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Synthesis of hierarchical mesoporous titania with interwoven networks by eggshell membrane directed sol–gel technique

Qun Dong [a], Huilan Su [a,*], Di Zhang [a], Zhaoting Liu [a], Yijian Lai [b]

[a] *State Key Lab of Metal Matrix Composites, Shanghai Jiaotong University, Shanghai 200030, PR China*
[b] *Instrumental Analysis Center, Shanghai Jiaotong University, Shanghai 200030, PR China*

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Abstract

Hierarchical mesoporous titania with interwoven networks was successfully prepared through a surface sol–gel process followed by a calcination treatment and using eggshell membrane (ESM) as the biotemplate. The biotemplating synthesis was systematically investigated by controlling calcination temperature (550–800 °C), heating rate (1–35 °C/min), impregnant pH value (1–3), and so on. Different from traditional immersion techniques, the nucleation, the growth, and the assembly of mesoporous TiO_2 in our work depended more on some reactions involving ESM biomacromolecules. As-prepared ESM-morphic TiO_2 was composed of intersectant fibers assembled by 6 nm nanocrystallites at 3D with hierarchical pores from 2 nm up to 8 μm.

Keywords: Interwoven networks; Porous titania; Hierarchy; Eggshell membrane; N_2 adsorption

1. Introduction

Nature always fascinates scientists and engineers with numerous examples of exceptionally fantastic building materials. It has long been using the bottom-up means to assemble nanomaterials from nanoscopic to macroscopic scale with sophisticated structure and ordering [1–3], that show much unique properties, as compared with many man-made top-down materials. Thus, the exploration of bioinspired morphosynthesis strategies, using self-assembled organic superstructures, organic additives, and/or templates with complex functionalization patterns, to construct inorganic materials with controlled morphologies, has drawn a lot of attention. Quite a list of biological species were imitated to synthesize hierarchical functional materials, including DNA [4], viruses [5], skeletal plates [6], butterfly wings [7], shell membranes [8], silk fibers [9], papers [10], and wood [11], etc.

Although emulsion foams [12], water-in-oil microemulsion [13], and pseudovesicular double emulsions [14] have been used as the templates to achieve the morphogenesis of inorganic materials, there are few feasibly techniques to construct practical and functional hierarchical nanomaterials. However, pursuing mild, versatile, and feasible techniques is the endless objective for materials scientists and chemists. In this way, mimicing and replicating the morphologies of natural materials must be one of the most potent shortcuts to construct hierarchical structures with complicated architectures [15]. To attain this goal at a rudimentary level, the feasible approach should be interfacial sol–gel process [16]. In such a route, sol ingredients would undergo surface preferred gelation and interact with bioelements (proteins, polysaccharides, functional residues). Therefore, biotemplate-directed synthesis in the sol–gel system proves an ideal approach to the design and construction of advanced materials with predetermined physical and chemical properties.

Mesoporous titania has outstanding chemical and physical properties, and widespread applications in

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* Corresponding author. Tel.: +86 21 62933106; fax: +86 21 62822012.
E-mail address: hlsu@sjtu.edu.cn (H. Su).

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photovoltaics [17], photocatalysis [18], ductile ceramics [19], pigmentation [20], optics [21], and so on, which depend more on the phase and crystallite size of building particles and relevant hierarchical structures. Therefore, the design of hierarchical mesoporous titania with tailored structures and morphologies would provide promising properties. Herein, we chose a convenient biomaterial eggshell membrane (ESM) as the biotemplate, in view of the special proteins patterns and functional residues of the ESM biomacromolecules, to synthesis hierarchical interwoven titania through a sol–gel approach followed by thermal decomposition.

2. Experimental details

Commercial ornithic eggs were gently broken and cleaned up. Consequently, eggshell membrane (ESM) was readily separated from the $CaCO_3$ shell and washed with distilled water. Fresh membrane was conserved as the template for further experiments. The interfacial sol–gel process went along as follows. In a typical procedure, titanium tetrachloride ($TiCl_4$) was added slowly (ca. 1 mL/min) into ice water under stirring to obtain 0.04 M $TiCl_4$ colloid medium, and the pH values of the media were adjusted to 1, 2, and 3 by adding 1 M NaOH solution, respectively. The membrane was immersed in the above colloid media for 13 h at room temperature, then rinsed with distilled water and dried naturally. The gel-ESM hybrids were calcined at 400, 550, 700, and 800 °C under air atmosphere for 1.5 h (heating rate 35, 18, and 1 °C/min), respectively. In all cases, the resulting white sheets were obtained and stored in vacuum for further characterizations.

The samples were analyzed with TGA in a universal V2.4F TA instruments analyzer in an oxygen atmosphere at the heating rate of 10 °C/min. X-ray diffraction (XRD) measurements were carried out on a Rigaku D/max 2550 V instrument operating at a voltage of 40 kV and a current of 200 mA with Cu Kα radiation ($\lambda = 1.5406$ Å) in the range of 20–90°. The morphology and composition of the samples were investigated on a FEI Sirion 200 field emission gun scanning electron microscope (FESEM) operated at an acceleration voltage of 5 kV attached to an X-ray microanalyser. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained as a bright field image and examined by selected area electron diffraction (SAED), conducted on a JEOL JEM-2010 instrument operated at an acceleration voltage of 200 kV and a JEOL JEM-2100F instrument working at 200 kV accelerating voltage, respectively. The nitrogen adsorption and desorption isotherms were measured by using a Micromeritics ASAP 2010 M + C system. All the samples were degassed at 180 °C before the actual measurements. For the BJH (Barret–Joyner–Halenda model), the pore-size distribution was obtained from the analysis of the adsorption branch of the isotherms.

3. Results and discussion

The avian eggshell is composed of multilayered membrane and calcified extracellular matrix, thereinto the eggshell membrane (ESM) is formed by the collagen and glycoprotein between the egg white and the mineralized shell [22]. FESEM shown in Fig. 1 reveals the interwoven and coalescing fiber network with average fiber width ranged from 400 nm to 6 μm. Herein, the special structures were targeted for the synthesis.

3.1. *Effect of calcination temperature*

TGA results indicate that the ESM template started pyrolyzing at 200 °C and absolutely pyrolyzed by 550 °C. The ESM-templated hybrids containing titanic and titanyl precursors also decomposed around 200 °C, and 18.3% (by mass) inorganic matters remained when the template was completely removed at 550 °C. XRD patterns of original ESM and the gel-ESM hybrids as well as the sinters at 400 °C are shown in Fig. 2, respectively. The pH values of the media were all kept at 2. XRD results indicate that

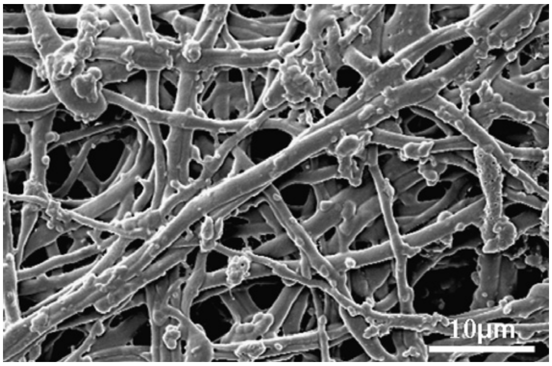

Fig. 1. FESEM image showing hierarchical interwoven structures of the natural eggshell membrane.

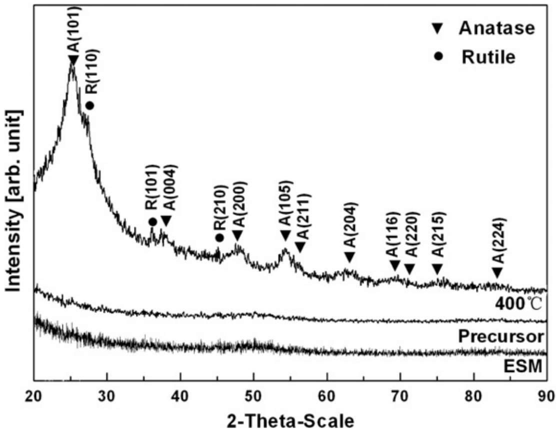

Fig. 2. XRD patterns of ESM, gel-ESM precursor, and the sinter prepared at pH 2.