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Effect of glucose on self-assembly of free-standing air–water interfacial lamellar ZrO_2 films

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ABSTRACT

A series of free-standing air–water interfacial ZrO_2 films have been self-assembled, using sodium dodecyl sulfonate (SDS) as template, glucose (Glu) as cosurfactant and zirconium(IV) butoxide as precursor. The formed nanostructures of ZrO_2 films have been carefully characterized by X-ray diffraction (XRD) and transmission electron microscope (TEM). Results show that the as-prepared ZrO_2 films display significant structural changes by adjusting the mass ratios of Glu to SDS. An architectural model based on SDS packing and charge-density matching has been proposed to illustrate the effect of Glu on various self-assembled nanostructures of ZrO_2 films.

1. Introduction

Nanocomposite functional films based on inorganic/organic hybrids have drawn much attention due to their attractive properties of the mechanically and thermally stable inorganic framework and the flexibility and special chemical activity of organic species. In order to gain high-ordered nanostructures and excellent physical and chemical properties for these inorganic/organic nanomaterials, a soft chemistry preparation method named self-assembly [1–3] has created a great deal of interest. In particular, the template-directed self-assembly technology has been established to be an effective strategy for the design of a variety of well-ordered nanostructures for inorganic/organic films. A number of anionic, cationic and nonionic surfactants have been employed to direct the self-assembly of metallic oxide/surfactant films. Ozin and co-workers [4] first reported free-standing and oriented air–water interfacial mesoporous silica films templated by an cationic surfactant of $CH_3(CH_2)_{15}N(CH_3)_3Cl$. As well, Yang [5,6], Zhao [7–9] and Stucky [10,11] did a lot of work on self-assembly of surfactant-templated amorphous and crystalline metallic oxide/surfactant hybrid films, e.g. TiO_2, ZrO_2 and SnO_2. In addition, White [12–14] prepared a series of surfactant-directed air–water interfacial silica films with high-periodic nanostructures. In our previous work, we synthesized many kinds of free-standing air–water interfacial metallic oxide/anionic surfactant films by the similar self-assembly method. Those prepared films displayed periodic nanostructures with different curvatures, e.g. lamellar [15,16], multiring [17–19] and mesoporous structures [20]. It was found that some employed cosurfactants (e.g. gelatin) had great influence on the formed nanostructures of the self-assembled films.

Recently, glucose (Glu) has been chosen as a promising candidate for the structural modification of free-standing metallic oxide/surfactant films, owing to its capability to form hydrogen bonds with the organic functional groups. By hydrogen-bonding interactions, Glu successfully directed the self-assembly of polymer nanotubes [21] and induced the helicity of foldamer gelators [22]. Additionally, it was reported by Wei et al. [23] that the hydrogen-bonding interactions between Glu and tetraethyl orthosilicate resulted in mesoporous sol–gel silica materials. Accordingly, Glu is expected to change the nanostructures of surfactant-templated metallic oxide films, but there are few work focused on this interesting research.

In this work, a series of free-standing air–water interfacial ZrO_2 films templated by the composite of sodium dodecyl sulfonate (SDS) and glucose (Glu) will be prepared by a self-assembly method. The effect of Glu on self-assembled nanostructures of ZrO_2 films will be discussed in detail.

2. Experimental

2.1. Chemicals

Zirconium(IV) n-butoxide ($Zr(OC_4H_9)_4$, Alfa Aesar), sodium dodecyl sulfonate (SDS, Alfa Aesar, 99%), chlorhydric acid (Nanjing chemical reagent Co., Ltd., 36–38%) and D-(+)-glucose (Sinopharm

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Chemical Reagent Co., Ltd., AR) were used as purchases without any further treatment. Deionized water was used for all manipulation.

2.2. Preparations

Preparation for ZrO_2 films was as follows. It should mention that the added SDS mass was a fixed value of 0.15 g and a number of mass ratios of Glu to SDS (Glu/SDS) were controlled at 1/1, 4/3, 2/1, 3/1 and 4/1, respectively. Take the self-assembly of ZrO_2 film with Glu/SDS (1/1) for example. First, 0.15 g sample of SDS and 0.15 g of Glu were mixed with 18.4 ml deionized water in a 25 ml beaker by magnetically stirring at 40 °C for 10 min, resulting in the template solution. Meanwhile, 0.84 g of zirconium(IV) n-butoxide, 0.64 ml of HCl and 2.0 ml of H_2O were mixed in a 10 ml beaker by stirring for 5 min, leading to the transparent precursor solution. Then, the precursor solution was first transferred to a Petri dish with a diameter of 90 mm and a depth of 10 mm and subsequently, the template solution was added as a coating. After keeping under static conditions at 21 °C for a growth time of 12 h, the free-standing white ZrO_2 film could be clearly observed at the air–water interface. In addition, a comparison experiment was carried out for SDS-templated ZrO_2 film by the similar self-assembly process. For further investigation of Glu effect, the SDS mass was increased to 0.3 g and two kinds of Glu/SDS mass ratios were chosen at 1/1 and 2/1, respectively. The preparation for these ZrO_2 films was as the same as the described self-assembly process for ZrO_2 film templated by Glu/SDS (1/1).

2.3. Characterizations

The self-assembled ZrO_2 films were transferred to glass substrates and dried for 24 h and then, the substrates were directly detected by X-ray powder diffraction (XRD) with a Bruker D8 Advance diffractometer, using monochromatic Cu Kα radiation operated at 40 kV and 40 mA. A fresh ZrO_2 film came from the self-assembled system was ultrasonically dispersed for 10 min and dropped to a copper grid, which was observed by a JEOL-2100 transmission electron microscopy (TEM) operated at 200 kV and equipped with a Gatan 794 charge-coupled device (CCD) camera.

3. Results and discussion

3.1. Structures of self-assembled ZrO_2 films with SDS (0.15 g)

In 2θ degree range between 2 and 10°, small angle XRD (SAXRD) patterns of ZrO_2 films with SDS (0.15 g) are displayed in Fig. 1. It is noteworthy that no obvious diffraction peaks are appeared in the wide 2θ range from 10 to 80°, suggesting all these assembled ZrO_2 films are amorphous. It has been proved that the strongest XRD peaks existed in low 2θ angles (<10°) indicate well-ordered nanostructures have been obtained in the assembled inorganic–organic films [15–20]. The formed nanostructures could be in the form of lamellae, mesopores or multirings, where the recorded d value corresponds to the lamellar spacing or the mesoporous diameter. For ZrO_2 film directly templated by SDS, the predominant XRD peak is appeared at 2θ = 2.70°, corresponding to d_a = 3.26 nm.

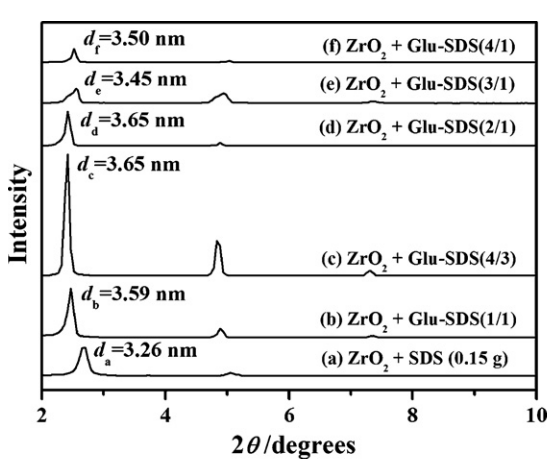

Fig. 1. SAXRD patterns of self-assembled ZrO_2 films templated by 0.15 g of SDS (a), Glu/SDS with mass ratios of 1/1 (b), 4/3 (c), 2/1 (d), 3/1 (e) and 4/1 (f).

When Glu is added into the self-assembly system, obvious decreased 2θ angles are observed for those assembled ZrO_2 films templated by the Glu/SDS composite. In the presence of Glu/SDS (1/1) template, the strongest diffraction peak of ZrO_2 film displays a slightly sharp shape with a relatively small peak width and this peak is located at 2θ = 2.46°, corresponding to an increased d_b value of 3.59 nm. When the Glu/SDS mass ratio increases to 4/3, the diffraction peak width for ZrO_2 film is dramatically decreased, indicating a much higher ordered nanostructure of this sample. The strongest diffraction peak is appeared at 2θ = 2.42°, indicating an increased d_c value of 3.65 nm. When Glu/SDS ratio continues to increase from 2/1 to 4/1, the diffraction peak widths of ZrO_2 films are broadened and have more or less changes for the peak positions. The diffraction peaks of these films are located at 2θ = 2.42°, 2.56° and 2.52°, corresponding to d_d = 3.65 nm, d_e = 3.45 nm and d_f = 3.50 nm, respectively. Remarkably, ZrO_2 film templated by Glu/SDS (3/1) has a much broad peak width and interestingly, another obvious diffraction peak is appeared at 2θ = 4.94°, which indicates a significant change for the formed nanostructure of this film. According to the peak widths for the strongest diffraction peaks of ZrO_2 films, it seems that the formed ordered nanostructures of these self-assembled ZrO_2 films templated by Glu/SDS follow the sequence of Glu/SDS (4/3) > Glu/SDS (1/1) > Glu/SDS (2/1) > Glu/SDS (3/1) > Glu/SDS (4/1).

For the self-assembled ZrO_2 film templated by SDS, a number of irregular ribbons and spheres are observed by TEM images in Fig. 2(a) and (b). A typical ribbon is composed of many aggregated layers in three-dimensional (3D) space, as seen in Fig. 2(c). Note that there are some ambiguous two-dimensional (2D) lamellar structures resided in the obtained ribbons. The black lamellae mean ZrO_2 species and the white lamellae indicate SDS template. From the TEM observation in Fig. 2(d), mesoporous structures are clearly observed for the microstructure of spheres and the estimated mesoporous diameter is in consistent with d_a = 3.26 nm recorded by XRD in Fig. 1(a).

Fig. 3 displays TEM and HRTEM images of ZrO_2 film templated by Glu/SDS (1/1). This film is comprised by a great many irregular ribbons, as indicated in Fig. 3(a). Note that there are no sphere-like structures observed for this sample. In comparison with ZrO_2 film with SDS, a small amount of dark pieces came from the overlapping of ZrO_2 ribbons indicate a better dispersion for this film. Fig. 3(b) shows that a typical ribbon is mainly composed of distorted lamellar structures. The black lamellae are organized by ZrO_2 species and the white lamellae are composed of Glu/SDS template. It could be clearly seen from Fig. 3(c) that this ribbon is organized by more than two layers. The further microstructure of these ribbons displays a great number of mesoporous structures and a few distorted lamellar structures. The spacing value between distorted lamellae is of 3.60 nm, which is estimated from the high resolution TEM (HRTEM) image in Fig. 3(d). This result agrees well with the XRD result of d_b = 3.59 nm in Fig. 1(b).

When Glu/SDS (4/3) template is added to the self-assembly system, a number of well-dispersed ribbons could be clearly observed for the as-synthesized ZrO_2 film, as indicated in Fig. 4(a). This indicates that the increased Glu molecules have a dispersion effect on the assembled ZrO_2 ribbons. Fig. 4(b) displays a typical ribbon