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Synthesis of gold nanoplates in lamellar liquid crystal

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ABSTRACT

Single-crystalline gold nanoplates have been synthesized in a lamellar lyotropic liquid crystal (LLC) composed of a nonionic surfactant, $C_{12}E_4$ (tetraethylene glycol monododecyl ether) and the chloroauric acid ($HAuCl_4$) solution. The sizes of gold nanoplates can be varied from several hundreds of nanometers to a few microns in width by changing reaction conditions. The factors which influence the product morphology, like LLC composition, capping agent and reaction temperature are studied by small-angle X-ray scattering (SAXS), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The mechanism analysis indicates that the LLC plays an important role for the consequent growth of single-crystal anisotropic plates by providing an ordered reaction medium and a limited growth space.

1. Introduction

Synthesis of one- or two-dimensional (1D or 2D) nanostructures for gold and silver attracts much attention for their potential important applications in catalysis [1], sensing [2], recording media [3], optics [4], and so on. Among them, the anisotropic nanoparticles ranging from rods [5,6] to cubes [7], disks [8], belts [9,10], wires [11] and other special morphologies [12–15] have been widely fabricated by solution-based [16], electrochemical [17], photochemical [18,19], templating [20,21] and seeding growth methods [22]. In particular, exploration on gold nanoplates or planar nanoparticles becomes more and more popular because of their novel functions [23–30].

Besides using the homogeneous solution to fabricate the anisotropic nanomaterials, other mediums with ordered structure were also used as "soft templates" or confined reaction media. For gold anisotropic nanomaterials, Qi and coworkers have synthesized Au nanowires in lamellar LLC composed of $C_{12}E_4$ (tetraethylene glycol monododecyl ether) and $HAuCl_4$ solution [31]. Niu and coworkers fabricated novel spherical three-dimensional (3D) dendritic gold–polypyrrole nanocomposites mediated by soft supramolecular micelles [32]. Huang et al. demonstrate the rapid synthesis of a large quantity of uniform-sized gold nanocubes by an electrochemical method, using a surfactant solution and acetone [33]. The nanostructured, ionic liquid-based gels has also been used to template the formation of new Au nanoparticle morphologies by Firestone et al. [34]. We also prepared gold nano- and microplates from hexagonal LLC comprising a poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (PEO-PPO-PEO) block copolymers [35,36]. In this paper, we use a lamellar LLC constructed mainly by $C_{12}E_4$ and $HAuCl_4$ solution to synthesize gold nano- and microplates. The poly(*N*-vinyl-2-pyrrolidone) (PVP) acting as the capping agent is added in some systems. The effects of different factors like capping agent, temperature and composition on size and shape of products have been studied. A possible growth mechanism is proposed to explain the LLC's confining effect.

2. Experimental

2.1. Materials

The nonionic surfactant, tetraethylene glycol monododecyl ether ($C_{12}E_4$, Brij 30), was obtained from Sigma–Aldrich Co. Poly(*N*-vinyl-2-pyrrolidone) (PVP, ≥95.0%) with an average molecular weight (g/mol) of 25,000–40,000 (K30) was purchased from Shanghai Runjie Reagent Co. Hydrogen tetrachloroauric acid ($HAuCl_4 \cdot 4H_2O$, ≥99.9%), was purchased from Shanghai Reagent Co. The water used was highly purified with the resistivity $\geq 18.0\,M\Omega\,cm$. All chemicals were used as received without further purification.

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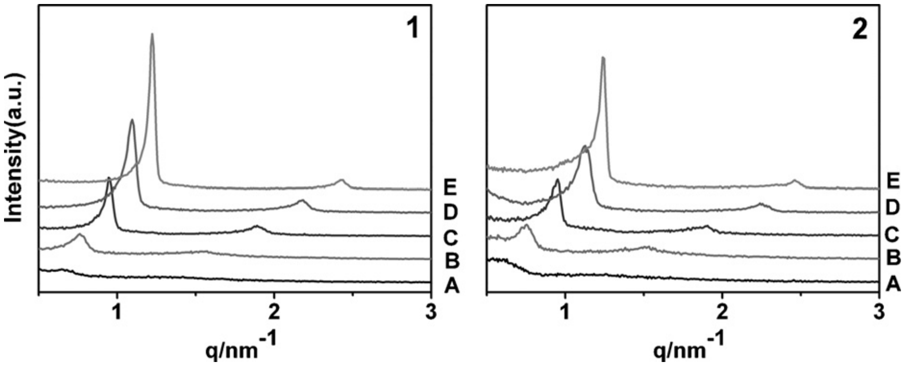

Fig. 1. SAXS patterns of lyotropic lamellar systems measured 3 weeks after preparation: (1) $C_{12}E_4$–H_2O; (2) $C_{12}E_4$–$HAuCl_4$ aqueous solution (0.015 M). Curves A, B, C, D and E corresponds to systems with $C_{12}E_4$ concentration (wt%) of 33%, 40%, 50%, 60% and 67%, respectively.

2.2. *Instrumental characterization*

2.2.1. *SAXS characterization*

The small-angle X-ray scattering measurements were carried out in a special SAXS camera (Hecus Mbraun X-ray Systems, Graz, Austria) with a Ni-filtered Cu Kα radiation (0.154 nm) operating at 50 kV and 40 mA. The sample-to-detector distance is 277 mm. The temperature is kept at $25 \pm 0.1\,^{\circ}$C. The relative positions of SAXS scattering peaks along the scattering vector (q) axis are used to determine the lyotropic phase structure. For the lamellar structure, the peak positions should obey the relationship of 1:2:3:4 [37]. The repeat spacing between the lamellar layers can be determined from the first scattering peak position (q_1) as $d = 2\pi/q_1$.

2.2.2. *TEM and SEM observation*

TEM observations were performed with a JEM-100CX II (JEOL) electron microscope operated at an accelerating voltage of 100 kV. Samples were prepared by dropping a dispersion of the products on Formvar-coated copper grids (230 meshes). SEM images were taken on a JEOL JSM-6700F system (operated at 10 kV).

3. Results and discussion

3.1. *Synthesis of gold nanoplates*

The lyotropic liquid crystalline behavior of $C_{12}E_4/H_2O$ binary system has been studied in detail [38]. Based on its phase diagram, $C_{12}E_4$ can form the lamellar phase at a wide range of concentration (weight percentage of 25–80%) when mixed with water at room temperature. In our study, we selected five concentrations of $C_{12}E_4$ (wt% = 33%, 40%, 50%, 60% and 67%) to construct the templates. For the synthesis of gold nanocrystals, aqueous tetrachloroauric acid solutions (0.015 or 0.03 M) instead of water were used to form lamellar phases with $C_{12}E_4$. All samples were sealed in glass tubes and left at room temperature for further study.

3.2. *Characterization of LLC and gold nanoplates*

3.2.1. *LLC phase structures*

SAXS patterns of studied lyotropic samples without and with gold nanoplate preparation are shown in Fig. 1. The relative positions of SAXS scattering peaks along the scattering vector (q) axis indicate clearly that all systems here keep the structural characteristics of a lamellar phase. Their repeat spacing (d) values are listed in Table 1, exhibiting a decreasing tendency with the increase of $C_{12}E_4$ concentration. Comparing systems with or without $HAuCl_4$ in Fig. 1, the d values are similar to each other, suggesting little influence of products on the template structure. With the prolonged reaction time, the lamellar structure with small $C_{12}E_4$ concentration would be destroyed to a certain degree due to the oxidation of oxyethylene (EO) groups, accompanying with the disappearance of the characteristic birefringence of LLC. The EO-type nonionic surfactants can act as the reducing agent to slowly reduce Au^{III} ions to Au^0 through the oxidation of their oxyethylene groups [39,40].

3.2.2. *Characterization of gold nanoplates*

The reduction process takes about 3 weeks to finish in the absence of PVP. TEM images shown in Fig. 2 are taken from samples produced in different LLC systems (A_2–E_2). The obtained nanoplates, with a few to several 10 μm in size along their longest smooth edges, present hexagonal, truncated triangle, and triangular geometries. It can be noted that the nanoplate size is reduced with increasing $C_{12}E_4$ concentration. Under a higher reductant concentration condition, the reduction of $AuCl_4^-$ ions should go faster and form more gold nuclei, which may favor the formation of nanoplates with smaller sizes [25]. The selected area electron diffraction (SAED) pattern in Fig. 2F reveals that the produced Au nanoplate is a face-centered cubic (fcc) single crystal with a preferential growth direction along the Au (1 1 1) plane [23].

To confirm the plate nature of the products, their morphologies were also characterized by scanning electron microscopy (SEM). The SEM image in Fig. 3A clearly shows micrometer-scale plates accompanying with small quantities of spherical particles as by-products. The chemical composition of these plates was further identified by energy-dispersive X-ray spectroscopy (EDX) as pure metallic Au because of the strong signal corresponding to Au in EDX spectrum (Fig. 3B).

Table 1
Repeat spacings (d) for LLC systems with compositions corresponding to those in Fig. 1

System	d (nm)
A_1	9.53
B_1	8.07
C_1	6.59
D_1	5.73
E_1	5.14
A_2	9.89
B_2	8.24
C_2	6.54
D_2	5.57
E_2	5.07