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RESEARCH PAPER

Study on the Doping and Interactions of Metal Nanoparticles in the Lyotropic Liquid Crystals

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Abstract: The hydrophilic silver and hydrophobic gold nanoparticles are doped simultaneously or separately into different regions of a lyotropic liquid crystal (LLC) with long-range structural order built with the AOT/isooctane/ water ternary system. A stable lamellar hybrid is produced under suitable conditions. Polarized optical microscopy (POM) and small angle X-ray scattering (SAXS) are used to compare the phase changes upon various doping manners. The interactions between doped particles and surfactant bilayers are analyzed and compared in detail. Factors affecting the stability of inorganic/organic hybrids are also discussed. The doped hydrophobic particles affect the equilibrium of van der Waals and Helfrich interactions between them and the membranes. When hydrophilic particles are incorporated into LLC aqueous region, electrostatic force will be dominant. The results suggest that it is the balance of electrostatic, van der Waals, and Helfrich forces in the lyotropic liquid crystal that determines the hybrid structure.

Key Words: Lyotropic liquid crystal; Lamellar phase; Nanoparticles; Small angle X-ray scattering

Assembling inorganic functional nanoparticles into a two- or three-dimensional ordered structure is becoming a potential way to fabricate devices with novel chemical, optical, magnetic, and electronic properties[1]. Among techniques for such researches, templated assembling now attracts much attention because of its convenience and various patterns. Lyotropic liquid crystal (LLC) with a long-range structural order is a useful template used to assemble functional nanomaterials, because of its inherent tunability and many other useful characteristics[2−7]. Such hybrid materials may yield novel physical properties and are also very promising in view of possible technological applications[8].

In the 1990s, single-phase systems, combining a lyotropic lamellar phase and oil- or water-stabilized magnetic particles, have been described by Fabre *et al*.[9] and Menager *et al*.[10], respectively. Since then, most studies have concentrated on the ferrofluid and SDS (sodium dodecyl sulfate)[7, 9−13]. Wang *et al*.[14] and Chen *et al*.[15] attempt to direct silver nanoparticles (NPs) into the hydrophilic or hydrophobic regions of LLCs built from SDS or AOT (sodium bis-(2-ethylhexyl) sulfosuccinate), respectively. However, it is very difficult to obtain stable lyotropic lamellar systems with both aqueous and organic colloidal silver particles doped simultaneously. In the present report, to further understand the doping mechanism of metal nanoparticles in the LLC phase and to elucidate the way in which it affects the stability and the order in this complex system, we chose the lamellar LLC of AOT-water-isooctane ternary system as the matrix, to extend this pioneering work to dope silver and gold NPs, respectively, or simultaneously into different regions of LLC, and study the factors of incorporated particles affecting the stability of inorganic/organic hybrids.

1 Experimental section

1.1 Reagents and instruments

AOT, $AgNO_3$, $NaBH_4$, isooctane, and oleic acid are all A.R. grade and purchased from Aldrich. $HAuCl_4$ (A.R. grade) is from Shanghai chemical reagent Co. All reagents are used as received. The resistivity of water is more than 18 MΩ·cm. The textures of LLC are observed under Motic (Beijing, China) polarized optical microscopy. SAXS experiments are per-

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formed on an HMBG-SAX X-ray small angle system (Austria) with Ni-filtered Cu K_α radiation (0.154 nm) operating at 50 kV and 40 mA. The scattering vector, q, is defined as $q=4\pi\sin(2\theta/\lambda)$, where 2θ is the scattering angle and λ is the X-ray's wavelength. The position (q_{max}) of the first Bragg peak is related to the lamellar spacing (d), $d=2\pi/q_{max}$.

1.2 Methods

Oleate capped silver colloidal hydrosols are prepared according to Ref.[14], and gold organosols are obtained as described previously[16]. Lamellar lyotropic samples are prepared by dissolving an appropriate amount of AOT in water and adding precisely defined volumes of isooctane. When preparing the lyotropic lamellae, the hybrid systems are made spontaneously by using a silver hydrosol instead of pure water or a gold organosol instead of pure isooctane, respectively, for single doped samples, and simultaneously for dual doped samples. The ternary system of AOT-isooctane-water has a wide range of lamellar phase, however, the system allows very limited amount of isooctane in the lamellae, only around 10%–30% AOT(w)[17]. Therefore, in this study, we have selected systems with AOT composition (w(AOT)) at 15% and 25%. Considering the effect of the NPs' concentration on the hybrid samples' stability and the matching of NP sizes to spacings of the template, the concentrations of doped NPs are all 1.0×10^{-3} mol·L^{-1}, and Ag, Au NP sizes are selected at (5.6±1.9) nm and (4.5±1.7) nm, respectively[14, 18].

2 Results and discussion

2.1 POM observation

Fig.1 shows the textures of 15% and 25% AOT lyotropic liquid crystals. In Fig.1(a–d), the typical Malta cross droplets indicate the lamellar structure in these samples. Among them, Fig.1a and Fig.1d display oily-streak textures; however, the apparent luminance of Fig.1b and Fig.1c are darker, suggesting that there are some isotropic regions in the samples, i.e., their long-range orders are lower[19]. For 15% AOT liquid crystals, their repeated spacings are large, which is helpful to hold NPs. However, the larger spacings also make the AOT bilayer's undulation more influenced by the particles' doping. On the basis of the observation of the sample's texture, the order of 15% AOT liquid crystals is pure sample > dual-doped sample > doped with Ag hydrosol sample > doped with Au organosol sample.

As shown in Fig.1(e–h), liquid crystalline oily-streak textures, and apparent luminance are much clearer as AOT concentration increases, reflecting a higher long-range order of the sample's structure[19, 20]. However, there are still some dark visual fields that can be seen in the dual-doped sample, suggesting the existence of some isotropic areas in the system. From these, we can draw a rough conclusion that the arrangement of 25% AOT lyotropic phase's structural order is: pure sample > doped with Au organosol sample > doped with Ag hydrosol sample > dual-doped sample.

2.2 SAXS investigation

Fig.2(a–d) shows SAXS curves of 15% AOT liquid crystals. The first peaks of the scattering curves are obvious, whereas the second and third peaks are very weak, reflecting the imperfect lamellar structure. Nevertheless, the curves of 25% AOT samples display three distinct peaks, in Fig.2(e–h), corresponding to well-defined lyotropic lamellae. Thus, the AOT concentration's increasing of liquid crystal is favorable to the holding of the lamellar structure. The repeated distances (d) of LLCs can be calculated through $d=2\pi/q$, as shown in Table 1. The spacings of pure samples decrease obviously as the AOT concentrations increase, reflecting that the liquid crystalline structure is dominated by the content of templating agents in the samples.

According to Kotlarchyk *et al*.[21], the thickness of the water layer (d_W) in undoped liquid crystal is calculated by using a suggestion $d_W=0.098W\cdot d_S$. Wherein, W is the water/AOT molar ratio, and d_S (the thickness of the surfactant bilayer) is taken as 1.9 nm. The thickness of the organic layer (d_O) can be estimated as $d_O=d_W[w(i\text{-}C_8H_{18})/w(H_2O)]/[\rho(i\text{-}C_8H_{18})/\rho(H_2O))$[16]. In this formula, $\rho(i\text{-}C_8H_{18})$ is the density of isooctane, about 0.7 g·mL^{-1}. Therefore, the repeated distances of AOT lyo-

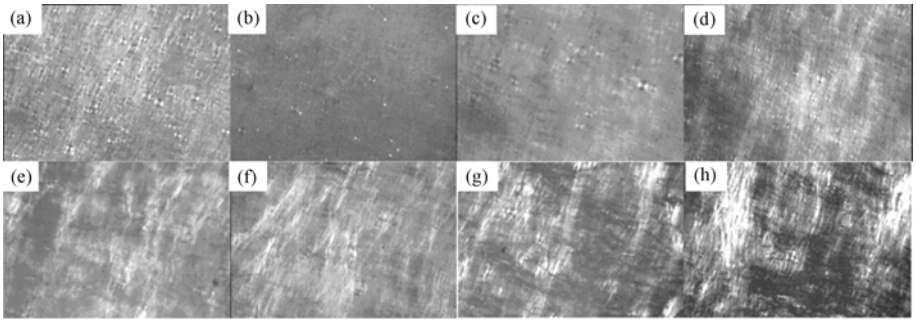

Fig.1 Textures of 15%(a–d) and 25%(e–h) AOT lyotropic lamellar phase
(a, e) pure samples; (b, f) doped with Au organosol; (c, g) doped with Ag hydrosol; (d, h) dual-doped; AOT: sodium bis-(2-ethylhexyl) sulfosuccinate