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Shape-controlled synthesis of gold icosahedra and nanoplates using Pluronic P123 block copolymer and sodium chloride

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ABSTRACT

Gold icosahedra with an average diameter of about 600 nm were easily prepared by heating an aqueous solution of the amphiphilic block copolymer, poly(ethylene oxide)$_{20}$–poly(propylene oxide)$_{70}$–poly(ethylene oxide)$_{20}$ (Pluronic P123), and hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4 \cdot 3H_2O$) at 60 °C for 25 min. When sodium chloride ($NaCl$:$HAuCl_4$ molar ratio=10:1) was added to this aqueous solution, gold nanoplates were produced. The chloride ion was found to be a key component in the formation of the gold nanoplates by facilitating the growth of {111} oriented hexagonal/triangular gold nanoplates, because similar gold nanoplates were produced when LiCl or KCl was added to the aqueous solution instead of NaCl, while gold nanocrystals having irregular shapes were produced when NaBr or NaI was added.

1. Introduction

Gold crystals have attracted intensive interests in modern science, due to their unique physicochemical, optical, electrical, mechanical properties, and wide range of potential applications such as catalysis, sensing, and biolabeling [1–5]. It is well known that the characteristic properties of gold crystals including nanomaterials are strongly dependent on their morphologies. Therefore, the shape-controlled synthesis of gold crystals is important for achieving their potential applications. Numerous synthetic methods have been successfully developed to prepare gold crystals with various shapes, such as rods [6], plates [7], cubes [8], octahedra [9], decahedra [10], and icosahedra [11]. However, the development of a simple and environmentally benign route to prepare gold crystals with well-defined shapes is a still challenging task for scientists.

Various poly(ethylene oxide)–poly(propylene oxide)–poly (ethylene oxide) block copolymers (Pluronics) having different block lengths have been widely used in the fields of pharmaceuticals and biomedical materials, due to their non-toxicity and amphiphilicity [12]. Also, it was recently found that these Pluronics can act as both a reducing agent and colloidal stabilizer in the synthesis of gold nanomaterials having various sizes and shapes. For example, Alexandridis group reported the preparation of gold nanoparticles with an average diameter of about 10 nm using various Pluronics [13]. Han et al. recently reported that gold icosahedra having sizes ranging from 100 nm to 1 μm could be prepared using various Pluronics (F88, F85, P104, and P105) by heating for 1 day at 17–40 °C without using any other chemical reducing reagents [14].

Our group prepared various gold crystals with different sizes and shapes such as gold nanowires [15], nanosheets [16], and microparticles [17] by applying various reduction methods, such as UV light, visible light irradiation, and heating, to a series of Pluronics. Herein, we report a facile one-step synthetic route (heating at 60 °C for 25 min) for the preparation of gold icosahedra and/or nanoplates from hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4 \cdot 3H_2O$) in an aqueous solution of Pluronic P123 block copolymer and sodium chloride (NaCl) under mild conditions. The present approach is environmentally friendly since it involves only water, NaCl, and nontoxic Pluronic P123 polymer.

2. Experimental section

2.1. Chemicals and materials

Hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4 \cdot 3H_2O$) was purchased from Sigma-Aldrich. Pluronic P123 block copolymer (Poly(ethylene oxide)$_{20}$–poly(propylene oxide)$_{70}$–poly(ethylene oxide)$_{20}$) was provided by BASF. Sodium chloride (NaCl), sodium bromide (NaBr), sodium iodide (NaI), lithium chloride (LiCl), and potassium chloride (KCl) were purchased from Daejung chemical.

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Distilled water was used in all of the syntheses and all other reagents were used without any further purification.

2.2. *Preparation of gold icosahedra/plates*

Pluronic P123 block copolymer (1.18 g, 0.20 mmol) was dissolved in 6 mL of distilled water. To the homogeneous polymer solution, an aqueous solution (1 mL) containing a predetermined amount of NaCl (0, 0.0001, 0.001, 0.01, 0.1, 0.5, and 1 mmol) was added. The final concentration of the Pluronic P123 solution was 14 wt%. Finally, $HAuCl_4 \cdot 3H_2O$ (39.4 mg, 0.1 mmol) was added to the reaction mixture and heated to 60 °C with magnetic stirring. After 25 min of heating, the crude products were centrifuged and washed with water/ethanol several times. To investigate the effect of cations and anions on the formation of the gold plates, 0.1 mmol of various halide salts, viz. LiCl, KCl, NaBr, or NaI, instead of NaCl, was added to the reaction mixture.

2.3. *Characterization*

Scanning electron microscopy (SEM) images were obtained on a JEOL JSM 6330-F. Transmission electron microscopy (TEM) was performed using a JEOL JEM-3010 and a JEOL JEM-200CX. UV–Vis spectra were acquired using an Agilent 8453E spectrometer. X-ray diffraction analysis was carried out using a Bruker D5005 X-ray diffractometer and the 3C2 beam line at the Pohang Accelerator Laboratory.

3. Results and discussion

Fig. 1(a) and (b) show the representative SEM images of the gold nanomaterials prepared by the reduction of $HAuCl_4$ in an aqueous solution of Pluronic P123 at 60 °C for 25 min. The majority of the particles are icosahedral in shape with an average size of 590 ± 90 nm (calculated from 200 particles), although a very small amount of gold plates, decahedra and irregular-shaped particles also coexisted. Some degree of surface roughness on the icosahedra is thought to be originated from the Pluronic P123 polymer remaining on the surface of gold icosahedra. (See Supplementary Materials) The X-ray powder diffraction (XRD) pattern of the gold icosahedra synthesized by the above method is shown in Fig. 1(c). The five peaks corresponding to the diffractions from the (111), (200), (220), (311), and (222) planes of face-centered cubic (fcc) gold, respectively, indicate that the icosahedra are pure fcc crystalline gold [18]. The intensity ratio of the (111) and (200) diffraction peaks was 2.36, which is much higher than the bulk value of 1.88, indicating that the as-prepared icosahedra were abundant in {111} planes [19]. This result is in good agreement with the inference that the gold icosahedron is enclosed by 20 triangles with {111} faces [14].

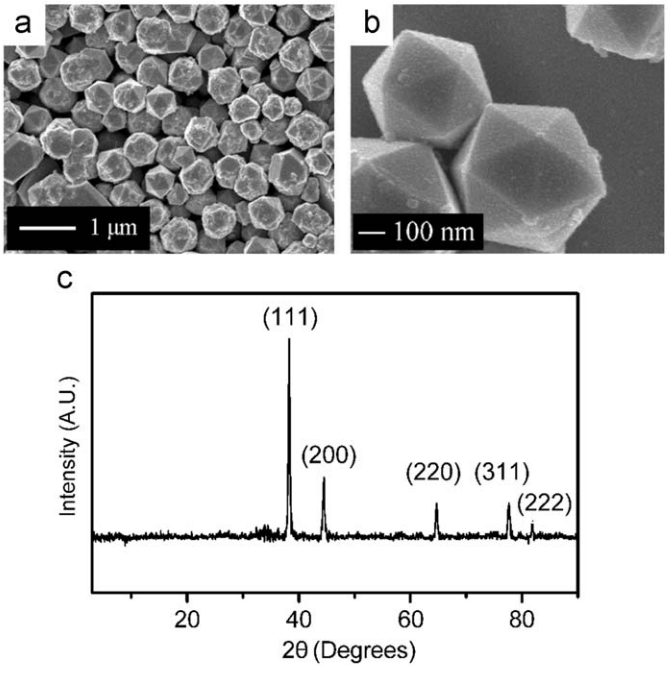

Fig. 1. SEM images of gold icosahedra (a) at low magnification and (b) at high magnification synthesized by heating an aqueous solution of Pluronic P123 and $HAuCl_4$ at 60 °C. (c) X-ray diffraction pattern of the gold icosahedra.

Fig. 2 shows the UV–Vis absorption spectra of the aqueous solution of Pluronic P123 containing $HAuCl_4$ on heating at 60 °C recorded as a function of time. The strong absorption band centered at ~330 nm, originating from the metal–ligand charge transfer (MLCT) band of $AuCl_4^-$ [20] decreased gradually over time, indicating the gradual disappearance of the gold salts at 60 °C. This decrease coincides with the increase in the intensity of the new broad band at around 600 nm, which originates from a surface plasmon resonance (SPR) band of the gold crystals [21], indicating that the small-sized gold crystals were produced during the reduction of the gold salt. After 25 min, no further change in the UV–Vis spectra was noticed, suggesting that the reaction had finished. The broad plasmon band in the > 600 nm range and the red-shift of the SPR band compared to that of typical spherical gold nanoparticles imply that the as-synthesized gold icosahedra had an anisotropic morphology, sharp corners, and larger size than typical gold nanoparticles [17]. The gold icosahedra precipitated as soon as they were prepared, whereas aggregations between the gold icosahedra did not occur. Therefore, they could be easily redispersed in various solvents,

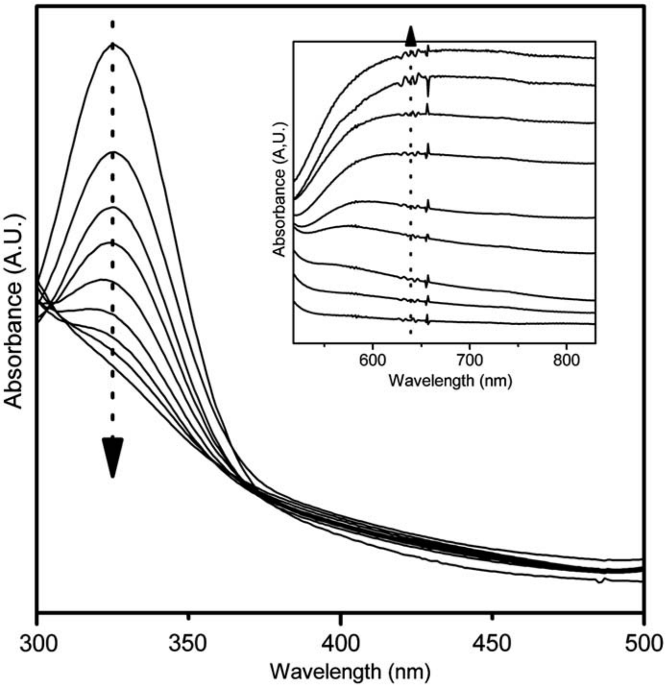

Fig. 2. Time-evolution UV–Vis spectra of an aqueous solution of Pluronic P123 and $HAuCl_4$ on heating at 60 °C. The inset shows the SPR absorption of the gold icosahedra versus the reaction time. The UV–Vis spectra from top to bottom correspond to 1, 3, 5, 7, 10, 13, 16, 20, and 25 min after heating, whereas the corresponding time scale of the inset figure is from bottom to top.

such as water, ethanol, tetrahydrofuran, and chloroform by gentle stirring or ultrasonication.

It is well known that Pluronic block copolymers can act as both reductants and colloidal stabilizers. In the presence of Pluronic polymers, it has been suggested that the oxidation of the PEO block reduces $AuCl_4^-$ ions bound to pseudocrown ether cavities formed from the PEO coils and results in Au(I) ions, which finally follow the equilibrium $3Au(I) \leftrightarrow 2Au + Au(III)$ to yield gold particles [13]. Furthermore, our experiment reveals that Pluronic P123 can selectively adsorb on Au crystal faces to promote the anisotropic growth toward the formation of gold icosahedra. Generally, a gold icosahedron, which is a type of multiple-twinned particle (MTP), achieves a low total free energy by assuming a twinned structure with the lower energy {111} facets. However, this twinned structure exhibits strong reactivity toward oxidative etching, because of the lattice distortions and surface defects [22]. Moreover, the strain energy originating from the twin defects increases as the size of the MTP increases [11]. Hence, it is generally thought that MTPs are not stable when they grow to a large size. However, in our system, it can be thought that the surface capping ability of Pluronic P123 reduces the surface energy, so as to offset the strain energy of the twinned structure and protects the gold icosahedra from oxidative etching. Thus, Pluronic P123 stabilizes the growth of large multiple-twinned icosahedra.

The chloride ion (Cl^-) is known to be able to interact with a gold surface and, thus, promote the anisotropic growth of gold crystals [23]. In the present case, we observed that the shape of the gold crystals could be changed from icosahedra to plates by introducing sodium chloride (NaCl). Fig. 3 shows the SEM images of the gold nanocrystals prepared at different NaCl concentrations. As the molar ratio of NaCl to the gold salt increases from 0 to 10, the size and shape of the gold icosahedra become smaller and more irregular, respectively, and their content in the product decreases, while that of the gold nanoplates increases. For example, when a molar ratio of NaCl to the gold salt of 10 was used, gold nanoplates having hexagonal, triangular, and truncated triangular shapes with edge lengths of about 1–6 μm (Fig. 3(f)) were mostly obtained.

Fig. 4(a) shows a typical TEM image of a single gold icosahedron produced by the above method without the addition of NaCl and the inset in Fig. 4(a) shows the corresponding selective-area electron diffraction (SAED) pattern. The lattice spacings of 2.36, 2.03, 1.23, and 1.17 Å obtained from the SAED pattern indexation can be assigned to (111), (200), (311), and (222) reflections of fcc gold crystal, respectively.

Fig. 4(b) shows the TEM image of a hexagonal gold nanoplate synthesized with the addition of NaCl (NaCl to gold salt molar

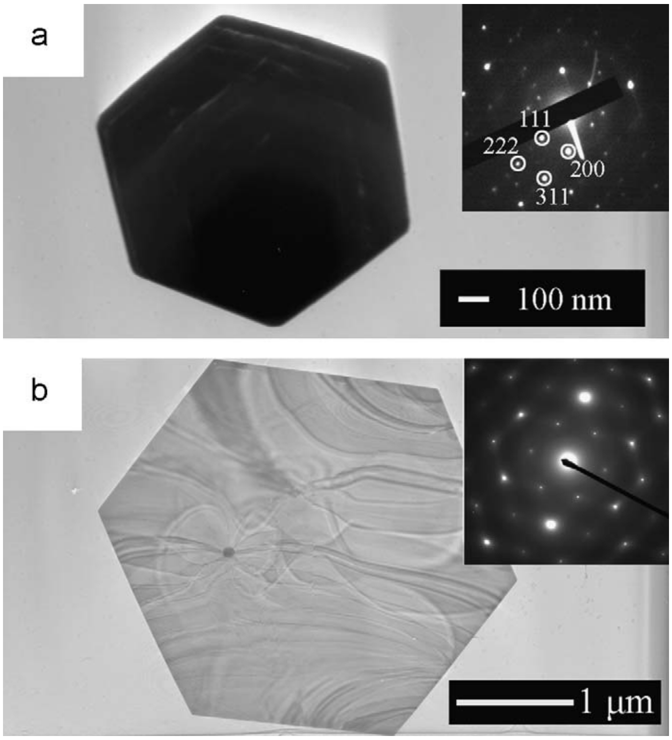

Fig. 4. TEM images of (a) a gold icosahedron and (b) a gold hexagonal plate. The insets represent the SAED patterns of the corresponding gold nanocrystals.

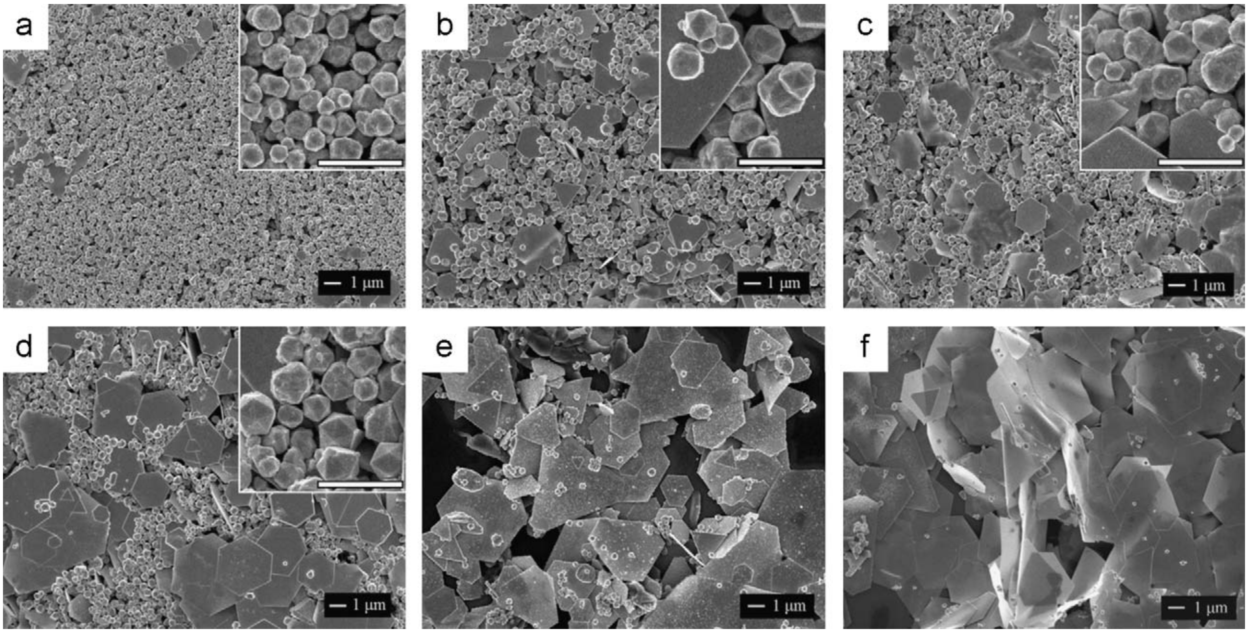

Fig. 3. SEM images of the gold nanocrystals synthesized in the presence of NaCl at a molar ratio of NaCl to $HAuCl_4$ of (a) 0.001, (b) 0.01, (c) 0.1, (d) 1, (e) 5, and (f) 10. The insets in (a)–(d) show the high magnification images of the corresponding samples, respectively. The white scale bars in the inset images indicate a length of 1 μm.

Table 1
X-ray diffraction intensity ratio between (111) and (200) facets of the gold nanocrystals synthesized in the presence of various concentrations of NaCl.

	Molar ratio, [NaCl]:[$HAuCl_4$]						
	Without NaCl	0.001:1	0.01:1	0.1:1	1:1	5:1	10:1
Intensity ratio of the (111) to the (200) diffraction peak	2.36	2.77	3.24	3.18	3.21	3.25	4.06

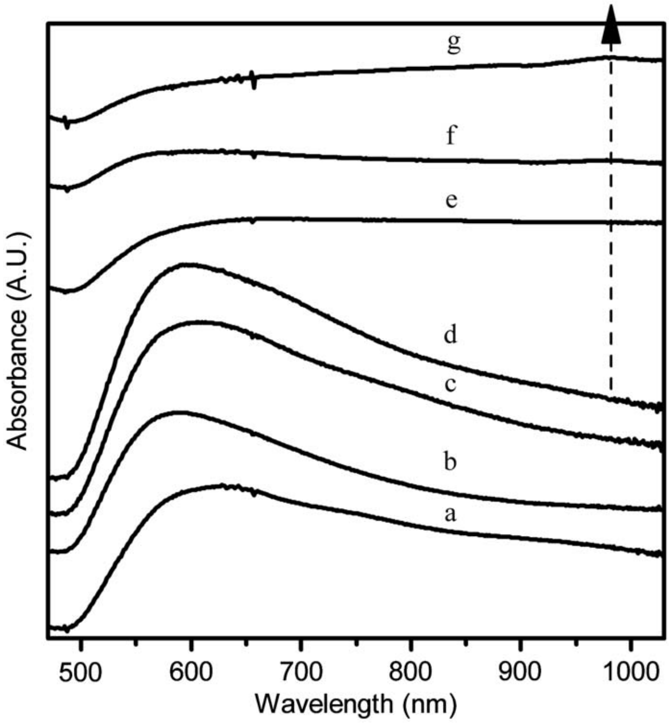

Fig. 5. UV–Vis spectra of gold nanocrystals synthesized in the presence of NaCl at a molar ratio of NaCl to $HAuCl_4$ (a) 0, (b) 0.001, (c) 0.01, (d) 0.1, (e) 1, (f) 5, and (g) 10.

ratio=5). The band-like patterns on the surface of the gold nanoplate are due to its deformation or bending during the irradiation of the electron beam [24]. The related SAED pattern in the inset of Fig. 4(b) shows hexagonally arranged diffraction spots, indicating that the gold nanoplates are single crystalline with the surface covered with (111) facets [25].

While the SEM and TEM results show only a small portion of the samples, the XRD analysis provides further information on the overall structures and compositions of the gold crystal mixtures. Table 1 shows the intensity ratio of the (111) to the (200) peak in the XRD spectra of the gold nanocrystals obtained at different NaCl concentrations. All of the samples exhibit higher intensity ratios of the (111) to the (200) diffraction peak than the bulk value, indicating that the gold icosahedra and plates are essentially composed of {111}-dominant facets, as already reported [14,26]. As can be clearly seen in Table 1, the intensity ratio of the (111) to the (200) peak increases with increasing concentration of NaCl. This XRD analysis matches well with the SEM images in Fig. 3, and indicates that the relative number ratio of the (111)-faceted single-crystalline gold nanoplates to the total number of products increases with increasing concentration of NaCl. Therefore, the XRD analysis provides further evidence that NaCl facilitates the growth of the (111) oriented hexagonal/triangular gold nanoplates.

The optical properties of gold nanomaterials are highly dependent upon the crystal size and shape [27]. Fig. 5 shows the UV–Vis spectra of the gold nanocrystals synthesized at different NaCl concentrations. It is found that all of the samples displayed the characteristic SPR absorption band. There is no significant difference in the UV–Vis spectra between the samples produced with low NaCl concentrations (NaCl to gold salt molar ratio=0, 0.001, 0.01, and 0.1, Fig. 5(a–d)). However, in the case where higher NaCl concentrations were used (NaCl to gold salt molar ratio=1, 5, and 10), the as-synthesized gold crystals show a broad absorption band in the near-infrared (NIR) region (Fig. 5(e–g)). At these concentrations, the intensity of the broad absorption band in the NIR region increases as the ratio of gold nanoplates to icosahedra increases. Moreover, when a molar ratio of NaCl to the gold salt of 5 or 10 was used, an SPR absorption shoulder located at around 980 nm appeared, which originates from the in-plane dipole plasmon resonance of the gold nanoplates [28]. These results imply that the optical properties of the gold nanocrystals can be tuned by simply changing the NaCl concentration.

From the above experimental results, we can conclude that NaCl promotes the formation of gold nanoplates. It is well known that Cl^- ions chemisorb on the surface of gold to form a hexagonal closed packed adlayer on the Au (111) surface and inhibit the growth along the $\langle 111 \rangle$ direction [28]. Thus, it promotes the crystal growth perpendicular to the $\langle 111 \rangle$ direction required for the formation of the flat gold nanoplates. It is thought that the crystal growth mechanism involves the competition between the chemisorption ability of Cl^- ions to produce nanoplates and the capping ability of Pluronic P123 to produce icosahedra. Besides, from the experimental results, we can conclude that the degree of formation of the single crystalline gold nanoplates is proportional to the concentration of Cl^- ions. It has been reported that a combination of oxygen (O_2) from the air and Cl^- ions promotes the dissolution and etching of twinned seeds. Single-crystal seeds are more stable than twinned seeds in this oxidative environment, owing to the lack of twin boundary defects on the surface [29]. On the basis of this model, we believe that the increase of the Cl^- concentration caused by adding a larger amount of NaCl enhanced the oxidative dissolution selectively, so that more single-crystal seeds were produced than twinned seeds [30]. As a result, the ratio of single crystalline gold nanoplates to multiple-twinned icosahedra increases as the concentration of NaCl increases. Also, it is thought that the oxidative etching of the gold icosahedra was responsible for the decrease in the size of the gold particles and the increase in the ratio of the irregular-shaped particles to icosahedra [11].

To clarify the role of the Cl^- ion in the growth of the gold nanoplates, other halogen salts, viz. lithium chloride (LiCl), potassium chloride (KCl), sodium bromide (NaBr), and sodium iodide (NaI), were added to the aqueous solution instead of NaCl. The concentration of each halogen salt was equimolar to $HAuCl_4$. The size and shapes of the gold crystal mixtures obtained using a molar ratio of LiCl and KCl of 1, shown in Fig. 6(a) and (b), respectively, were found to be almost identical to that obtained using a molar ratio of NaCl of 1, shown in Fig. 3(d). Furthermore, the X-ray and UV–Vis spectra were also found to be almost identical. Therefore, only the chloride ion affects the shape controlled synthesis of the gold nanocrystals, whereas the cation

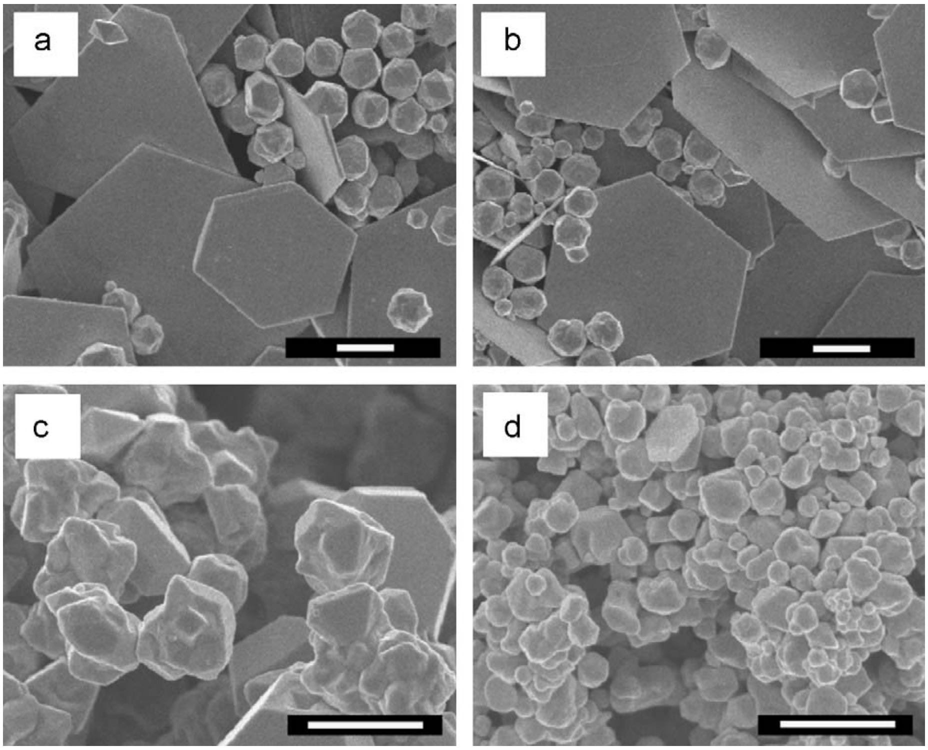

Fig. 6. SEM images of gold nanocrystals synthesized in the presence of (a) LiCl, (b) KCl, (c) NaBr, and (d) NaI at a molar ratio of 1 with respect to $HAuCl_4$. The white scale bars indicate a length of 1 μm.

in the halide salt has no effect. However, when NaBr and NaI were used, irregular-shaped gold nanoparticles were obtained instead of mixtures of gold icosahedra and nanoplates, as shown in Fig. 6(c) and (d), respectively. While the hexagonal packed adlayer of chloride ions is well aligned with the Au (111) surface, the bromide or iodide ion adlayer has a large mismatch with the Au (111) surface and generates interfacial strain [31,32]. This strain prevents the gold crystals from growing with extended (111) faces and, thus, gold particles with irregular shapes are produced instead of gold icosahedra and nanoplates. Moreover, the interfacial strain is thought to be relieved through the distortion of the morphology of the gold crystals with defect formation [23]. For these reasons, the gold nanoparticles synthesized by the above method in the presence of NaBr and NaI have a distorted and irregular morphology. In addition, iodide ions can chemisorb more strongly to the gold surface than bromide ions and generate more interfacial strain, due to higher degree of mismatch with the Au (111) surface [32,33]. Hence, iodide ions retract and distort the gold growth more strongly than bromide ions, so that the size of the resulting gold particles (280 ± 260 nm) is smaller than that of the particles synthesized in the presence of bromide ions (840 ± 160 nm).

4. Conclusion

In this work, we presented a simple and economical method (at 60 °C for 25 min) for the synthesis of gold icosahedra and nanoplates using environmentally benign reagents. The amphiphilic block copolymer, Pluronic P123, was found to be an efficient reducing agent and colloidal stabilizer for the anisotropic growth of gold icosahedra. The chloride ions (Cl^-) released from sodium chloride (NaCl) promoted the growth perpendicular to the ⟨111⟩ direction required for producing gold nanoplates. The ratio of gold icosahedra to nanoplates could be controlled simply by changing the concentration of NaCl. The gold nanocrystals synthesized by our method showed unique surface plasmon resonances depending on the ratio of gold icosahedra to nanoplates. The unique properties of these shape-controlled gold nanomaterials could have potential applications in chemical or biological sensing, the hyperthermia treatment of tumors, optical coatings, and catalysts.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2009.09.020.

References

[1] M.A. El-Sayed, Acc. Chem. Res. 34 (2001) 257–264.
[2] E. Hutter, J.H. Fendler, Adv. Mater. 16 (2004) 1685–1706.
[3] K.L. Kelly, E. Coronado, L.L. Zhao, G.C. Schatz, J. Phys. Chem. B 107 (2003) 668–677.
[4] M.-C. Daniel, D. Astruc, Chem. Rev. 104 (2004) 293–346.
[5] M. De, P.S. Ghosh, V.M. Rotello, Adv. Mater. 20 (2008) 4225–4241.
[6] C. Wang, Z. Ma, T. Wang, Z. Su, Adv. Funct. Mater. 16 (2006) 1673–1678.
[7] Z. Li, Z. Liu, J. Zhang, B. Han, J. Du, Y. Gao, T. Jiang, J. Phys. Chem. B 109 (2005) 14445–14448.
[8] D. Seo, J.C. Park, H. Song, J. Am. Chem. Soc. 128 (2006) 14863–14870.

[9] C. Li, K.L. Shuford, Q.-H. Park, W. Cai, Y. Li, E.J. Lee, S.O. Cho, Angew. Chem. Int. Ed. 46 (2007) 3264–3268.
[10] A. Sánchez-Iglesias, I. Pastoriza-Santos, J. Pérez-Juste, B. Rodríguez-González, F.J. García de Abajo, L.M. Liz-Marzán, Adv. Mater. 18 (2006) 2529–2534.
[11] J. Xu, S. Li, J. Weng, X. Wang, Z. Zhou, K. Yang, M. Liu, X. Chen, Q. Cui, M. Cao, Q. Zhang, Adv. Funct. Mater. 18 (2008) 277–284.
[12] A.V. Kabanov, E.V. Batrakova, V.Y. Alakhov, J. Controlled Release 82 (2002) 189–212.
[13] T. Sakai, P. Alexandridis, Langmuir 20 (2004) 8426–8430.
[14] C. Zhang, J. Zhang, B. Han, Y. Zhao, W. Li, Green Chem. 10 (2008) 1094–1098.
[15] J.-U. Kim, S.-H. Cha, K. Shin, J.Y. Jho, J.-C. Lee, Adv. Mater. 16 (2004) 459–464.
[16] S.-H. Cha, J.-U. Kim, K.-H. Kim, J.-C. Lee, Mater. Sci. Eng. B 140 (2007) 182–186.
[17] S.-H. Cha, K.-H. Kim, W.-K. Lee, J.-C. Lee, J. Solid State Chem. (2009) 1575–1580.
[18] Z. Li, A. Friedrich, A. Taubert, J. Mater. Chem. 18 (2008) 1008–1014.
[19] F. Kim, S. Connor, H. Song, T. Kuykendall, P. Yang, Angew. Chem. Int. Ed. 43 (2004) 3673–3677.
[20] S. Kundu, L. Peng, H. Liang, Inorg. Chem. 47 (2008) 6344–6352.
[21] J. Zhang, H. Liu, Z. Wang, N. Ming, Adv. Funct. Mater. 17 (2007) 3295–3303.
[22] Y. Xiong, J.M. McLellan, Y. Yin, Y. Xia, Angew. Chem. Int. Ed. 46 (2007) 790–794.
[23] A. Rai, A. Singh, A. Ahmad, M. Sastry, Langmuir 22 (2006) 736–741.
[24] Y. Chen, X. Gu, C.-G. Nie, Z.-Y. Jiang, Z.-X. Xie, C.-J. Lin, Chem. Commun. (2005) 4181–4183.
[25] S. Goy-López, E. Castro, P. Taboada, V. Mosquera, Langmuir (2008) 13186–13196.
[26] C.S. Ah, Y.J. Yun, H.J. Park, W.-J. Kim, D.H. Ha, W.S. Yun, Chem. Mater. 17 (2005) 5558–5561.
[27] S.S. Shankar, A. Rai, A. Ahmad, M. Sastry, Chem. Mater. 17 (2005) 566–572.
[28] S.S. Shankar, S. Bhargava, M. Sastry, J. Nanosci. Nanotech. 5 (2005) 1721–1727.
[29] Y. Xia, Y. Xiong, B. Lim, S.E. Skrabalak, Angew. Chem. Int. Ed. (2009) 60–103.
[30] M. Tsuji, N. Miyamae, M. Hashimoto, M. Nishio, S. Hikino, N. Ishigami, I. Tanaka, Colloids Surf. A Physicochem. Eng. Aspects (2007) 587–598.
[31] O.M. Magnussen, B.M. Ocko, R.R. Adzic, J.X. Wang, Phys. Rev. B 51 (1995) 5510–5513.
[32] O.M. Magnussen, Chem. Rev. 102 (2002) 679–725.
[33] B.M. Ocko, G.M. Watson, J. Wang, J. Phys. Chem. 98 (1994) 897–906.