Self-Assembled Nanodisks with Targetlike Multirings Aggregated at the Air−Water Interface

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Since the synthesis of inorganic mesoporous materials by the use of surfactant molecules as the structure-directing template was first reported in 1992,[1,2] this noteworthy method has been used and extended to a variety of oriented material self-assembly.[3−8] Air−water interfacial films can find a wide range of useful technological applications, e.g. in the biological, medical, foodstuffs, and domestic areas. Over the past decade, J. W. White's group has investigated the self-assembly of a series of inorganic oxide films floating at the air−water interface, such as silica,[9−11] titania,[12,13] and zirconia.[14] Indeed, to investigate a new subject in the material science and nanoscience areas, some attention has been put into the research of inorganic films located at the air−water interface.[15,16]

Herein, we report the self-assembly of zirconia by mixing its precursor with another solution containing surfactant as well as gelatin. The resulting zirconia product consists of many disks with diameters ranging from ∼100 nm to ∼2 μm. These disks can be assembled inside the aqueous system. Meanwhile the disks rise gradually and eventually form a visible film at the air−water interface. Remarkably, the structure of zirconia disks templated by surfactant has been found to be targetlike multirings with a d spacing of ∼3.3 nm. We propose that a successful multiring self-assembly depends on two different template-functions from the same surfactant, excellent tenacity of the zirconia layers and strong ability of the gelatin to stabilize and disperse the disks. To our knowledge, this oxide-based multiring nanostructure has never been reported before.

In our experiments the hydrolysis of organozirconate was employed as an essential process to produce the zirconia film, which can be controlled by template, stabilizer, pH value, etc. The film was prepared by the following procedure: 0.58 mL of 10.8 M hydrochloric acid was first added dropwise to 2.2 mmol of zirconium(IV) butoxide. After the addition of 1.0 mL of water, the mixture was stirred magnetically for 10 min, and then the clear solution obtained was transferred to a plastic container with a diameter of 80 mm and a depth of 10 mm. Subsequently a solution of 0.15 g of sodium dodecyl sulfate (SDS) and 0.15 g of gelatin in 18.4 mL of water was poured gently over the clear solution in the container. The hydrolysis of organozirconate was carried out under strong acidic conditions (pH = 0.5). Finally the container was sealed and left undisturbed for 2−5 days at room temperature (∼21 °C). The film grew gradually on the solution surface, and by 1 day a quite visible film was present at the air−water interface in the container. It was then transferred to the glass substrates and characterized by scanning electron microscope (SEM, JEOL-6380LV), transmission electron microscope (TEM, JEOL-2100), and X-ray diffraction (XRD, Bruker D8).

The SEM images (Figure S1) show clearly the aggregation of many disklike particles with diameters of ∼0.5 to ∼2 μm in the zirconia film obtained from the air−water interface. Furthermore, detailed analysis of the TEM images (Figure 1) of the film demonstrates the existence of well-monodispersed disks with
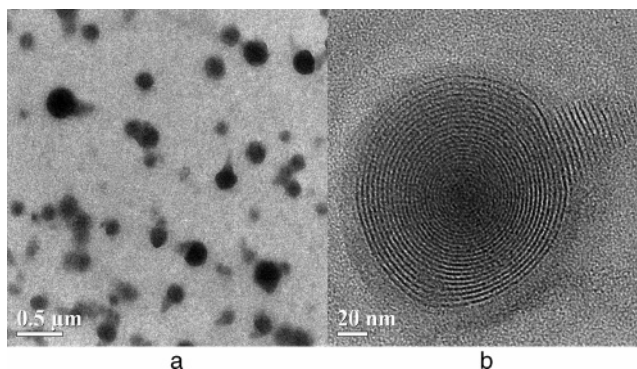

Figure 1. Typical TEM micrographs of zirconia disks from a fresh sample. Zirconia film was transferred into pure water and then treated by ultrasonication, after which some visible suspensions of the film still remain in the water. In our measurement, only clear colloid solution containing well-monodispersed particles was selected to drop onto a carbon-coated copper grid.

relatively smaller diameters (∼100 to ∼300 nm). However, other disks in the film, as shown in Figure S1, are too large to be well dispersed into clear colloid solution (Figure 1). For all disks with the colors of deep dark, dark, and gray in Figure 1a, the difference in the color of the disks depends on their thickness and diameter. Namely, the larger the disk volume is, the darker the disk color will be. There are also some tadpole-like particles, in which a particle is composed of a disk and a tail (Figure 1a). Repeated experiments have demonstrated that these disks are of targetlike multiring structures. One typical image of the targetlike disk with a layered tail is shown in Figure 1b. In addition, Figure 1a reveals that many tails have broken away from the disks due to the weak linkage between disk and tail. In our other TEM observations, the free tails and the targetlike disks without a tail (Figure S2) can also be easily observed.

To gain a better understanding of the orderliness of the transferred zirconia films prepared at the air−water interface, we performed an XRD scan on the sample. Figure 2a displays the intensity versus angle pattern of the zirconia film in the 2θ range 2°−10°. It should be mentioned that no obvious reflections from 10° to 36° can be detected. The observed reflections at d = 3.27, 1.75, and 1.25 nm are similar to the reported data for SDS,[17] whose reflections are assigned to d = 3.86, 1.94, and 1.29 nm corresponding to the (001), (002), and (003) planes respectively (SDS tends to pack into a lipidlike bilayer structure, whose width is about 3.86 nm). This comparison can provide a pathway to understand the function of surfactant as a template in the zirconia disks.[12,13] The strongest reflection at d = 3.27 nm implies that a high degree of order has been retained in the film. This d spacing coincides well with the observation in the HRTEM micrograph (Figure 2b) in which the d spacing of a targetlike disk is determined to be ∼3.3 nm.

Figure 3 illustrates our proposed mechanism for the formation of characteristic morphologies for zirconia films. Stucky et al.[18]
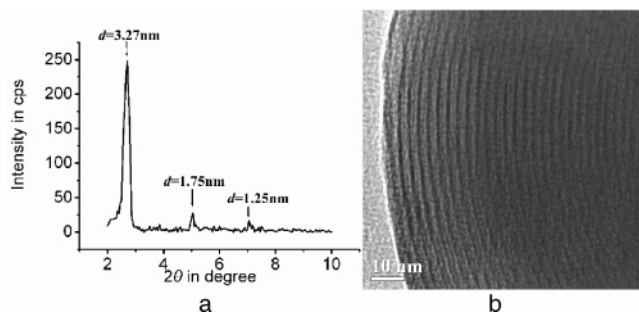
Figure 2. (a) Representative XRD pattern of a piece of dried zirconia film. (b) High-resolution transmission electron micrograph (HRTEM) of a zirconia disk.
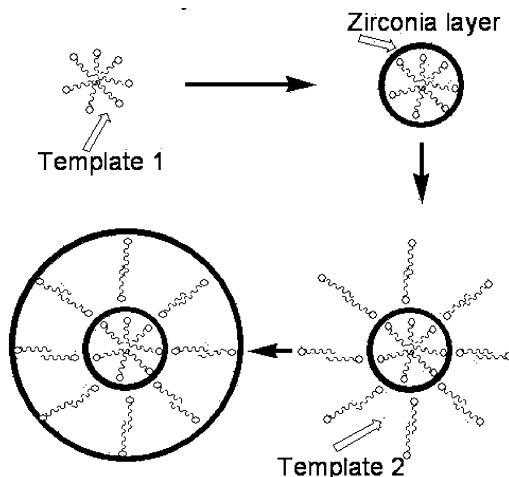

Figure 3. Mechanism of targetlike zirconia disk templated by surfactant molecules.

have summarized two typical mechanisms of surfactant-templating inorganic species, resulting in the formation of layered or mesoporous structures. Here, in Figure 3, these two mechanisms have been combined to template a targetlike disk. First, a disklike SDS micelle (template 1) induces primary ring formation. The smallest zirconia ring from its precursor hydrolysis carries positive charges in the strong acidic condition, which can interact with the negatively charged SDS headgroups through electrostatic interactions. In the next stage, two SDS molecules can be coupled through van der Waals forces to produce a dimeric bar, which can serve as a new template (template 2). This template plays a key role in the subsequent self-assembly processes. The direct evidence to support the formation of this dimeric bar model comes from the facts that on one hand the molecular length of SDS is reported to be 2.2 nm[13] and on the other hand the measured d spacing of the bar is ~3.3 nm in Figure 2. Thus, an observed d spacing is just less than twice the length of a SDS molecule, which satisfies the requirement for the formation of a dimeric structure. Additionally, the tenacity of the zirconia layer plays a determining role in the target assembly. Because the zirconia layer tension is inversely proportional to the disk diameter, the formation of the layers near the center of the disk is a key step.

Interactions between various polymers and surfactant SDS have been investigated extensively due to related applications in biological, chemical, and material areas. Clearly, the stable binding between gelatin peptide chains and SDS molecules have been verified by previous studies.[19,20] The gelatin, as a polyelectrolyte, with a formal isoelectric point of pH = 5.5 in the strong acidic system (pH = 0.5), will carry positive charges and bind to template (SDS) headgroups. This electrostatic interaction is so strong that gelatin peptide chains can wrap assembled zirconia disks very well, making these disks well monodispersed during rising and growth in the solution.

We propose that the formation of the interfacial film takes place by means of aggregation of the self-assembled particles. These particles are born and grow in the bulk of the aqueous solution, rather than at the air−water interface directly (Figure S3). Meanwhile, these insoluable particles with a density less than that of water will rise gradually. In general, chemical reactions occurring in aqueous solution will always precipitate insoluble solid inorganics to the bottom of the reactor. More remarkably, this film fabrication method in the presence of gelatin, as reported in this communication, allows the sucessful self-assembly of targetlike zirconia nanodisks.

Supporting Information Available: SEM and additional TEM observations, and a scheme to describe the growth process of the interfacial film. This material is available free of charge via the Internet at http://pubs.acs.org.

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