have the ability to interact with gold salts,

it was found to be important for inducing the anisotropic growth of gold crystals, resulting in the formation of gold microparticles.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2009.03.029.

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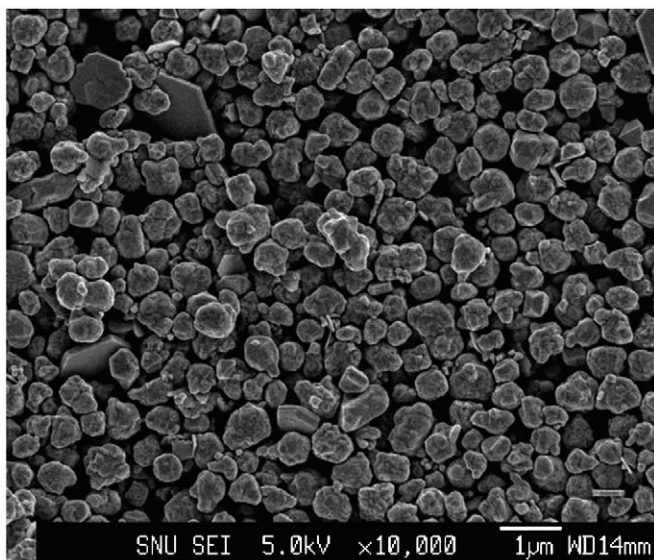[45] N.R. Jana, X. Peng, J. Am. Chem. Soc. 125 (2003) 14280.

Fig. 6. SEM image of gold microparticles prepared from 1 day irradiation with a UV light at a KBr to $HAuCl_4$ ratio of 0.01.