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Effect of proteins on the self-assembly of multiring structural ZrO_2 nanodisks

Hongjun Ji, Xiaoheng Liu, Xin Wang*, Xiaodong Wu, Xujie Yang, Lude Lu

Key Laboratory for Soft Chemistry and Functional Materials of Ministry of Education, Nanjing University of Science and Technology, Nanjing 210094, China

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ABSTRACT

Compared to the air–water interfacial zirconia film with regularly multiring structure self-assembled by using zirconium(IV) butoxide as precursor, sodium dodecyl sulfonate (SDS) as template and gelatin (G) as stabilizer, another kind of multiring structural ZrO_2 nanodisks has been prepared in the presence of the globular protein bovine serum albumin (BSA). X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM) and X-ray photoelectron spectroscopy (XPS), etc. have been used to characterize morphologies, high ordered structures and components for the assembled ZrO_2 film. Results show that both G and BSA could help to assemble multiring structural ZrO_2 films. The difference is that the multiring nanodisk assembled with BSA seems to be relatively defective compared to the product prepared with G, due to the better ability of G to stabilize the micelles of surfactant templates. Remarkably, this self-assembly method may be widely applied in preparing many functional metal oxide nanofilms and proteins will play important roles in assembling well ordered structures inside those films.

1. Introduction

Some inorganic metal oxide nanofilms at the air–water interface have been prepared by a "from down to up" self-assembly method [1,2] with surfactant as template, containing well ordered nanostructures, e.g. lamellar structures and mesoporous structures. White and co-workers [3–5] and we [6–8] have reported some research works on air–water interfacial TiO_2 film and ZrO_2 film self-assembled with versatile anionic and cationic surfactants, e.g. sodium dodecyl sulfonate (SDS) and tetradecyltrimethylammonium chloride (C_{14}TAC). Recently, interesting interactions between surfactants and proteins have attracted our attentions. For instance, interesting interactions between SDS and bovine serum albumin (BSA) have been investigated by surface tension, fluorescence and light scattering, etc. [9–17], resulting in some classical models, e.g. necklace and bead model [9–11,16–17].

Accordingly, in this work, we will report a kind of zirconia-based film with multiring structures, which is self-assembled with the BSA–SDS complex acted as the stabilizer-template and zirconium alkoxide acted as the precursor. A special effort is made to investigate the effects of proteins (gelatin and BSA) on the ZrO_2 film with ordered multiring structure.

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 BSA (Sigma) were used as purchased.

2.2. Preparations

Preparation for the self-assembly ZrO_2 thin film was as follows. First, 0.15 g SDS and 0.15 g BSA were mixed with 18.4 ml deionized water in a 25-ml beaker by stirring magnetically at 40 °C for 10 min to prepare the surfactant solution. It should be mentioned that in our previous work the same mass weight of gelatin (G) was used to prepare ZrO_2 film with almost all the same conditions. At the same time, the precursor solution was prepared by stirring 0.84 g zirconium(IV) *n*-butoxide, 0.64 ml HCl and 2 ml H_2O in a 10-ml beaker for 5 min. Then, the precursor solution was transferred to a Petri dish with a diameter of 90 mm and a depth of 10 mm, and subsequently, the surfactant solution was poured as a coating. The film growing process works well under static conditions at room temperature (21 °C) over a reaction time of 6–24 h. Well-formed film could be clearly observed at the air–water interface.

2.3. Characterizations

ZrO_2 film was transferred to a glass substrate and dried for 24 h, and then the substrate was directly detected by X-ray diffraction

* Corresponding author. Tel.: +86 25 8431 5054; fax: +86 25 8431 5054.
E-mail address: wangx@public1.ptt.js.cn (X. Wang).

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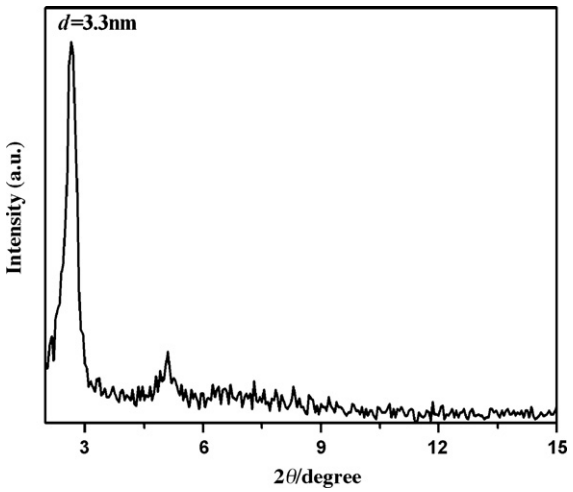
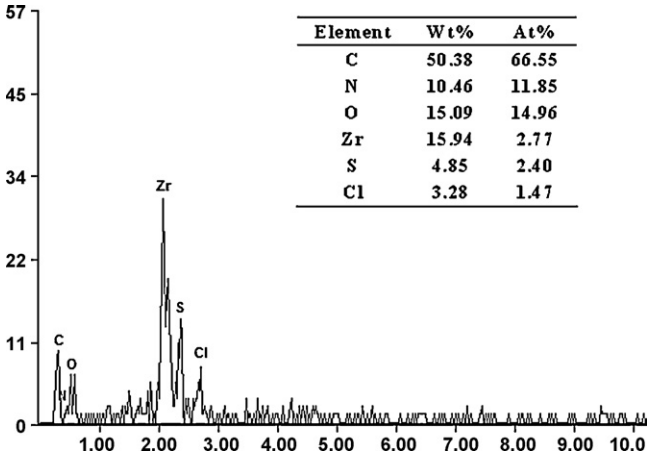


Fig. 1. XRD pattern of ZrO_2 film assembled with BSA.



Element	Wt%	At%
C	50.38	66.55
N	10.46	11.85
O	15.09	14.96
Zr	15.94	2.77
S	4.85	2.40
Cl	3.28	1.47

Fig. 3. EDS image of ZrO_2 film assembled with BSA.

(XRD) with a Bruker D8 diffractometer, using monochromatic Cu Kα radiation operated at 40 kV and 30 mA. Scanning electron microscope (SEM) of JEOL-6380LV and EDS with EDAX Genesis2000 were applied to detect the dried film. X-ray photoelectron spectroscopy (XPS) was performed with a PHI5300-spectrometer (PerkinElmer) with Mg Kα X-ray source. The fresh film dropped to a copper grid after ultrasonic dispersion for 10 min was observed by a JEOL-2100 transmission electron microscopy (TEM) at 200 kV and a Gatan 794 charge-coupled device (CCD) camera. Fluorolog-1040 (JobinYvoh Horiba) was used for fluorescence measurements. The excited wavelength was kept at 280 nm. Note that SDS and SDS–BSA diluted in deionized water keep the same concentrations as that in the self-assembly experimental of ZrO_2 film.

3. Results and discussion

3.1. Morphology and structure

In 2θ degree range between 2° and 15°, XRD pattern of ZrO_2 film is displayed in Fig. 1. Note that no obvious diffraction peaks are observed after 15°. The strongest diffraction peak at 2θ degree of 2.65° with a *d* spacing of 3.3 nm suggests a well-ordered structure consisted in the as-synthesized ZrO_2 film.

From SEM image in Fig. 2, many disk-cluster particles are observed with diameters ranging from 0.5 μm to 2 μm. Note that some large gaps between those disk-clusters, resulting in low density for ZrO_2 film. EDS image in Fig. 3 shows that the elements S, N and Zr are clearly observed, indicating that SDS, BSA and ZrO_2 have been successfully assembled in the as-prepared ZrO_2 film. The detailed element contents are shown in the table present in Fig. 3.

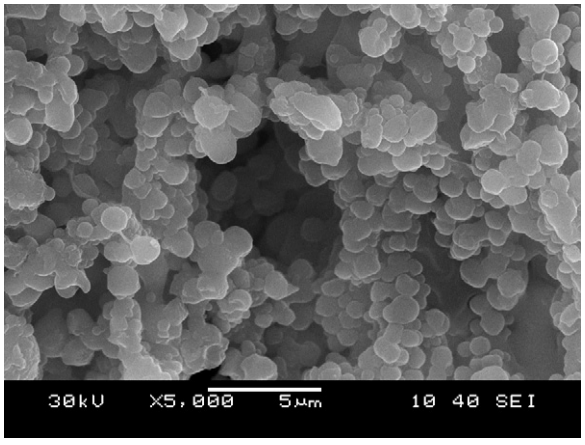


Fig. 2. SEM image of ZrO_2 film assembled with BSA.

TEM images of ZrO_2 film in Fig. 4 display a novel multiring structure. Many defective-multiring structures have been observed as seen in Fig. 4(a). The black layers inner those multirings were attributed to ZrO_2 and the white layers should be the SDS–BSA complex. Furthermore, the *d* spacing between those multirings was measured ~3 nm in consistent with the XRD characterization result ~3.3 nm in Fig. 1. Interestingly, some intact-multiring structures were also observed in Fig. 4(b), which were similar to our previous ZrO_2 film with target-like multiring structures self-assembled by using SDS as template and gelatin as stabilizer and dispersant [6]. Furthermore, every perfect multiring nanodisk in the film with G had a small tail associated with the formation mechanism. The *d* spacing between the perfect multirings measured 3.27 nm, which was in consistent with the XRD result for the film prepared with BSA in Fig. 1. TEM results show that both proteins could help assemble multiring structural ZrO_2 films. The product assembled with G displayed especially perfect multiring disk-like structure, which could be attributed to the more stable interaction between G and SDS. Accordingly, the relatively unstable interaction between BSA and G had more difficulties in forming substantial regular multiring structures, resulting in many defective multiring structures as seen in Fig. 4(a).

As shown in Fig. 5, the domain XPS peaks $Zr3d_{5/2}$ and N 1s were assigned to Zr^{4+} in ZrO_2 and N^{3-} in BSA with binding energies at 183.1 ev and 400 ev, respectively. Note that an obvious shoulder in Fig. 5(a) with the binding energy at 185.3 ev belongs to $Zr3d_{3/2}$ in ZrO_2. Meanwhile, XPS spectra of other elements, including C 1s, O 1s and S 2p (not shown) were obtained, suggesting SDS, ZrO_2 and BSA have been successfully assembled in this as-prepared ZrO_2 film. Since XPS was a useful characterization for analysing relative atomic concentrations, the elements Zr/S/N ratio was 2.5/2.3/1, according to our experimental XPS peak areas and their relative sensitivity factors.

For the further analysis of the effect of BSA, the fluorescence spectra are displayed in Fig. 6. The emission peak of the ZrO_2 film self-assembled with SDS at 310 nm corresponded to SDS. However, in the presence of BSA in our film preparation, the emission peak at 325 nm was blue-shifted compared to that of BSA at 342 nm due of the Trp fluorophore in BSA. Meanwhile, the emission peak at 310 nm disappeared, suggesting the complex interactions in this self-assembly system. Furthermore, in the mixture solution of SDS–BSA with the same concentration as SDS, the maximum emis-