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In situ photopolymerization and photophysical properties of a surfactant-encapsulated polyoxometalate in casting film

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ABSTRACT

In this paper, we constructed an ordered self-organized film possessing a well-defined layered structure by using a polymerizable surfactant-encapsulated polyoxometalloeuropate, $(DMDA)_9EuW_{10}O_{36}$ (DMDA: dodecyl(11-methacryloyloxyundecyl)dimethylammonium bromide). The in situ polymerization of the film through UV irradiation was investigated by using ^1H NMR and FTIR spectra, and X-ray diffraction. The results show that 68% of the monomers that connect to the complex in the film have been polymerized at the utmost. In contrast to the virgin layered structure of the casting film which possesses a layer spacing of 2.7 nm, the layer thickness increases to about 3.3 nm after the in situ polymerization. The lifetime and the quantum yield of the polyoxometalate in the casting film were found to increase due to the change of the layered structure after in situ polymerization. Thus, the present results provide an effective way to tune the photophysical properties of the film through alteration of the layered structure. In the meantime, the stability of the casting film in the alkaline solution was improved after in situ polymerization.

1. Introduction

Polyoxometalates (POMs) are discrete, molecularly defined, inorganic metal–oxygen clusters with sizes ranging from approximately one to several nanometers. These clusters exhibit various topologies and diverse chemical and electronic properties, leading to potential applications in catalysis, optics, magnetism, medicine, and biology [1–3]. However, the application of these inorganic clusters in functional materials and thin film devices remains a challenge because of their inherent limitations, such as the poor processibility as inorganic crystalline or powdered materials and the incompatibility in weak polar organic solvents. Therefore, the development of suitable methods and technologies to protect and utilize POMs has become a focus topic in POM chemistry. An effective strategy is to introduce POMs into organic matrices through ion-replacing reaction; i.e., the cationic surfactants can replace the counterions of POMs, forming surfactant-encapsulated clusters (SECs) [4–6]. In this way, the surface of POM is covered with an organic component, so that not only is the solubility of POMs promoted in regular organic solvents, but also well-ordered thin films can be easily prepared by solvent casting and LB techniques [7–9]. Furthermore, some inherent properties of POMs are well kept and directly associated with their aggregated structures in various assemblies [6,7,10]. For example, the change of layered structure can be employed to regulate the photophysical properties of Eu^{3+}-containing SECs [10]. The previous results suggest the possibility of assembling SECs into various matrices such as silica sol–gel [11], polymer [9], and liquid crystal [12] systems by an appropriate modification of organic components covered on the surface of POMs. And the introduced matrices can effectively protect POMs from outside etching, which can greatly improve the stability of POMs against solution pH and electrolytes [11]. It is especially important to fabricate the antietching ordered ultrathin film, as it is helpful for developing potential applications in corrosion-resistant coatings of metal surfaces [13].

To obtain more stable structure-controlled ultrathin films, we herein report an effective method for the construction of polymerized organized film of a polymerizable surfactant-encapsulated cluster (P-SEC) by simply solvent casting and following photo-induced polymerization, as shown in Scheme 1. The reason that we selected a typical luminescent POM, $Na_9EuW_{10}O_{36}$, is that it possesses the highest quantum yield among the known luminescent POMs [14], and its complex LB film and casting film have been well examined [10,15,16]. By using X-ray diffraction (XRD), ^1H NMR, Fourier transform infrared (FTIR), and emission spectra, we characterized the relationship of the assembly structure with photophysical properties of the organized casting film before and after the in situ polymerization through UV light irradiation. We further compared the stability of the casting film before and after polymerization in water and sodium hydroxide solution. The present investigation provides a simple and effective route for con-

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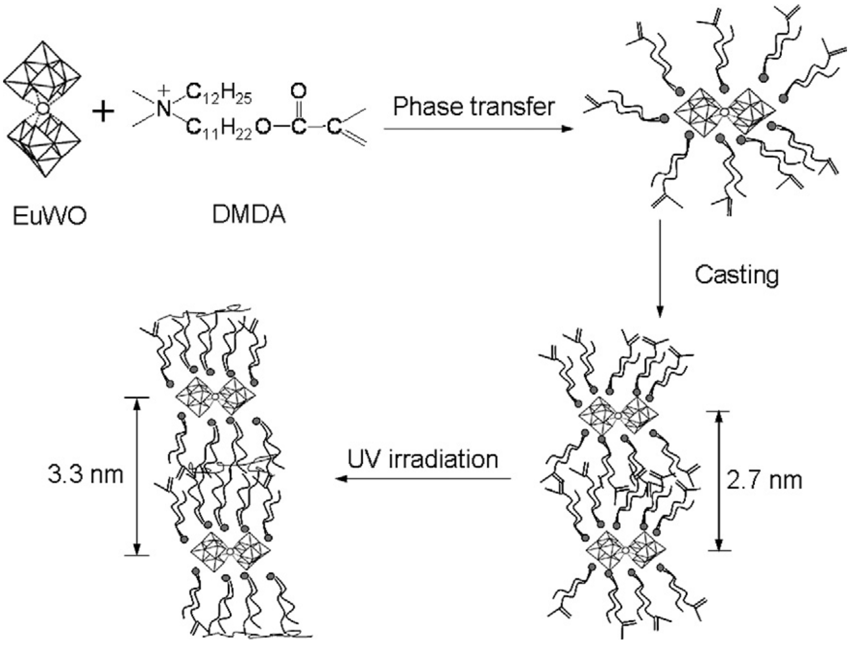

Scheme 1. Schematic illustration of the preparation of the hybrid complex and the packing structure of P-SEC in its casting film before and after in situ polymerization.

trolling the photophysical properties and the stability of the P-SEC ultrathin film.

2. Materials and methods

2.1. Materials

The polymerizable surfactant, dodecyl(11-methacryloyloxyundecyl)dimethylammonium bromide (DMDA), and luminescent POM, $Na_9EuW_{10}O_{36}\cdot 32H_2O$ (EuWO), were prepared according to a published procedure [9,14]. The polymerizable surfactant-encapsulated cluster, P-SEC, was synthesized as described in the previously reported procedure [9].

2.2. Characterization

FTIR spectral measurements were performed on a Bruker VERTEX 80V FTIR spectrometer equipped with a MCT detector (512 scans), which were recorded with a resolution of 4 cm^{-1}. XRD was carried out on a Rigaku X-ray diffractometer (D/max rA, using Cu$K\alpha$ radiation at a wavelength of 1.542 Å), and the data were collected from 0° to 10°. Luminescent measurements were performed on a HITACHI F-4500 Fluorescence spectrophotometer. The luminescent lifetimes were recorded on a Spex 1934D phosphorescence spectrophotometer. ^{1}H NMR spectra with tetramethylsilane as internal reference were recorded on a Bruker UltraShield 500 MHz spectrometer.

The in situ polymerization experiment was carried out using a 300-W high-pressure Hg lamp as the light source in an hour at room temperature. The distance between the lamp and the samples was kept at 10 cm. The samples were maintained in contact with air during irradiation.

3. Results and discussion

3.1. Aggregated structure and photophysics of P-SEC in casting film

We investigated the aggregated structure of the P-SEC in casting film by employing FTIR spectroscopy, an effective tool for examining the molecular structure and dynamics of alkyl chains with high sensitivity [17]. As shown in Fig. 1A, the bands at 2924 and 2852 cm^{-1} are assigned to the antisymmetric (d^-) and symmetric (d^+) stretching vibrations of the methylene group, respectively. It is well known that d^- and d^+ bands are strong indicators of the chain conformation: low wavenumbers (2915–2918 and 2846–2850 cm^{-1}) of the bands are characteristic of highly ordered alkyl chains [18], while their upward shifts (2924–2928 and 2854–2856 cm^{-1}) are indicative of the increase in gauche conformers, implying that the alkyl chains conformation tends toward disorder. On the basis of this regularity, the observed frequencies at 2924 and 2852 cm^{-1} for the casting film of P-SEC at room temperature reveal the presence of relatively disordered alkyl chains though they are not completely disordered. In the previous research results [19], we have reported that the order of the alkyl chains conformation in the patterned thin film of SECs is associated with the chain number and chain length on the surface of POMs. Smaller alkyl chain number and shorter chain length on the SECs normally make the alkyl chains disordered. For all casting and LB films of EuWO encapsulated by the surfactants with simple double long alkyl chains such as dioctadecyldimethylammonium cation (DODA), the alkyl chains are ordered [10]. In the present case, although the methacryloyl is chemically connected to the terminal of undecyloxy chain, longer than the other chain (dodecyl) of DMDA, the increase of gauche conformation in P-SEC casting film should be mainly derived from the distortion due to the introduction of methacryloyl group at the terminal of alkyl chains,

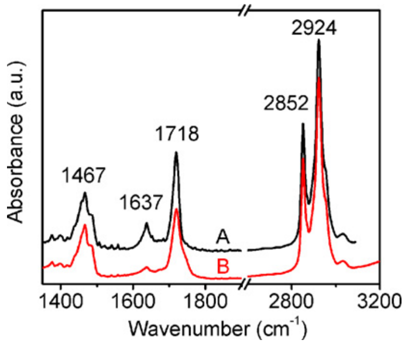

Fig. 1. FTIR spectra of the P-SEC casting film (A) before and (B) after UV light irradiation.