

Controllable Morphology Formation of Gold Nano- and Micro-plates in Amphiphilic Block Copolymer-based Liquid Crystalline Phase

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A new and simple method is used to control formation of gold nanoparticles in lyotropic liquid crystal. Triangular or hexagonal nano- and micro-plates can be obtained in PEO–PPO–PEO-based hexagonal liquid crystals after adding a small amount of cationic surfactant, CTAB. All plates are single crystals and mostly characterized by orientation along the [111] direction. Their sizes are even longer than 10 μm . The selective adsorption of CTAB on certain crystallographic facets is the main point of supposed mechanism.

Recently, metal and semiconductor nanoparticles of non-spherical shapes such as rods, wires, belts, cubes, and disks become much attractive because some special properties originated from their anisotropic shapes can not be obtained from conventional spherical particles.^{1–6} In particular, preparation of disk-like or plate-like nanoparticles is now a new and interesting research focus. For example, silver nanodisks or nanoplates with perfectly and truncated triangular shapes have been synthesized by different methods.^{6–8} The shape of flat nanoparticles is found to strongly affect the spectral position of the surface plasmon band, indicating potential applications in optics.^{6–8} For gold nanoparticles, various preparation methods are extensively reported and reviewed in past decades.⁹ Different chemical and physical approaches are contributed to fabricate gold nanostructures of anisotropic shapes particularly nanorods with controllable aspect ratios.^{1,10,11} However, few reports concern systems of gold nanodisks or planar nanoparticles though Milligan has observed gold nanoplates since 1964.¹² Zhou et al., Tsuji et al., and Ibano et al. obtained mixtures of triangular, square, hexagonal gold nanoplates with nanospheres by ultraviolet irradiation, microwave-polyol, or photoreduction method, respectively.^{13–15} Malikova et al. prepared gold nanoplates with different shapes using salicylic acid as reducing agent in aqueous solution.¹⁶ Stoeva et al. got the plate-like gold superlattices also from inverse micelles.¹⁷ The produced gold nanoplates from above mentioned methods, however, are usually of small size or not single crystals.

We report here a new and simple method for the large-scale preparation of gold nanoplates and microplate in lyotropic liquid crystal (LLC) mainly made of poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) (PEO–PPO–PEO) block copolymers. Pluronic P123 (EO₂₀PO₇₀EO₂₀, BASF Corp.) with weight percent of 45% is chosen to form hexagonal LLC phase with aqueous solution of HAuCl₄ (0.03 M) at room temperature on the basis of the phase diagram¹⁸ reported in literature. Herein, PEO–PPO–PEO molecules self-assemble into cylinders with PEO blocks in water domains. The PEO blocks play

the roles both as reducer for AuCl₄[–] and also as the stabilizer for nanoparticles.¹⁹ As a well-known capping ligand, cetyltrimethylammonium bromide (CTAB) is added into LLC to control the growth of gold nanocrystals.^{11,20}

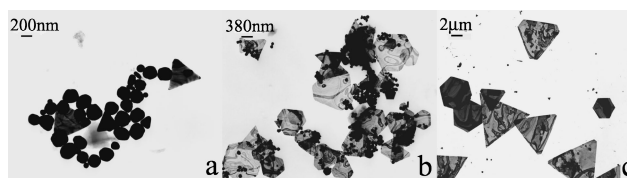


Figure 1. TEM images of gold nano- and micro-crystals formed in the hexagonal liquid crystal of P123 (45%)–HAuCl₄ aqueous solution systems with adding CTAB (a) 0, (b) 0.5%, (c) 1% after three days.

In the ordered cylindrical arrays self-assembled from PEO–PPO–PEO, the reduction occurs in the aqueous domain and PEO blocks will slowly reduce Au^{III} ions to Au by oxidation of their oxyethylene groups.¹⁹ Morphologies of gold products are observed under a JEM-100CX II (JEOL) TEM operated at 100 kV. Figure 1 shows various products formed with or without adding CTAB to P123 (45%)–HAuCl₄ system. Spherical nanoparticles are main products coexisting with few triangular nanoplates when no CTAB is added. It can be noted that increasing CTAB to 0.5%, more plate-like gold nanocrystals appear in products mixed with spheres and plates (Figure 1b). However, adding 1% CTAB into the LLC results in much larger gold plates as shown in Figure 1c and Figure 2. Most particles exhibit equilateral triangular, hexagonal, and truncated triangular shapes with the edge size even longer than 10 μm . The triangles and hexagons are characterized by a uniform contrast, indicating single-crystalline structures.

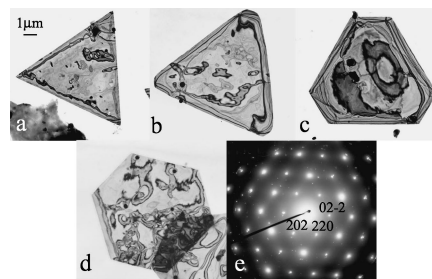


Figure 2. Different TEM images observed in P123 (45%)–CTAB (1%)–HAuCl₄ system after three days. (a) equilateral triangle, (b) and (c) truncated triangle, (d) hexagon. Electron diffraction pattern (e) is obtained from the triangular microplate.

TEM images of plate-like gold microcrystals with various shapes and electron diffraction (ED) pattern are shown in Figure 2. The hexagonal ED pattern clearly suggests a face-centered cubic (fcc) single crystal with atomically flat surface and its $[111]$ orientation parallel to the electron beam. The sharp spots represent different lattice planes of $(02\bar{2})$, (220) , and (202) , respectively. Similar results are obtained from other microcrystals (Figures 2b–2d). Such orientational ordering is indicative of the faceted morphology of the Au nanoparticles and their inherent anisotropy. This finding is important since many optical and electronic properties of the nanocrystals depend on the orientation.

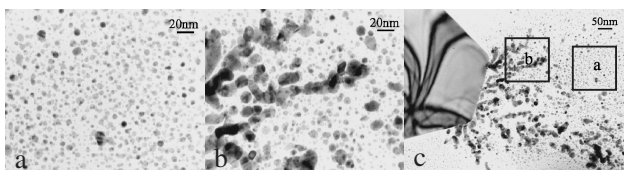


Figure 3. TEM images observed during growth of gold nanoplates after 20 h. (a) small nanoplates, (b) formation of larger plate-like nanoparticles, and (c) aggregation and fusion of small particles onto a large nanoplate. (a) and (b) are enlarged images corresponding respectively to specified area in (c).

What leads to different morphologies of products? From above analysis, it is reasonably concluded that the cationic surfactant, CTAB, plays the critical role on the nucleation of anisotropic gold nanocrystals. It has been reported that the headgroups of CTAB can adsorb on Au surface.^{11,20} When CTAB is introduced into reaction systems, the selective adsorption on certain crystallographic facets during particles growth is believed to affect nanoparticles shape. Therefore, such binding prevents the growth of other facets and results in the formation of plate-like microcrystals. This process may preferentially take place on $\{111\}$ facets to stabilize the plates.^{5,6} With CTAB concentration increasing from 0.5 to 1%, the effect of adsorption induces higher nanocrystal surface coverage and favors a large-scale production of microplates. The TEM images observed during the aggregation and fusion of small particles onto larger ones (Figure 3) are supporting evidences for this mechanism.

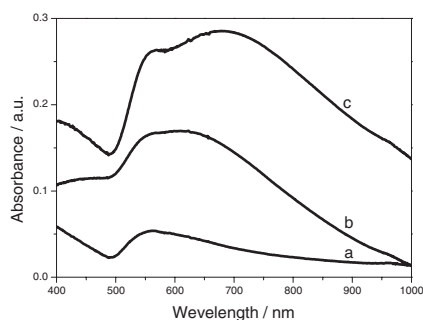


Figure 4. UV-vis absorption spectra of gold nano- and microcrystals prepared respectively from P123 (45%)–HAuCl₄ (0.03 M) systems with adding CTAB (a) 0, (b) 0.5%, and (c) 1% after 3 days.

Optical properties of nanostructured materials are strongly related to their shape and size. The UV-vis spectra of samples containing gold particles are depicted in Figure 4. The character-

istic surface plasmon band for the spherical particles is observed at $\lambda_{\max} = 563$ nm (Figure 4a). Its unsymmetrical shape may result from big particles and the plate-like by-products. For anisotropic metallic nanoparticles including silver and gold nanodisks or nanorods, it is well known that two or more plasmon resonances, the transverse and longitudinal bands, are expected.^{6,11} With increasing quantity and size of microplates, the peak around 563 nm broadens (Figure 4b) and two peaks centered respectively around 570 and 690 nm can be noted (Figure 4c), which can be attributed to the transverse and the longitudinal plasmon bands, reflecting the anisotropic nature of gold microplates.

In summary, we establish a new and simple method to prepare nano- and micro-plates. The added CTAB molecules play the most important role in controlling the shape and size of particles by adsorbing selectively on certain crystallographic facets. The result suggests an effective way to produce particles with controllable shape and size and a clue to understand the mechanism for crystal growth.

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