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High-Yield Synthesis of Gold Microplates Using Amphiphilic Block Copolymers: Are Lyotropic Liquid Crystals Required?

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Summary: High-yield synthesis of gold microplates is achieved through autoreduction of hydrogen tetrachloroaureate (III) hydrate ($HAuCl_4 \cdot 3H_2O$) in aqueous solutions of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer (Pluronic L64, $EO_{13}PO_{30}EO_{13}$) at ambient conditions, in the absence of added energy, reductant, or other surfactants. The formation by the amphiphilic block copolymer of lyotropic liquid crystals (e.g., ordered cylindrical/hexagonal or lamellar phases) is not required for templating the formation of such microplates.

Keywords: block copolymers; Gold microplates; lyotropic liquid crystals; nanoparticles; poly(ethylene oxide); poly(propylene oxide); template

Introduction

Dimensional-controlled synthesis of metal nanomaterials, in addition to size-controlled synthesis, has been attracting significant attention in the literature, motivated by emerging nanotechnology applications.[1–13] Dimensionality can play a critical role in modulating the properties of materials due to, for example, the different ways that electrons interact in three-dimensional (3D), 2D, 1D and 0D structures.[1–13]

Several methods have been proposed for the preparation of, e.g., gold nanostructures with various shapes and dimension, such as spherical nanoparticles (0D), nanowires (1D), nanoplates (2D) or cubes (3D).[1–13] Template-directed synthesis methods using inorganic mesoporous materials, surfactants, or block copolymers constitute promising routes for controlling the nanostructure.[1–13]

Templates generated by the self-assembly of amphiphilic molecules are particularly attractive for materials synthesis because of their reproducible (thermodynamically driven) formation and tunable structure and characteristic dimensions in the nanoscale. In particular, polymer templates can form matrices that afford processability, mechanical and chemical stability, morphological versatility, as well as novel properties of the resulting nanocomposite material.[14–18]

Self-assemblies of block copolymers of the poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) ($EO_xPO_yEO_x$) family[19] are commonly used as templates for the synthesis of nanoporous inorganic nanomaterials.[20,21] Variation of the block copolymer molecular characteristics (e.g., block length, block ratio), concentration, solvent quality (e.g., solvent type, mixtures of solvents), and temperature allows for a unique tunability of the phase behavior and corresponding nanostructure.[22–28] For example, self-assembled $EO_xPO_yEO_x$ block copolymers can transform from spherical micelles in a solution of a selective solvent (e.g., water or formamide that are selective for PEO) to lyotropic liquid crystals (micellar cubic, hexagonal and lamellar) with an increase in the block copolymer concentration (at a fixed temperature).[22,24,29,30]

In the context of on-going efforts in our research group that aim to capitalize on the

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advantages that block copolymers confer as templates for nanomaterials synthesis and organization,[31,32] we have discovered that $EO_xPO_yEO_x$ block copolymers can act as very efficient reductants and stabilizers in the synthesis of gold nanocolloids from hydrogen tetrachloroaureate (III) hydrate ($HAuCl_4 \cdot 3H_2O$) in air-saturated aqueous solutions at ambient temperature in the absence of additional reductant or energy input.[33–36]

In particular, we have established that the size of the gold nanocolloids can be controlled on the basis of the amphiphilic character afforded by $EO_xPO_yEO_x$ block copolymers: PEO-induced metal ion reduction and PPO-promoted block copolymer adsorption on the surface of gold nanoparticles.[33–36] For example, the lower $AuCl_4^-$ reduction activity exhibited by block copolymers with shorter PEO blocks gives rise to larger particles because the metal ion reduction on the particle surface is more prevalent than that in the bulk solution in this case.[33–36] Following our initial papers,[33–36] a number of reports have appeared in the literature following up on the subject of metal nanoparticle synthesis in $EO_xPO_yEO_x$ solutions, with experimental and modeling findings that confirm and generalize our results, and provide additional information on the size control and colloidal stabilization of the resulting nanoparticles.[37–41]

The results that we have obtained support the hypothesis that the interplay between the (i) block copolymer adsorption on different facets of the growing metal crystal and (ii) crystal growth kinetics (rate of metal ion reduction) could determine the shape of the metal colloids.[33–36] This raises a question on what effect the ordered (lyotropic liquid crystal) structures formed by $EO_xPO_yEO_x$ block copolymers might have on the shape of the metal colloids formed in such templates.

Recently, the synthesis of gold nanorods and plates has been reported inside self-assemblies of $EO_xPO_yEO_x$ block copolymers.[10–12] In particular, Kim et al.[10] have discussed the formation of gold nanowires in the lamellar lyotropic liquid crystal phase of $EO_{20}PO_{70}EO_{20}$ block copolymers (Pluronic P123) with the aid of UV irradiation, and of gold plates in high-polymer-content melt through thermal reduction above 70 °C. These authors found the block copolymer to act as "a capping reagent and/or a template".[10] Wang et al.[11,12] have reported gold plate synthesis in the hexagonal phase of $EO_{20}PO_{70}EO_{20}$ block copolymers with the aid of small amount of surfactants (e.g., CTAB, TBAB). While these authors recognized that the gold plates thus formed did not replicate the hexagonal (cylindrical) lyotropic liquid crystal (LLC) structure of the block copolymer, they concluded that "the LLC phase provides an ideal reaction environment to control the shape of gold particles".[12] The relative function of the $EO_xPO_yEO_x$ block copolymers (e.g., as a reductant and/or a capping reagent) and of the lyotropic liquid crystals (as template) for shape determination is difficult to establish from the above studies, because of the external energy input used for $AuCl_4^-$ reduction, the presence of ionic surfactants, and/or the lack of control experiments.

In order to elucidate the role of the $EO_xPO_yEO_x$ block copolymers and the lyotropic liquid crystals that they form as templates for gold plate synthesis, we examined a system with well-known phase behavior,[22] which exhibits both lyotropic liquid crystals (hexagonal and lamellar) and micellar solutions. These different structures will serve as controls on the effect of self-assembly. We report here the high-yield, one-pot synthesis of gold microplates at ambient conditions through autoreduction of $AuCl_4^-$ in aqueous solutions of $EO_{13}PO_{30}EO_{17}$ block copolymer (Pluronic L64) across a wide concentration range.[22]

Different from recent studies, the methodology that we present here requires neither external energy input for $AuCl_4^-$ reduction nor the addition of ionic surfactants as structure-directing agents, but still results in high yields. Furthermore, lyotropic liquid crystals are not required as templates for microplate formation.

Experimental

Gold colloids were synthesized following the procedure we reported elsewhere.[33–36] In summary, a hydrogen tetrachloroaureate (III) hydrate ($HAuCl_4 \cdot 3H_2O$; 99.9 + %, Aldrich) aqueous (18.2 MΩ cm, Millipore-filtered water) solution was mixed with 20, 50 or 70 wt% $EO_{13}PO_{30}EO_{13}$ block copolymer (Pluronic L64, MW 2900, BASF Corp.) aqueous solutions. At the 20, 50 and 70 wt% concentrations (points a, b and c in Figure 1), $EO_{13}PO_{30}EO_{13}$ block copolymers form micellar solution, hexagonal and lamellar lyotropic liquid crystals, respectively, at ~30 °C.[22,30] This phase behavior enables us to examine the effects of self-assembly structure on the size and/or shape of Au colloids formed.

The $AuCl_4^-$ concentration at the start of the reaction was 2×10^{-3} mol L^{-1}. Following agitation for ~10 sec, the samples were left standing at ~30 °C for ~3 days for the reaction to proceed. The colloids obtained in the micellar solutions precipitated after the reaction was completed. The gold colloids obtained in the lyotropic liquid crystal phases remained dispersed well after the end of the reaction (Figure 2), most likely due to the higher viscosity of the organized polymer matrix.

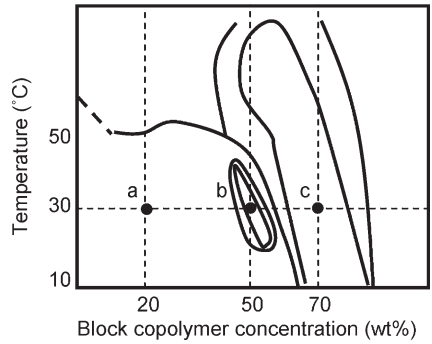

Figure 1.
Phase diagram of $EO_{13}PO_{30}EO_{13}$ in water, adapted from ref. 22. Points a, b and c represent the block copolymer concentrations (self-assembled structures) that we have considered here: 20 (micellar solution), 50 (hexagonal LLC) and 70 wt% (lamellar LLC) $EO_{13}PO_{30}EO_{13}$.

Results and Discussion

In the micellar solutions[22,30] triangular and hexagonal microplates (of side up to ~10 μm and thickness ~20 nm) formed in high yield, together with small amount of

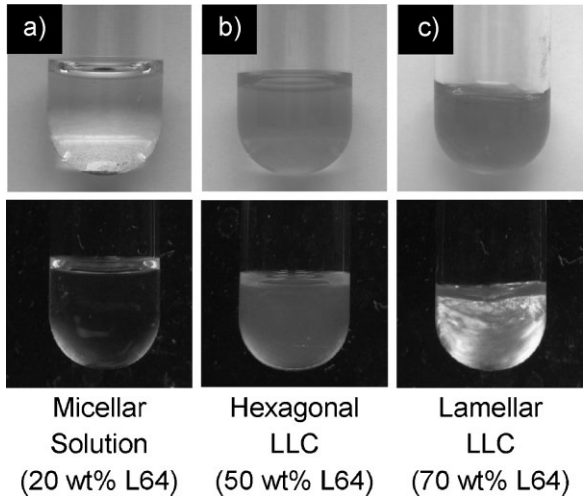

Figure 2.
Photographs, obtained under (top) normal and (bottom) polarized light, of micellar solution (a), hexagonal LLC (b) and lamellar LLC (c) samples, following the formation of gold microplates. The photographs under polarized light confirm that the isotropic micellar solution and the birefringent LLC organization are retained after the plate formation. Note that the gold microplates remain well dispersed in the LLC media.

spherical particles (~50 nm diameter). Figure 3a shows a scanning electron micrograph (SEM) of the plates formed in the micellar solution (observed using a S-4000 instrument by Hitachi, following drying of the gold colloids on an SEM sample holder). Triangular and hexagonal plates also formed in the lyotropic liquid crystal phases. In particular, gold microplates (side up to ~5 μm), smaller than those in the micellar solution, formed in the hexagonal phase (Figure 3b). The size of the microplates formed decreased further (side up to ~2.5 μm) in the lamellar phase (see Figure 3c). These results demonstrate that lyotropic liquid crystals are not required as templates for the formation of gold microplates. Moreover, the type of self-assembled structure does not affect the yield. Electron diffraction patterns obtained by aligning the electron beam perpendicular to the surface of a plate (see Figure 3c inset), reveal spots of hexagonal symmetry, indicating that these plates are single crystals bound mainly by {111} faces.[5,9]

Synthesis of triangular or hexagonal gold nanoplates similar to the ones we present here has been reported with the use of aspartate as a reductant/stabilizer,[5] photoreduction with an anionic phospholipid as a stabilizer,[6] microwave-induced reduction with polyvinylpyrrolidone as a stabilizer,[7] poly(vinyl alcohol) as a reductant/stabilizer and matrix,[8] and upon heating with polyamine as a reductant/stabilizer.[9] The nanoparticle shape control is typically attributed to an interplay between the faceting tendency of the stabilizing agent and the growth kinetics (rate of supply of Au^0 to the crystallographic planes).[3–5] For example, Shao et al. have concluded that gold plates are formed via crystal growth caused by aspartate binding to {100} facets.[5] Sau and Murphy have synthesized gold nanoparticles of multiple shapes by sequential addition of gold seeds into aqueous solutions containing $HAuCl_4$, ascorbic acid (AA) (as a reducing agent), cetyltrimethylammonium bromide (CTAB) (having no reduction activity), and in some cases a small quantity of $AgNO_3$.[4] Since CTAB molecules appear to bind more strongly to the {100} than the {111} facets,[3] the concentration ratio of CTAB to AA can control the formation and deposition of Au^0 onto either the {111} or both the {100} and {111} facets, and thus shape control (cubes and rods or octahedra, respectively) has been achieved.[4]

In our methodology that utilizes $EO_xPO_yEO_x$ block copolymers as reductants, the particle size/shape is dictated by the relationship between metal ion reduction activity in the bulk solution and on the particle surface.[34,35] The $AuCl_4^-$ reduction activity in the case of the $EO_{13}PO_{30}EO_{13}$ block copolymer that we consider here is lower (because of the shorter PEO block length) than that of other $EO_xPO_yEO_x$ block copolymers that we have previously examined,[34,35] thus $AuCl_4^-$ reduction on

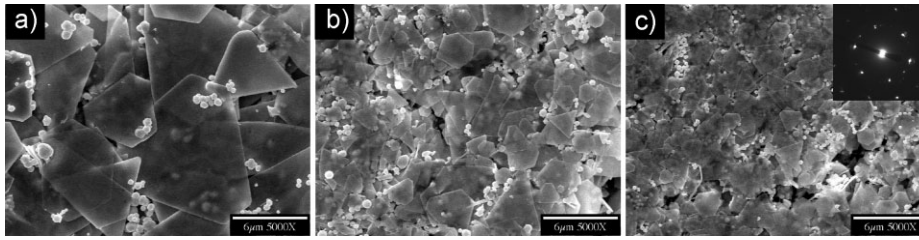

Figure 3.
SEMs of gold microplates synthesized in aqueous (a) micellar solutions of 20 wt% $EO_{13}PO_{30}EO_{13}$ block copolymers, (b) hexagonal lyotropic liquid crystal phase of 50 wt% $EO_{13}PO_{30}EO_{13}$ block copolymers, and (c) lamellar lyotropic liquid crystal phase of 70 wt% $EO_{13}PO_{30}EO_{13}$ block copolymers. The inset in (c) is an electron diffraction pattern of the microplates observed by transmission electron microscope (JEM-2010, JEOL Ltd.).

the particle surface is more significant than that in the bulk solution. This favors the growth of particles which, in the (current) case where the block copolymers prefer to adsorb on the lower atomic density {100} facets,[13] results in the formation of plates with a preferential growth direction along the {111} facets, due to $AuCl_4^-$ reduction in the vicinity of the adsorbed polymers. The decrease of the plate size with increasing block copolymer concentration is most likely due to a decrease of $AuCl_4^-$ reduction activity that is caused by the more entangled polymer conformation at higher concentrations.[34,35]

Conclusions

High-yield synthesis of gold microplates can be achieved in micellar solutions and also in lyotropic liquid crystals formed by $EO_{13}PO_{30}EO_{13}$ amphiphilic block copolymers in aqueous solutions at ambient conditions, in the absence of any external energy input, other reductant, or ionic surfactant addition. The plates formed in the liquid crystal matrix remain well dispersed for extended periods of time. The plate morphology is attributed to $AuCl_4^-$ reduction on the {100} facets (promoted by the lower reduction activity of the shorter PEO length block copolymers that adsorb there), rather than the shape-directing action of lyotropic liquid crystals as templates. These findings signify that ordered (lyotropic liquid crystal) structures formed by amphiphiles are not always necessary as templates for the formation of anisotropic nanomaterials. The work that we present here and related activities in our group[31–36,42,43] exemplify the utility of functional amphiphilic polymers for nanomaterial synthesis in a size- and shape-controlled manner.

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