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Synthesis of Gold Nanoparticles Using Lamellar Liquid Crystal of Protic Ionic Liquids

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Gold spherical nanoparticles and nanoplates with triangular, pentagonal or hexagonal shapes are synthesized by reduction of $H[AuCl_4]$ in lyotropic liquid crystal (LLC) mainly made of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymers and protic ionic liquids (PILs) $[Pyrr][NO_3]$. Lyotropic liquid crystal was characterized by small-angle X-ray scattering measurements. Transmission electron microscopy and UV-VIS spectroscopy show the formation of spherical nanoparticles and nanoplates.

Key Words: Gold nanoparticles, Nanoplates, Lyotropic liquid crystal, Protic ionic liquid.

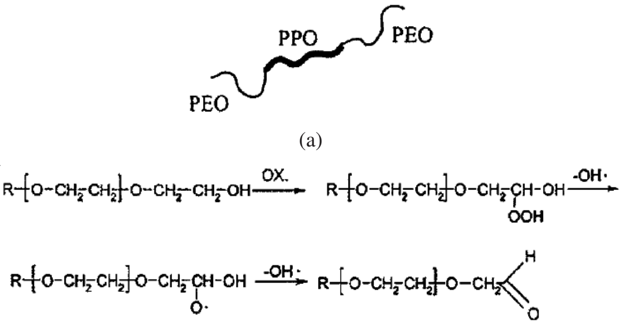
INTRODUCTION

In recent years metal nanoparticles have attracted active attention due to their unique optical, electronic, magnetic and catalytic properties which are different from those of the bulk states[1]. Among the different metal particles, gold nanostructures have stimulated great research because of their fascinating optical, electronic and chemical properties and promising applications in nanoelectronics, biomedicine, sensing and catalysis[1,2]. Many techniques have been exploited to prepare shape-controlled gold nanoparticles, including polyol synthesis[3], microwave-polyol synthesis[4], laser ablation[5], seed-mediated growth[6], lyotropic liquid crystal (LLC)[7], hydrogel templates[8], layer-by-layer assembly (LBL)[9] and the Langmuir-Blodgett technique[10,11].

At the same time, there is considerable interest in the use of room temperature ionic liquids (ILs) as promising substitutes for volatile organic solvents. Ionic liquids are organic salts with melting points near room temperature, which have received a great deal of attention as green and designer solvents owing to their unique properties such as negligible vapour pressure, nonflammability, high chemical and thermal stability, high polarity, high ionic conductivity, wide electrochemical window and tunable physico-chemical properties including dissolving ability and solvent miscibility[12-15], protic ionic liquids (PILs) are a subset of ionic liquids that can be easily produced trough the proton transfer between Bronsted acids and bases. Protic ionic liquids exhibit some special qualities compared to aprotic ionic liquids because of the presence of the proton donor and acceptor sites, which makes them also useful in biology[16] and as proton-conducting media in polymer membrane fuel cells, double-layer capacitors or dye-sensitized solar cells[17,18]. Meanwhile, the ease with which protic ionic liquids form hydrogen-bonded network put them to be good candidates as non-aqueous self-assembling media[19]. Recently, the advantages of amphiphilic ionic liquid derivatives in the introduction of ordered self-organized structures have been reported. For example, long chain ionic liquids have been used as synthetic templates in the preparation of mesoporous silica[20-22]. But the use of liquid crystals formed by protic ionic liquids as templates in nanoparticle synthesis has been scarcely reported. In this paper, we report the formation of gold nanoparticles from lyotropic liquid crystals (LLC) made of poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) (PEO-PPO-PEO) block copolymers in protic ionic liquid pyrrolidinium nitrate ($[Pyrr][NO_3]$). The transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS) and UV-VIS absorption spectrum were employed to characterize the gold nanoparticles. In this process, $H[AuCl_4]$ was reduced by the block copolymers PEO-PPO-PEO and there were no other reducing agents were added or other reductive methods were employed. The mechanism for oxidative degradation of ethoxyl groups of PEO-PPO-PEO are shown in Fig. 1[23].

EXPERIMENTAL

The amphiphilic block copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, Mn = 5800) is purchased from Sigama. Hydrogen tetrachloroauric acid ($HAuCl_4{\cdot}4H_2O$, ≥ 99.9 %) is purchased from Shanghai Reagent Co. Water used in the experiment was triply distilled. All chemicals are used as received without further purification.



(a)

(b)

Fig. 1. Schematic of molecular structure of P123(a) and mechanism for oxidative degradation of ethoxyl groups (b)[23].

Synthesis of protic ionic liquid pyrrolidinium nitrate ([Pyrr][NO$_3$]): [Pyrr][NO$_3$] was synthesized according to the procedure reported by Anouti *et al.*[24]. Pyrrolidine (17.85 g, 0.39 mol) is placed in a three-neck round-bottom flask immersed in an ice bath and equipped with a reflux condenser, a dropping funnel to add the acid and a thermometer to monitor the temperature. Under vigorous stirring, conc. nitric acid (68 %, 23.03 g) is added dropwise to the pyrrolidine (1 h). As this acid-base reaction is strongly exothermic, the mixture temperature is maintained less than 25 ºC during the addition of the acid by use of the ice bath. Stirring is maintained for 6 h at ambient temperature, a low-viscous liquid is obtained. This new phase is yellow pale coloured. The residual pyrrolidine or acid is evaporated under reduced pressure and the remaining liquid is further dried at 50 ºC under reduced pressure to obtain the target ionic liquid. The water content of the final product was determined by Karl Fischer titration to be 0.42 %.

Synthesis of gold products: On the basis of studied by our group, pluronic P123 can form a lamellar phase at higher concentration (weight percentage of 52-82 %) when mixed with [Pyrr][NO$_3$] at room temperature. In present study, 70 % P123 is selected where lamellar liquid crystal can be formed. To prepare gold nanoparticles, tetrachloroauric acid solution (0.02 or 0.05 mol L^{-1}) in protic ionic liquid [Pyrr][NO$_3$] instead of water is used to construct lamellar phase with PEO-PPO-PEO. The samples are sealed in glass tubes and left at room temperature for further study.

Small-angle X-ray scattering (SAXS) measurement: Phase behaviors of lyotropic liquid crystals are investigated by SAXS on a HMBG-SAX X-ray small angle system (Austria) with Ni-filtered CuK$_\alpha$ radiation (0.154 nm) operating at 50 kV and 40 mA. The sample-to-detector distance is 27.8 cm. The temperature is kept at 25 ºC. The relative positions of SAXS scattering peaks along the scattering vector (q) axis are used to determine the lyotropic phase structure. For lamellar structure, the peak positions should obey the relation 1:2:3:4.

Characterization of products: Morphologies of gold particles are observed under a JEM-100CX II (JEOL) transmission electron microscope operated at 100 kV. To prepare transmission electron microscopy (TEM) samples, the reacted mixtures are dispersed in ethanol under sonication. A little drop of resulting dispersion is put onto a Formvar-covered copper grid (230 mesh) for TEM measurement. The optical properties of obtained gold products dispersed in water are characterized on a HP 8453E UV-VIS spectrometer.

RESULTS AND DISCUSSION

Different macroscopic phenomena: The change in colour indicates the occurrence of chemical reaction. Fig. 2 shows the change in colour with the time for lyotropic liquid crystal system containing 0.05 mol L^{-1} HAuCl$_4$. As can be seen, the sample shows transparent yellow when the sample are prepared only after 4 h. Then, the colour change into opaque yellow when it was left at room temperature for 1 day and it change into dark brown after 5 days. After that, the increase of time does not cause the change of colour.

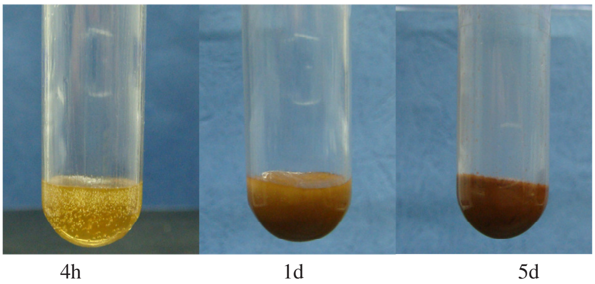


Fig. 2. Appearance of Pl23-[Pyrr][NO$_3$] (HAuCl$_4$) lamellar liquid crystal (70-30 wt %) after different reaction time. HAuCl$_4$ concentration is 0.05 mol L^{-1}

Lyotropic liquid crystal phase structures: Small-angle X-ray scattering patterns of liquid crystal template (70 % P123) and hybrids with different gold atom concentrations are given in Fig. 3. As can be seen, all of them exhibit two clear and typical scattering peaks, accompanying with the third nearly undistinguishable peaks. The ratio of the scattering factors (q) at the 1st, 2nd and 3rd Bragg peaks is 1:2:3, indicating a lamellar structure, which is kept well when lyotropic liquid crystal is added into HAuCl$_4$. The typical repeat distance (d) for lyotropic liquid crystal determined from the first peak position (q1) without HAuCl$_4$ is calculated as 12.1 nm and it increases to 12.8 nm when HAuCl$_4$ is added because of the swelling effect of particles formed in lyotropic liquid crystal phase. In addition, the intensity of peaks 1 and 2 become drastically weaker for systems having Au(III) reduction compared with those of the template, which may originate from the deterioration of long-range ordering in the lyotropic liquid crystal phase by included gold particles and decreased viscosity due to oxidation of ethylene oxide chains in polymer molecules.

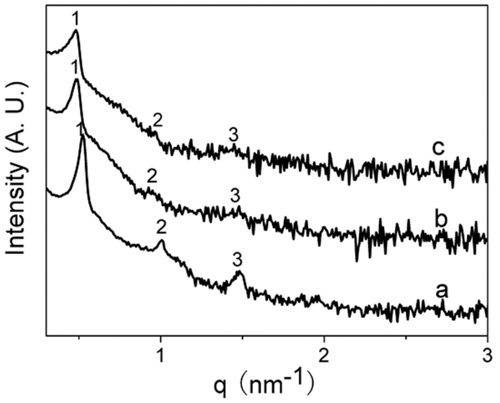


Fig. 3. SAXS patterns of P123 (70 %) lamellar liquid crystal phases measured 10 days after preparation. Concentrations of HAuCl$_4$ (mol L^{-1}) are: (a) 0, (b) 0.02 and (c) 0.05

Structural characterization of gold products: In the lamellar lyotropic liquid crystal system self-assembled from P123, the reduction occurs and poly(ethylene oxide) blocks will slowly reduce Au(III) ions to Au through oxidation of their oxyethylene groups[23,25-26]. TEM images for samples produced from different $HAuCl_4$ concentration are shown in Fig. 4. As can be seen, spherical nanoparticles (*ca.* 100 nm) coexist with some nanoplates. Upon an increase of the $HAuCl_4$ concentration to 0.05 mol L^{-1}, the aggregation of gold naoparticles occurs, which results in larger gold plates particles. The plate-like particles are mainly nearly perfect hexagonal, pentagonal and triangular nanoparticles.

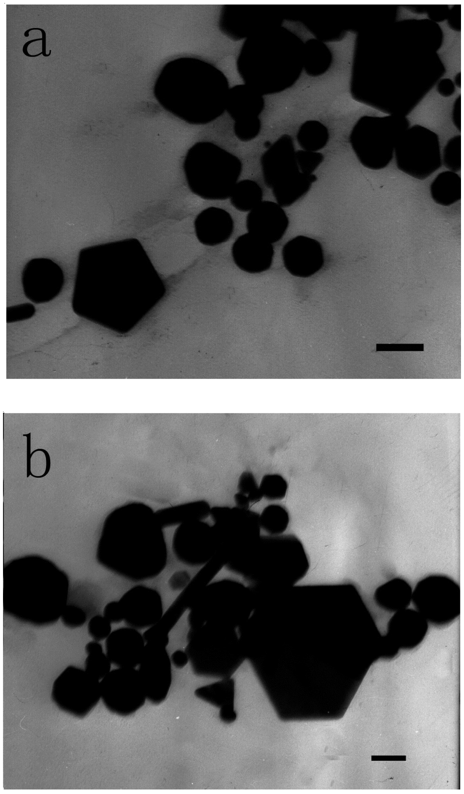


Fig. 4. TEM images of gold nanoparticles obtained from P123-$HAuCl_4$ (0.03 M) systems measured 10 days after preparation. Concentrations of $HAuCl_4$ (mol L-1) are: (a) 0.02 and (b) 0.05. Scale bar: 100 nm

Optical properties: Optical properties of prepared gold nanoparticles are strongly related to their shape and size. To further study such manipulation effect and monitor the products formation, the optical absorption properties of obtained product dispersions are recorded. As shown in Fig. 5a, the UV-VIS absorption curves for two investigated samples, the symmetrical shape of absorption peak reflects a uniform size distribution of spherical particles. On the basis of the shape of the curves in Fig. 5a, it is concluded that the main products of these three systems are spherical nanoparticles at the beginning of reduction. With extended reaction time, spectral changes of the above systems are depicted in Fig. 5b. The surface Plasmon resonance (SPR) band at 571 nm (Fig. 5a) is now red-shifted to 662 nm (Fig. 5b) and its shape becomes also unsymmetrical, reflecting the formation of larger particles and their aggregates mixing with some platelike structures (Fig. 4).

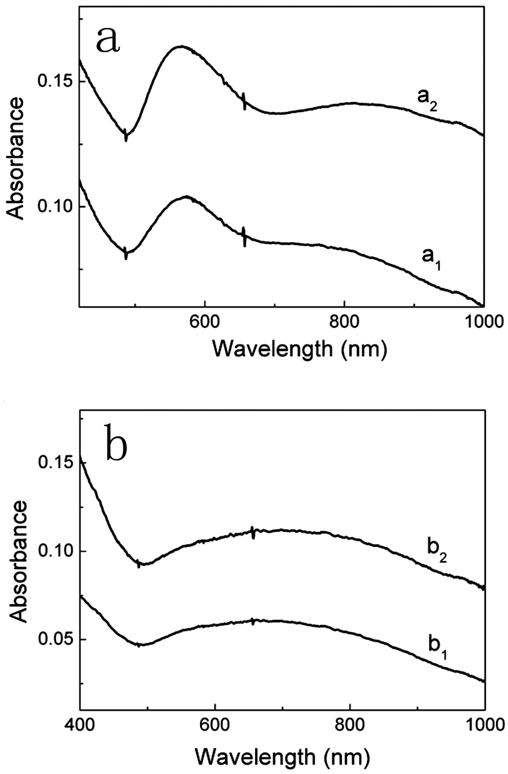


Fig. 5. UV-VIS absorption spectra of gold products prepared from P123-$HAuCl_4$ systems with $HAuCl_4$ concentration (mol L^{-1}) at (a_1) 0.02, (a_2) 0.05, (b_1) 0.02 and (b_2) 0.05. They are measured, respectively, at 1 day (a) and 10 days (b) after sample preparation

Conclusion

In summary, present study has demonstrated that protic ionic liquid, [Pyrr][NO_3], can form lyotropic liquid crystal with P123 in the system containing $HAuCl_4$, which can be used as soft templates to prepare gold nanoparticles. Gold particles are formed by reducing $HAuCl_4$ using the ethylene oxide chains in polymer molecules P123. Small-angle X-ray scattering results indicate the formation of lamellar liquid crystal and the typical repeat distance (d) for lyotropic liquid crystal increase when $HAuCl_4$ is added because of the swelling effect of particles formed in lyotropic liquid crystal phase. TEM measurements and UV/VIS spectra of the products show the coexistence of spherical nanoparticles coexist and nanoplates. Obtained results suggest that the lyotropic liquid crystal phase provides an ideal reaction environment to control the shape of gold particles.

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