Hierarchically ordered networks comprising crystalline ZrO$_2$ tubes through sol–gel mineralization of eggshell membranes

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A facile sol–gel coating procedure has been successfully applied for the ZrO$_2$ coating of eggshell membranes (ESM), resulting in hierarchically ordered thin films with a macroporous network structure comprising crystalline ZrO$_2$ tubes. This hierarchical material, which was obtained through sol–gel mineralization of the ESM template and subsequent calcination at 600 °C, was characterized by XRD, SEM, TEM, HRTEM, and nitrogen sorption measurements. It has been shown that this ZrO$_2$ material exhibits a macroscopic morphology of a film with a thickness about 15 μm; the film has a microstructure of macroporous networks composed of interwoven ZrO$_2$ microtubes with diameters less than 1.0 μm; the tube walls consist of tetragonal ZrO$_2$ nanocrystals with an average crystallite size about 6 nm. It shows a specific surface area of 55 m$^2$ g$^{-1}$ and a BET average pore size of 7.0 nm, which is mostly due to the ZrO$_2$ nanocrystals constituting the tube walls.

It has also been shown that calcination of the initial ESM/zirconium precursor hybrid at 700 °C resulted in significant fusion between neighboring ZrO$_2$ tubes accompanying a tetragonal-to-monoclinic phase transformation of zirconia.

Introduction

Porous inorganic materials with controlled pore structure and size have attracted much attention because of their wide potential applications in catalysis, sorption, separation, and optics. In general, strategies for synthesizing these materials rely on the use of templates, the size and nature of which dictate the pore dimensions and architecture. For example, three-dimensional (3-D) ordered macroporous materials have been fabricated by using various templates including colloid crystals,1-4 polyurethane foams,5 and emulsions6 whereas ordered mesoporous materials have been synthesized by templating organized assemblies of surfactants7 and block copolymers.8,9 Macroporous networks have also been prepared by employing polymer gels,10,11 polymer membranes,12,13 and bicontinuous microemulsions14,15 as templates. In addition to synthetic templates, a variety of natural biological templates have been employed for the synthesis of porous materials with sophisticated structural ordering analogous to natural materials.16-22

Compared with artificial templates, biological templates are inherently complex and hierarchical;23,24 moreover, they are generally cheap, abundant, and environmentally benign. For instance, sophisticated macroporous materials have been produced by templating organic matrix isolated from cuttlebone25 and inorganic skeletal plates of echinoids.26 Notably, biological templates, such as organized bacterial threads18,19 and wood cellular structures,20,21 have been used to synthesize hierarchically ordered macroporous materials with bimodal porosity, which combined the good mass transport and accessibility of macroporous networks with the high surface area, selectivity, and catalytic properties of the smaller pore systems. Recently, we reported a novel synthesis of hierarchically ordered macroporous networks composed of TiO$_2$ tubes by using eggshell membranes (ESM) as templates via a sol–gel coating method.22 However, this ESM templating approach remains to be extended to the synthesis of hierarchically ordered networks of other oxide systems.

Zirconium dioxide has attracted increasing interest in the field of heterogeneous catalysis since it has redox properties as well as acidic and basic character.25 Its high chemical stability also favors its applications as a catalyst support, adsorbent, chemical sensor, and structural ceramic.26,27 Consequently, the fabrication and structural characterization of ZrO$_2$ nanoparticles27-29 and nanotubes30,31 have attracted much attention. On the other hand, many recent efforts have been devoted to the synthesis of porous ZrO$_2$ with controlled pore structure and size; examples include ordered mesoporous ZrO$_2$,9,26,32-34 ordered macroporous ZrO$_2$,5,35 and high-surface-area ZrO$_2$ aerogels.36 It is noteworthy that macroporous ZrO$_2$ network membranes have been easily fabricated by sol–gel coating36 of cellulose acetate (CA) membranes.37 However, in many cases the obtained porous ZrO$_2$ materials were not well-crystallized, which would largely limit their applications in catalysts. Furthermore, it would be highly desirable to synthesize hierarchically ordered porous ZrO$_2$ since the control of pore structure and size greatly influences the efficiency of the porous material in its applications. In this current work, we have applied the sol–gel coating procedure for the ZrO$_2$ coating of ESM consisting of interwoven organic fibers. For the first time, hierarchically ordered network membranes comprising crystalline ZrO$_2$ tubes have been prepared through the sol–gel mineralization of ESM.

Experimental

Materials

The zirconium precursor, zirconium propoxide (ZP, 70 wt% in propanol) was purchased from Fluka. Commercial eggs were locally available. All the other chemicals used in the experiments were of analytical grade and the water used was deionized.

Separation of eggshell membranes

Eggshell membranes (ESM), which are stable in aqueous and alcoholic media and undergo pyrolysis on heating, consist of the outer shell membrane, inner shell membrane, and limiting membrane surrounding the egg white.37 The outer shell
membrane, which can be easily isolated from eggshells, was used as a removable template in this work. The separation of the outer shell membrane from eggs has been described previously. Briefly, eggs were gently broken and emptied via the blunt end and the eggshells were washed with water. Then, the inner shell membrane and the limiting membrane were manually removed. The remaining eggshells were rinsed in 1 M HCl to dissolve the CaCO3, leaving the organic outer shell membrane. After the outer shell membrane was washed with water thoroughly, a solvent exchange process for the membrane was carried out by slowly increasing the ratio of 2-propanol to water until the membrane was in high purity with water thoroughly, a solvent exchange process for the membrane. After the outer shell membrane was washed manually removed. The remaining eggshells were rinsed in 1 M HCl to dissolve the CaCO3, leaving the organic outer shell membrane. After the outer shell membrane was washed with water thoroughly, a solvent exchange process for the membrane was carried out by slowly increasing the ratio of 2-propanol to water until the membrane was in high purity, similar to the case of polymer gels. Then, the dehydrated outer shell membrane was used as the ESM template for the ZrO2 coating.

Sol–gel mineralization of ZrO2

The sol–gel coating procedure previously used for the TiO2 coating of the ESM template was partly modified and applied for the ZrO2 coating. In a typical synthesis, the eggshell membrane was dipped into a closed vessel containing a 7% (w/w) solution of zirconium propoxide (ZP) in 2-propanol for 4 h, where an equimolar amount of acetyl acetone (acac) was added to lower the hydrolysis rate of ZP. After removal from this solution, the membrane coated with the precursor was dried in air at room temperature for 48 h. The resulting yellow hybrid material was then heated to 600 °C or 700 °C in an oven under air atmosphere to burn off the organics and crystallize zirconia.

It can be noted that for the synthesis of ESM-templated TiO2, the ESM template filled with the precursor titanium butoxide (TB) was hydrolyzed in 2-propanol/water (50:50 v/v) for 1 h before it was dried in air. However, our preliminary experiment showed that the same procedure was applied for the synthesis of ESM-templated ZrO2. Lots of irregular ZrO2 particles stuck on the surface of the membrane and the ESM template could not be replicated well, which could be attributed to the much faster hydrolysis rate of ZP. Consequently, ZP-coated ESM was directly dried in air without hydrolysis in the 2-propanol/water mixture in the present preparation. It was also found that if the dipping time of the ESM template in the ZP solution was shorter than 1 h, the precursor ZP did not form a complete coating on the surfaces of the ESM fibers, resulting in collapsed ZrO2 membranes upon drying and calcination. When the dipping time was varied from 4 to 24 h, the ESM template could be replicated well and the structure of the resulting ZrO2 material did not change considerably. Hence, a dipping time of 4 h was adopted in this work.

Characterization

Scanning electron microscopy (SEM) measurements were performed with an Amray 1910FE microscope. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) investigations were conducted on a JEOL JEM-200CX microscope and a Hitachi H-9000HAR microscope, respectively. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Dmax-2000 diffractometer with Cu Kα radiation. Thermogravimetric analysis (TGA) was carried out on a LCT-1 type thermoanalyzer in air. The specific surface area and average pore size were obtained from BET analysis after nitrogen sorption using a Micromeritics ASAP 2010 system.

Results and discussion

It has been documented that avian eggshells are formed by layered organization of calcified shell and organic eggshell membranes consisting of collagen-like proteins (collagen types I, V, and X) and glycosaminoglycans. Scanning electron microscopy (SEM) images present information about the membrane thickness and the larger pores in the initial membrane template. Typical SEM images of the initial ESM template are presented in Fig. 1. As shown in Fig. 1a, the membrane has a macroporous framework composed of interwoven and coalescing fibers ranging from 0.5 to 1.5 μm in diameter. A membrane thickness of about 25 μm can be estimated from the cross section image (Fig. 1b).

It is known that eggshell membranes contain plenty of amines, amides and carboxylic surface functional groups, which may interact with the zirconium precursor, anchoring the precursor molecules to the membrane fiber surface where the ZP coating can occur. The TGA curve of the resulting ESM/ZP hybrid is shown in Fig. 2, which suggests that the organic ESM template and the zirconium precursor started pyrolyzing around 210 °C and were completely pyrolyzed by 600 °C, leaving 11.3% (by mass) inorganic solid. Apparently, the residual inorganic fraction is very low; however, the real proportion between ZrO2 and the organic membrane is much higher considering the incomplete hydrolysis of the zirconium precursor under the present synthesis conditions. It was also found that the apparent residual inorganic fraction can be increased to more than 30% without changing the inner structure of the ZrO2 material by increasing the concentration of the ZP solution and by repeated dipping and drying. The XRD patterns of the ESM/ZP hybrid as well as the ZrO2 networks after calcination at 600 °C and 700 °C are shown in...
Fig. 3 XRD patterns of ESM-templated ZrO$_2$ samples: (a) as-synthesized ESM/ZP hybrid, (b) ZrO$_2$ networks obtained at 600 °C, (c) ZrO$_2$ networks obtained at 700 °C. T: tetragonal, M: monoclinic.

Fig. 4 SEM images of ESM-templated ZrO$_2$ networks obtained at 600 °C: a) overview of the surface, b) overview of the cross section, and c) higher magnification of the cross section showing the broken hollow tubes.

Fig. 5 TEM (a) and HRTEM (b) images of ZrO$_2$ tubes constituting the ZrO$_2$ networks obtained at 600 °C.
presence of mesopores. The Brunauer–Emmett–Teller (BET) surface area of the ZrO$_2$ networks was measured to be 55 m$^2$ g$^{-1}$ and the BET average pore size was estimated to be 7.0 nm, confirming the presence of mesopores within the tube walls composed of ZrO$_2$ nanocrystals. The surface area value is considerably larger than that for the 3-D ordered macroporous ZrO$_2$ (monoclinic) obtained by colloidal crystal templating (38 m$^2$ g$^{-1}$), and it is similar to that for the macroporous ZrO$_2$ networks obtained by sol–gel coating of CA membranes (54 m$^2$ g$^{-1}$) although it remains unclear whether this ZrO$_2$ material was crystallized. The combination of high surface area and high porosity of macroporous crystalline ZrO$_2$ networks is expected to enhance the wide and ever-growing range of applications of zirconia. Moreover, the unique hierarchical characteristic of the current macroporous networks composed of ZrO$_2$ tubes comprising tetragonal ZrO$_2$ nanocrystals might endow this material with unusual properties of technological importance. These results demonstrate that the procedure of sol–gel mineralization of ESM can be readily extended to systems of metal oxides other than TiO$_2$, which represents a versatile method for the biomimetic synthesis of hierarchically ordered networks of metal oxides.

Calcination of the ESM/ZP hybrid at elevated temperatures resulted in significant fusion between neighboring ZrO$_2$ tubes accompanying the tetragonal-to-monoclinic phase transformation of zirconia. Fig. 7 illustrates typical SEM images of the ESM-templated ZrO$_2$ networks after calcination at 700 °C, which shows that the obtained porous networks are much denser than the networks obtained at 600 °C. Although the

structure of a network consisting of hollow tubes is partly preserved near the surface of the membrane (Fig. 7a), the inner structure of the material looks more like a solid containing reticular hollow channels, the diameter of which is reminiscent of the diameter of the ESM fibers (Fig. 7b). This result is in good agreement with the general observations that the tetragonal-to-monoclinic phase transformation of zirconia is accompanied by volume expansion and loss of porosity. It is known that the tetragonal-to-monoclinic phase transformation of zirconia is of technological importance as it contributes to the toughening of ceramics. Therefore, it is expected that the obtained macroporous crystalline ZrO$_2$ networks may find applications as a structural ceramic.

Conclusion

A facile sol–gel coating procedure has been successfully applied for the ZrO$_2$ coating of eggshell membranes (ESM), resulting in hierarchically ordered membranes with a structure of macroporous networks comprising crystalline ZrO$_2$ tubes. This hierarchical material, which has a specific surface area of 55 m$^2$ g$^{-1}$ and a BET average pore size of 7.0 nm, was obtained through sol–gel mineralization of the ESM template and subsequent calcination at 600 °C. It shows a macroscopic morphology of a film with a thickness of about 15 μm; the film has a microstructure of macroporous networks composed of interwoven ZrO$_2$ microtubes with diameters less than 1.0 μm; the tube walls consist of tetragonal ZrO$_2$ nanocrystals with an average crystallite size about 6 nm. The combined benefits of macropores, microtubes, and mesopores can potentially be obtained in one film, which would make this material attractive for numerous applications including catalysis, separation, and sensors. It has also been revealed that calcination of the initial ESM/zirconium precursor hybrid at 700 °C resulted in a significant fusion between neighboring ZrO$_2$ tubes accompanying a tetragonal-to-monoclinic phase transformation of zirconia. These results suggest that the procedure of sol–gel mineralization of ESM represents a versatile method for the biomimetic synthesis of hierarchically ordered networks of metal oxides, which further demonstrates the great potential of bio-inspired materials chemistry.

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References
