Template-Directed Electrodeposition of Lamellar Platinum Nanostructures

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A simple method for electrochemical deposition of lamellar platinum nanostructure templated by lyotropic liquid crystal phase is developed. Small-angle X-ray scattering and transmission electron microscopy are used to characterize the template and deposit, respectively. Results indicate that the deposition potential and electrolyte concentration have great effects on the morphology of the product.

Because of the unique size-dependent physical and chemical properties, nanostructured materials present great promises and opportunities for a new generation of materials. Among the various preparation methods, templating synthesis is a useful approach.[1] In recent years, lyotropic liquid crystals (LLC) have been widely used as templates to obtain nanomaterials.[2–6] The formed liquid crystalline phases are of rich polymorphic structures with long-range periodicities, which can be controlled conveniently just by changing composition. Films[2] and nanowire arrays[5] have been electrochemically deposited from the normal and reverse hexagonal LLC template, respectively. To our knowledge, there is no report on the preparation of nanostructures templated from lamellar LLC by electrochemical approach, probably because of the difficulty to control the product morphology owing the high flexibility of the surfactant bilayers. In this work, we demonstrate the electrodeposition of platinum nanostructures from lamellar LLC of a nonionic surfactant, tetraethylene glycol monododecyl ether ($C_{12}EO_4$).

The template is composed of nonionic surfactant $C_{12}EO_4$ (purchased from Sigma Chemical Co.) and water as demonstrated by its well-known binary phase diagram.[6] The surfactant concentration is fixed at 50 wt %. For the template to deposit platinum nanostructures, the water phase is substituted by H_2PtCl_6 (AR, provided by Shanghai No. 1 Chemical Reagent Company) aqueous solution of different concentrations ($5.0–77.2 \times 10^{-3}$ mol/L). Electrochemical deposition experiments are conducted on a CHI604A electrochemical workstation, using a conventional three-electrode set-up, comprised of a platinum plate working electrode to which the copper grid with the Formvar support film for TEM is attached, a platinum plate counter electrode, and a saturated calomel reference electrode (SCE). The SAXS patterns of the lyotropic lamellar phases are recorded on a HMBG-SAX X-ray small-angle system (Austria) with Ni-filtered Cu Kα radiation (0.154 nm) operating at 50 kV and 40 mA. TEM images are obtained using a JEM-100 CX II transmission electron microscope operating at a voltage of 100 kV. The elemental composition of the products is analyzed on an EDAX/9100 energy dispersive X-ray (EDX) spectrometer operating at a voltage of 150 kV. All experiments are carried out at 25 °C.

Under the polarized optical microscope, all samples with different compositions are featured with oily streak texture, which is characteristic for the lamellar lyotropic phase. Figure

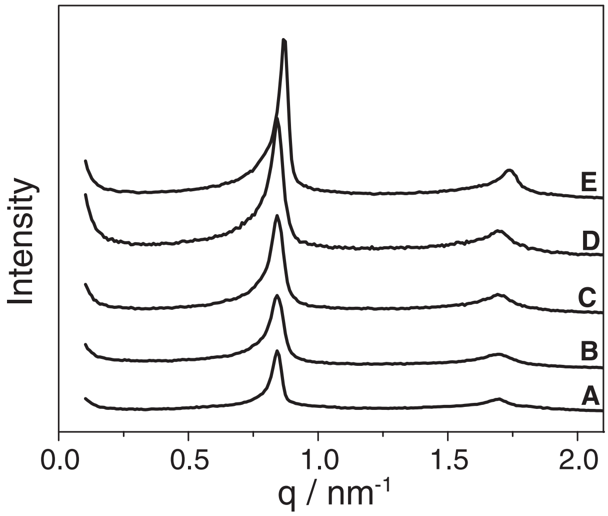

Figure 1. Typical SAXS curves of lamellar liquid crystals from 50 wt % $C_{12}EO_4$ with H_2PtCl_6 solutions of different concentrations ($\times 10^{-3}$ mol/L). (A) 5.0, (B) 10.0, (C) 19.3, (D) 38.0, (E) 77.2.

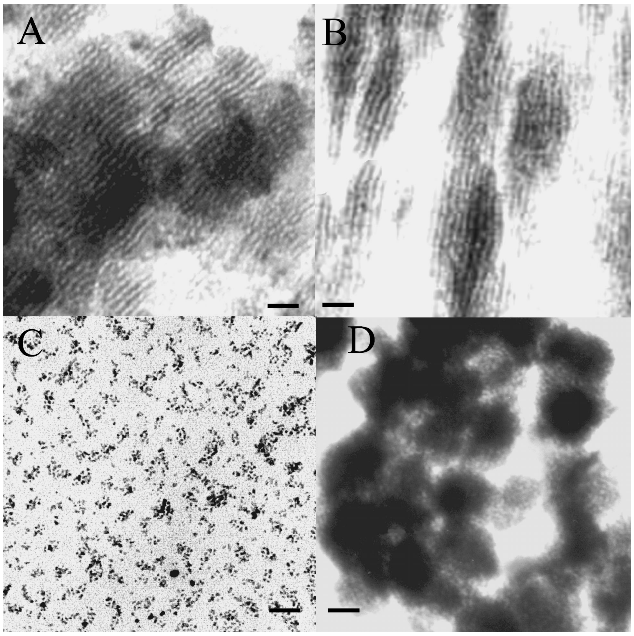

Figure 2. TEM images of products after 960 s deposition under different potentials (A) 0.2, (B), (C), and (D) 0.1 V (vs SCE) and different electrolyte concentrations ($\times 10^{-3}$ mol/L) (A), (B) 19.3, (C) 5.0, and (D) 77.2. Bar is 30 nm.

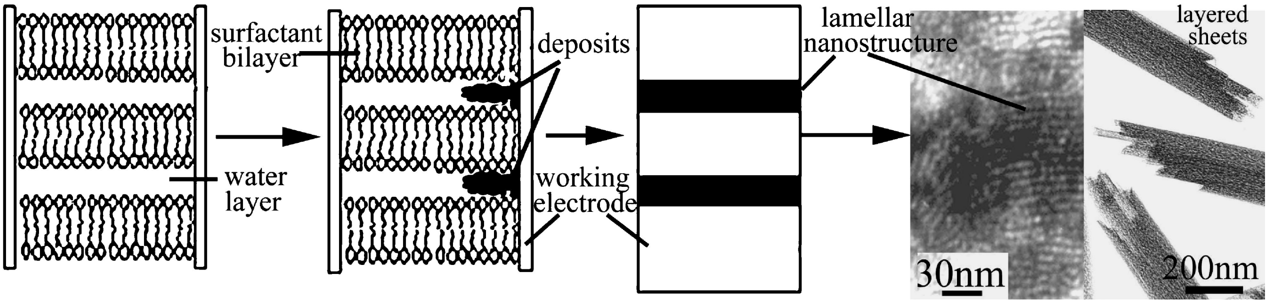

Figure 3. Schematic description of electrodeposition of lamellar platinum nanostructure templated by lyotropic liquid crystal.

1 presents the SAXS curves of the liquid crystalline phases with different electrolyte concentrations. The ratios of the scattering factors at the 1st and 2nd Bragg peaks of all samples are almost 1/2, indicating clearly that lamellar structures are kept well when the LLC are constructed with H_2PtCl_6 aqueous solution instead of water. According to Bragg equation, the typical repeat distance (d) is calculated as 7.46 nm, including the thicknesses of a surfactant bilayer and a water layer. For the sample prepared at 77.2×10^{-3} mol/L H_2PtCl_6, a shift of the scattering peaks towards the shorter d value is observed. This results from the enhanced hydration of $C_{12}EO_4$ molecules due to the interaction between $PtCl_6{}^{2-}$ anions and the oxyethylene groups, leading to a reduced repeat distance.

For the lyotropic lamellar phase consisted of H_2PtCl_6 aqueous solution (19.3×10^{-3} mol/L), potentiostatic deposition of platinum is carried out between 0.3 and −0.2 V for 960 s. In the potential range from 0.2 to 0.1 V, lamellar deposit is prepared with repeat distance of 7.0 nm or so, which is consistent with that of the template, as shown in Figure 2A (0.2 V) and Figure 2B (0.1 V). At more positive potential of 0.3 V, less reduction of H_2PtCl_6 results in the smallest amount of product. While the deposits become much thicker and the lamellar structures can only be seen from the edge of the product as the potential reaches more negative to 0 and −0.1 V. At the potential of −0.2 V, the reduction current increases quickly with disordered nanoparticles as the main products. All these results suggest that controlling the deposition potential is an important factor to obtain products replicating the template structure. The yield of deposited Pt nanostructure is evaluated both by TEM and cyclic voltammetry, indicating a best yield obtained at 0.2 V. Elemental composition analysis of the deposit by EDX spectrum confirms the metallic platinum nature.

H_2PtCl_6 concentration (C_H) also has obvious effect on the morphology of the deposits, which is studied by fixing the deposition potential and time at 0.1 V and 960 s respectively. C_H is varied from 5.0 to 77.2×10^{-3} mol/L to carry out electrodeposition. Under low C_H (5.0×10^{-3} mol/L) circumstance, there are no other deposits but separate nanoparticles obtained (Figure 2C). Increasing C_H to 10.0×10^{-3} mol/L, less regular lamellar structures are formed compared with Figure 2B. If C_H is increased further to 38.0×10^{-3} mol/L, the deposits become thicker and the lamellar structure is only kept partially. At even higher C_H of 77.2×10^{-3} mol/L, the deposits are all big disordered nanoparticles with diameter about 50 nm (Figure 2D), because of the fast reduction and aggregation of the product. Such morphology variations of the deposits can be explained as following. At low C_H (5.0×10^{-3} mol/L), the amount of the deposits is too small to form continuous structure of Pt, but leading to the formation of small nanoparticles. Increasing C_H (10.0 and 19.3×10^{-3} mol/L) is favorable for the formation of structured materials. The water layers in the templates direct the growth of products, which results in the regularly lamellar nanostructures. When C_H reaches as high as 38.0 and 77.2×10^{-3} mol/L, the reduction of Pt is fast and the flexible surfactant bilayers are not capable of controlling the growth of the products strictly in the water layers, which results in the formation of big nanoparticles far beyond water layer thickness. A schematic description of the deposition of lamellar nanostructures from the LLC template is shown in Figure 3.

In conclusion, platinum lamellar nanostructures have been electrodeposited from the LLC of the nonionic surfactant of $C_{12}EO_4$. Deposition potential and electrolyte concentration have great effects on the morphology of the products. Only by choosing suitable deposition potential and electrolyte concentration, can the nanomaterials duplicating LLC template structure be obtained.

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