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Macroporous honeycomb films of surfactant-encapsulated polyoxometalates at air/water interface and their electrochemical properties

Peiqin Tang, Jingcheng Hao *

Key Laboratory for Colloid and Interface Chemistry, Shandong University, Ministry of Education, Jinan 250100, PR China

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ABSTRACT

A series of surfactant-encapsulated polyoxometalates which have different compositions, shapes, and sizes, are able to self-assemble to the highly ordered honeycomb-structured macroporous films at the air/water interface without any extra moist airflow across the solution surface. The honeycomb film pores in the average diameter of 2–3 μm are obtained, which are independent of the polyoxometalates. It is speculated that the cooled micrometer water droplets act as the necessary templates for the formation of macropores, and the stability of these water droplets is crucial during the self-assembly. With increasing the concentration of surfactants, various morphologies from lowly ordered honeycomb films to highly ordered honeycomb films and then to disordered fragments can be modulated. The interfacial tension between chloroform solution and water droplets induces the changes of films. High-resolution TEM observations indicate a close-packed lamellar structure in the ordered honeycomb film walls. The self-assembly successfully performs the transfer of functional polyoxometalates from bulk solutions to interfacial films. Consequently, the produced honeycomb films present electronic activities, such as ferromagnetism and electrochemical properties. These detailed researches will enrich the studies based on materials obtained by encapsulations in cationic surfactants to construct newly nanostructures of polyoxometalates at interfaces, and promote the potential applications of the honeycomb films of surfactant-encapsulated polyoxometalates in advanced materials.

Contents

1. Introduction

Producing ordered porous membranes is always the fundamental and practical hotspot. Colloidal sphere templates [1,2], emulsion templates [3,4], and other "lithograph" [5] have been used to fabricate

* Corresponding author. Tel.: +86 531 88366074; fax: +86 531 88564464.
E-mail address: jhao@sdu.edu.cn (J. Hao).

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ordered porous materials by replicating periodic structures from inorganic oxides, colloidal metal particles, and polymers. These templating methods are advantageous to construct ordered arrays with controllable pores in a long range. However, because the pores are very dependent of the templates, they are still challengeable due to the order degree of templates and the removal of templates. Self-assembly is an effective method to produce ordered aggregations and porous films in surfactant chemistry [6] and material science. In 1994, François and his co-workers firstly found that when the carbon disulphide solutions of star-shaped polystyrene or polystyrene–polyparaphenylene block copolymers were cast on the solid substrates, under a moist airflow across the solution surface, polymers could self-assemble to the ordered porous patterns with the macropores in a hexagonal array after the solvent evaporation [7]. It has also been reported that some other star-like polymers [8,9], block copolymers [10–12], ligand-stabilized metal nanoparticles [13–15], and the newly investigated surfactant-encapsulated polyoxometalates [16] are able to self-assemble to ordered honeycomb films on solid substrates with a very necessary moist airflow across the solution surface. And the humidity is strongly influential on the self-assembly to honeycomb films.

Polyoxometalates (POMs) are novel inorganic macromolecules, which are in varieties of compositions, shapes, and nanoscaled sizes [17–21]. Furthermore, POMs are unique in their topological and electronic versatility, such as photoluminescence [22,23], magnetism [24–26], and electrochemical properties [27–29]. Thus POMs are attractively investigated in catalysis [30], medicine [31], molecular materials [32], and other applications [33]. In general, POMs are dissoluble and exist as giant ions in polar solvents. The oppositely charged surfactants or polyelectrolytes can electrostatically interact with POMs, and producing the hydrophobic surfactant-encapsulated polyoxometalates (HSEPs) complexes [34–36] which are novel inorganic–organic capsules with the head groups of surfactants interacting with POMs and the external hydrocarbon chains. It improves the stability and the solubility of POMs in nonpolar solvents by the surface modification [37]. Furthermore, it changes the surface properties of POMs so as to realize the integration of multifunctional POMs into ordered three-dimensional aggregations [38–40] and thin films. The thin films containing POMs has been extensively investigated by using layer-by-layer (LbL) self-assembly [41–44], Langmuir–Blodgett (LB) techniques [45–48], and solvent-casting method [49,50]. Very recently, a simple self-assembly has been reported by our previous work [51–53] that the ordered porous honeycomb films of surfactant-encapsulated POMs were fabricated by the solvent evaporation at the air/water interface without any extra moist airflow across the solution surface. However, whether the polyoxometalates with different shapes and sizes will influence the macropores of honeycomb films or not, the experimental proof of the formation of macropores templated by micrometer water droplets during the self-assembly, the detailed analysis for different film morphologies with increasing the concentrations of surfactants, the microstructure of the honeycomb films, and in particular, the functionally electronic properties of the honeycomb films based surfactant-encapsulated polyoxometalates always attract much attention and should be thoroughly investigated.

It is relatively young for studies of the honeycomb films containing polyoxometalates. However, polyoxometalates and porous films are all important to construct advanced materials. Herein, colloidal surfactants are introduced to successfully transfer the functional polyoxometalates to porous honeycomb films. A series of surfactant-encapsulated POMs are investigated by drop-casting their chloroform solutions onto the air/water interface without any extra moist airflow across the solution surface. It is thought that, at the air/water interface, the relative humidity of chloroform solution surface should be very high and enough to provide much water vapor around the solvent interface, which is useful to create a humid environment. Then the honeycomb films and their magnetic and electrochemical properties are detailedly investigated. These researches enrich the newly developed polyoxometalates chemistry, will promote the knowledge of the self-assembly of surfactant-encapsulated polyoxometalates. Furthermore, the electronic properties of honeycomb films containing nanoscaled polyoxometalates indicate that the honeycomb films of surfactant-encapsulated polyoxometalates are potentially applicable in the fields of catalysis and advanced materials.

2. Experimental section

2.1. Chemicals

The polyoxometalates crystals, including sandwich-shaped $\{Mn_2Bi_2W_{20}\}$ with a formula of $Na_6(NH_4)_4[(Mn(H_2O)_3)_2(WO_2)_2(BiW_9O_{33})_2]$ and the short axis diameter of 1.3 nm [17], ring-shaped $\{Mo_{154}\}$ with a formula of $Na_{15}[Mo_{154}O_{462}H_{14}(H_2O)_{70}]_{0.5}[Mo_{152}O_{457}H_{14}(H_2O)_{68}]_{0.5}$ ca.400 H_2O and the ring diameter of 3.6 nm [18], "Keplerate" spherical $\{Mo_{132}\}$ with a formula of $(NH_4)_{42}[Mo_{132}O_{372}(CH_3COO)_{30}(H_2O)_{72}]$ 300 H_2O 10 CH_3COONH_4 and the diameter of 2.9 nm [19], and hedgehog-shaped $\{Mo_{368}\}$ with a formula of $Na_{48}[H_xMo_{368}O_{1032}(H_2O)_{240}(SO_4)_{48}]$ ca.1000 H_2O, $x \approx 16$, and the long axis diameter of ~6 nm [20], were synthesized as described in the literatures. And a smaller Keggin heteropolytungstate $\{PW_{12}\}$ with a formula of $H_3PW_{12}O_{40}$ [21] was purchased from supplier. Dioctadecyldimethylammonium chloride ($C_{38}H_{80}ClN$, DODMACl) was purchased from Fluka. Triple-distilled water was used.

2.2. Preparation of honeycomb films at air/water interface

These POMs are able to dissolve in aqueous solutions to ionize nanoscaled giant anions and countered by small cations, such as Na^+, NH_4^+, and H^+. $\{Mn_2Bi_2W_{20}\}$ and $H_3PW_{12}O_{40}$ are stable in water and in acid solutions. However, due to the Mo^V in the composition of $\{Mo_{154}\}$, $\{Mo_{132}\}$, and $\{Mo_{368}\}$, the bubbling of pure nitrogen to expel oxygen is needed to prepare solutions. The freshly prepared aqueous solutions of POMs ($1.0\ mg\ mL^{-1}$, but $c_{\{Mo132\}} = 2.0\ mg\ mL^{-1}$, $c_{\{Mo368\}} = 0.5\ mg\ mL^{-1}$) were used. A series of solutions of DODMACl (0–$20\ mg\ mL^{-1}$) in chloroform (5.0 mL) were mixed with aqueous solutions of POMs (5.0 mL), respectively. Subsequently, the samples were stirred for 10 min to completely react. Then the samples were sealed and equilibrated at 25.0 ± 0.1 °C. After the complete phase separation, an amount of chloroform solution was dropped onto a calm pure water surface by using a microinjector. Finally, the thin architectures of $DODMA^+$-encapsulated POMs were self-assembled after the evaporation of chloroform. These films were directly transferred onto the analytical solid substrates by carefully dipping these substrates under the films and pulling them out of water. They were carefully dried by pure nitrogen for measurements. In addition, the precipitates of $(DODMA)_{10}\{Mn_2Bi_2W_{20}\}$ complexes were prepared by mixing $\{Mn_2Bi_2W_{20}\}$ and DODMACl at the molar ratio of 1:10. $(DODMA)_3\{PW_{12}\}$ complexes were prepared by mixing $\{PW_{12}\}$ and DODMACl at the molar ratio of 1:3. Then the precipitates were separated and dried for use, respectively.

2.3. Characterization of honeycomb films

Surface tension measurements of the upper water phases and the lower chloroform phases of the above prepared samples were performed on a Processor Tensiometer-K12 (Krüss Company, Germany) using the plate method at 25 °C. The morphologies of the prepared films were observed on a transmission electron microscope (TEM, JEM-100CX II, JEOL) at an acceleration voltage of 100 kV, a field-emission scanning electron microscope (SEM, JEOL JSM6700F), an atomic force microscope (AFM, Digital Instruments, NanoScope IIIa) in a contact mode, and an optical microscope (OM, Zeiss, Axioskop 40). High-resolution transmission electron microscopy (HRTEM) images were observed at an acceleration voltage of 200 kV (JEM-2010, JEOL)