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Self-patterning porous films of giant vesicles of $\{Mo_{72}Fe_{30}\}(DODMA)_3$ complexes as frameworks

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ABSTRACT

This work describes the preparation and properties of self-patterning porous films consisting of giant vesicles formed by a 2.5-nm-diameter, polyoxometalate (POM) cluster $\{Mo_{72}Fe_{30}\}$ macroanion, and a double-tailed cationic surfactant dimethyldistearylammonium bromide (DODMABr) in $CHCl_3$–CH_3OH mixture solvent (V_{CHCl3}: V_{CH3OH} = 3:1). These inverse vesicles with the diameter in the range of 0.45 ~ 1.3 μm in organic solution and the porous films consisting of the giant vesicles of the $\{Mo_{72}Fe_{30}\}(DODMA)_3$ complexes were characterized by SEM, TEM, XPS and AFM observations. Self-patterning of these giant vesicles into porous films that are highly ordered honeycomb films on solid surfaces can survive drying as the frameworks are firstly studied in detail. Water contact angle measurements proved that the porous films of $\{Mo_{72}Fe_{30}\}(DODMA)_3$ vesicles were endowed hydrophobic property from the hydrophilic surface. This porous film materials consisting of giant vesicles may be promising new options in many fields like photoelectrochemistry, sterilization, template, catalysis, in-situ synthesis.

1. Introduction

Because of the intriguing, well-defined, and highly symmetrical structures, inorganic polyoxometalates (POMs) [1], have attracted great attention. The POMs, a class of nanoclusters formed by transition metal, Mo, W, V, Cr, Fe, etc. oxide polyhedrals as building blocks, having uniquely physical and chemical properties, were extensively studied in many fields like catalysis, electrochemistry, photoresponse, biomedicine, template [1–8]. Considering their surface water ligand and inherent charge, POMs are very soluble in water to release small counterions such as Na^+, NH_4^+, etc. A typical example is the 2.5-nm-diameter, "Keplerate" $\{Mo_{72}Fe_{30}\}$ anion ($Mo_{72}^{VI}Fe_{30}^{III}O_{252}L_{102}\cdot xH_2O(x = 180, L = H_2O, CH_3COO^-, Mo_2O_{8/9}^{n-})$, $\{Mo_{72}Fe_{30}\}$ clusters exist as almost neutral molecules in crystal, but in water they behave like a weak acid: the water ligands attached to the Fe^{III} centers tend to partially deprotonate, thus making $\{Mo_{72}Fe_{30}\}$ clusters slightly negatively charged, i.e., carrying differently localized charges with the pH. The degree of deprotonation depends on the solution pH [9,10]. The hydrophilic POM surfaces can be adjusted to be hydrophobic by forming surfactant-encapsulated clusters (SECs), through encapsulating the inorganic macroanions with a protective shell of water-soluble cationic species (such as surfactants) via electrostatic forces [11].

Cationic species like surfactant, dioctadecyldimethylammonium bromide (DODMABr), having hydrophobic double-chain to dissolve in organic solvents can encapsulate $\{Mo_{72}Fe_{30}\}$ macroanions in water to transfer in organic solution for forming $\{Mo_{72}Fe_{30}\}$/DODMABr complexes. These organic–inorganic nanoscale hybrids can change the surface property of POMs to be hydrophobic in behavior. These complexes still retain amphiphilic property to dissolve in organic solvents and self-assemble to form various ordered aggregates such as thin hybrid films [12], vesicles [13], liquid crystals [14,15], gels with the structures of fibers [16], and so on. Among them, vesicles had attracted widespread attention because of their wide applications in drug delivery and release, synthesis of materials using vesicles as soft templates, etc. For example, the 2013 Nobel Prize in Physiology and Medicine was awarded to James E. Rothman, Randy W. Schekman and Thomas C. Südhof because of "their discoveries of machinery regulating vesicle traffic, a major transport system in our cells." Generally, vesicles were formed by amphiphilic molecules such as phospholipids, surfactants or their mixtures in aqueous solution. The structure of these vesicles could usually be destroyed once they were out of the water [17]. In recent years, our group and other researchers had fabricated successfully solid vesicles after evaporation of the solvent [18]. In organic solvents, those vesicles were formed by amphiphilic compounds of metal [19] or complexes of POMs and ordinary surfactants [9] or polymers [20]. Because their structural rigidity was improved, it could extend the application ranges of these vesicles.

Along with the much higher demands of film materials with specific functions, the research of organic–inorganic composite films have attracted great attention. Because of their unique structures and properties, POMs are often used to fabricate single- or multi-layer films in

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which surfactants or polymers were used as composite components [21–25]. To the best of our knowledge, very few self-assembled three-dimensional structures of the complexes of POMs and organic components were used to fabricate films as building blocks. Wu et al. fabricated honeycomb porous films using vesicles formed by surfactant-encapsulated clusters of $(DODA)_4H[Eu(H_2O)_2SiW_{11}O_{39}]$ [11]. The TEM images show that a few vesicles remaining in certain regions of the films were larger in volume and better in stability than those of the disappeared ones. Thus, to increase vesicle volume and stability as building blocks of films become the principal focus of research workers.

2. Experimental section

2.1. Chemicals and materials

$CH_3COONH_4{\cdot}4H_2O$ and $N_2H_4{\cdot}H_2SO_4$ were purchased from Kermel Co., Tianjing, China. Dioctadecyldimethylammonium bromide (DODMABr) was purchased from Fluka Co., USA. $CHCl_3$, and CH_3OH were purchased from Sinopharm Chemical Co. Ltd., China. $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, CH_3COOH, $FeCl_3{\cdot}6H_2O$, $CH_3COONa{\cdot}3H_2O$, HCl, NaCl, $CHCl_3$, and CH_3OH were purchased from Sinopharm Chemical Co. Ltd., China. Both carbon-coated copper grids and single-crystal silicon slides were purchased from Beijing Xinxing Braim Technology Ltd., Beijing, China. Ultrapure Millipore water with a resistivity of 18.25 MΩ cm was used in the preparation of aqueous solution. $Mo^{VI}{}_{72}Fe^{III}{}_{30}O_{252}L_{102}{\cdot}180H_2O$ ($L = H_2O/CH_3COO^-/Mo_2O^{n-}{}_{8/9}$), ab. $\{Mo_{72}Fe_{30}\}$, was synthesized according to the literature [26,27]. All chemicals were directly used without further purification.

2.2. Synthesis of nanometer molecules $\{Mo_{132}\}$ and $\{Mo_{72}Fe_{30}\}$

0.8 g $N_2H_4{\cdot}H_2SO_4$ was weighed to be added in 250 mL aqueous solution of 5.6 g $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ and 12.5 g CH_3COONH_4. The solution was then stirred for 10 min and 83 mL 50% CH_3COOH was subsequently added. The reaction solution with green color was stored in an open 500 mL Erlenmeyer flask at 20 °C without further stirring. After 4 d, the red–brown precipitated crystals were filtered off over a glass frit, washed with 90% ethanol, water-free ethanol, diethyl ether, and finally dried in air. The compound, $(NH_4)_{42}\{(Mo^{VI})Mo^{VI}{}_5O_{21}\{Mo^{V}{}_2O_4(CH_3COO^-)(H_2O)_6\}_{12}\{[Mo^{V}{}_2O_4(CH_3COO)]^+\}_{30}$, ab. $\{Mo_{132}\}$, was obtained.

1.4 g $\{Mo_{132}\}$ cluster was added to a stirred orange–red solution of 1.1 g $FeCl_3{\cdot}6H_2O$ and 1.1 g $CH_3COONa{\cdot}3H_2O$ in 75 mL H_2O. The resulting mixture was vigorously stirred in an open 100 mL Erlenmeyer flask (wide-necked) for 24 h. After acidification with 1 mL 1 mol L^{-1} HCl, 2.0 g NaCl was added, and the stirred reaction mixture was heated up to 90–95 °C, then filtered while still hot. The golden yellow filtrate was cooled down to 20 °C. Rhombic crystals of $\{Mo_{72}Fe_{30}\}$ with yellow color can be produced over a period of 2–3 d. The crystals were recovered by filtration through a glass frit, washed twice with a little iced water, and dried in air.

2.3. Preparation of $\{Mo_{72}Fe_{30}\}(DODMA)_3$ giant inverse vesicles

A stock solution of 8 mg mL^{-1} $\{Mo_{72}Fe_{30}\}$ was prepared by dissolving a certain amount of $\{Mo_{72}Fe_{30}\}$ in water. An amount of double chain cationic surfactant, DODMABr, was dissolved in $CHCl_3$-CH_3OH solvent (V_{CHCl3}: V_{CH3OH} = 3:1) and the concentration was 1 mg mL^{-1}. Three different volumes of 8 mg mL^{-1} $\{Mo_{72}Fe_{30}\}$ solution, 0.3 mL, 0.45 mL and 0.6 mL, were dropped on the top of 4 mL 1 mg mL^{-1} DODMABr organic solution, respectively. The three samples were mixed thoroughly and left for separation into two phases, and the organic phase was then put in an incubator (20 °C) for 3 weeks. The complexes of $\{Mo_{72}Fe_{30}\}(DODMA)_3$ in the $CHCl_3$–CH_3OH mixed solvent can self-assemble into vesicles.

2.4. Synthesis of porous films with $\{Mo_{72}Fe_{30}\}(DODMA)_3$ vesicles as building blocks

The porous films were prepared by breath figure method on the surface of single-crystal silicon. 10 μL three organic solutions of vesicles of $\{Mo_{72}Fe_{30}\}(DODMA)_3$ complexes which were formed by different volumes of 8 mg mL^{-1} $\{Mo_{72}Fe_{30}\}$ equilibrated with 4 mL 1 mg mL^{-1} DODMABr organic $CHCl_3$–CH_3OH (3:1) solution dropped onto the surface of the single-crystal silicon using a microinjector. The silicon wafer was placed in an atmosphere of nitrogen with a relative humidity of 80% adjusted by the flow rate of the nitrogen gas flow. After 3 min, the films were taken out and dried at room temperature. The porous films on a single-crystal silicon wafer can be obtained.

2.5. Characterizations of the giant inverse vesicles of $\{Mo_{72}Fe_{30}\}(DODMA)_3$ complexes in organic solvent and the porous films

A field-emission scanning electron microscope (FESEM, JEOL JSM6700F) was used to characterize the giant inverse vesicles of $\{Mo_{72}Fe_{30}\}(DODMA)_3$ complexes and the porous films. 5 μL organic solution of the vesicles of $\{Mo_{72}Fe_{30}\}(DODMA)_3$ complexes was directly dropped onto the single-crystal silicon wafer. X-ray spectroscopy (EDX) is carried out in the FE-SEM. The porous films of $\{Mo_{72}Fe_{30}\}(DODMA)_3$ complexes were fabricated on the single-crystal silicon wafer by using the breath figure method. All the samples were dried at room temperatures before testing. The morphology and microstructure of the samples were characterized using a JEOL JEM-1400 transmission electron microscope (TEM) and a JEOL JEM-2100F high-resolution transmission electron microscope (HR-TEM). All the samples were prepared on carbon-coated copper grids by the same method used for FE-SEM observations. The samples were irradiated with infrared light for 30 min and the solvent completely evaporated before measurements. Atomic force microscopic (AFM) IIIa (Digital Instruments) measurements were used in tapping mode (TM) with NSC35/Al BS silicon tips of a cantilever length 90 μm and a resonance frequency of 240–405 kHz. Water contact angle images of the film surface were captured at room temperatures with a CCD camera and the films were prepared on the glass slide.

2.6. Determination of composition of $\{Mo_{72}Fe_{30}\}$/DODMABr complexes

The molecular formula of $\{Mo_{72}Fe_{30}\}$ is $[Mo_{72}Fe_{30}O_{252}(CH_3COO)_{12}\{Mo_2O_7(H_2O)\}_2\{H_2Mo_2O_8(H_2O)\}(H_2O)_{91}]{\cdot}$ca.$150H_2O$ [28] with a molecular mass $M_{\{Mo72Fe30\}}$ = 18,644.8. So if an aqueous solution of 8 mg mL^{-1} $\{Mo_{72}Fe_{30}\}$ in a solution has a pH value of 2.91, then the number of H^+ given by each $\{Mo_{72}Fe_{30}\}$ can be calculated according to the following formula

$$\frac{10^{-2.91}}{8/18644.8} = 2.9 \quad (1)$$

Each $\{Mo_{72}Fe_{30}\}$ gives out about three protons and takes a net negative charge of three, so the composition of $\{Mo_{72}Fe_{30}\}$/DODMABr complexes could be calculated to be $\{Mo_{72}Fe_{30}\}(DODMA)_3$.

3. Results and discussion

We report a conceptually new fabrication for the complexes of a Keplerate-type polyoxomolybdate, $\{Mo_{72}Fe_{30}\}$, and a double-chain cationic surfactant DODMABr to produce the giant inverse vesicles in organic solvent (Fig. 1A). A certain amount of $\{Mo_{72}Fe_{30}\}$ in an aqueous solution was transferred by cationic $DODMA^+$ via electrostatic forces to form $\{Mo_{72}Fe_{30}\}$-$DODMA^+$ complexes in the $CHCl_3$–CH_3OH (3:1) mixed solution. The $\{Mo_{72}Fe_{30}\}(DODMA)_3$ complexes which was calculated can form giant inverse vesicles by self-assembly in the mixed