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Nanoporous gyroid TiO_2 and SnO_2 by melt infiltration of block copolymer templates

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ABSTRACT

Fabrication of meso-porous metal oxide thin films with high surface area is a crucial requirement for numerous applications, such as catalysis, photovoltaics and electronics. Despite considerable progress in fabrication of three-dimensional metal oxide nanostructures, it is still quite challenging to manufacture highly ordered structures over a large area in a controlled way. The main objective of this study is to demonstrate fabrication of interconnected, crack-free and highly ordered ceramic films using a nano-porous polymer with gyroid morphology as template. Titanium tetraisopropoxide and tin chloride dihydrate are used as precursors for nanostructured TiO_2 and SnO_2, respectively. Complete precursor infiltration into the template and successful transformation into metal oxides can be achieved by rational tuning of the template chemistry. As a result, thin films of nanostructured metal oxides with gyroid morphology, such as titania and tin dioxide, are created and thoroughly characterized by scanning electron microscopy, transmission electron microscopy, energy-dispersive analysis, x-ray diffraction and Brunauer–Emmett–Teller analysis.

1. Introduction

Meso-porous titania (TiO_2) and tin dioxide (SnO_2), both n-type semiconductors, are among the most promising materials for applications such as solar cells [1–3], batteries [4,5], photocatalysts [6] and gas sensors [7]. For these applications an optimal device needs to fulfill at the same time the maximization of interfacial area per volume and the interconnectivity between each interfacial element with the external circuit. Currently, the manufacture of well-defined nanostructures mainly depends on top-down nanolithography processes [8,9]. However, the resolution of the nanostructures, the material quality and the fabrication process of complex three-dimensional structures are normally rather limited for these techniques. And also, decreasing particle or feature size is generally accompanied with a decrease in the intrinsic thermal and chemical stability. Therefore, it is a significant challenge to demonstrate local control over material assembly on the 10-nm length scale in macroscopically extended layers of micrometer thickness.

The next generation of nanostructure processing could take advantage of bottom–up processes utilizing self-assembly which can overcome the problems listed above. Preparation of meso-porous TiO_2 and SnO_2 has been reported by using surfactant and block copolymers [10–13], but those are less successful compared with syntheses of mesoporous silica materials in terms of long range order and well-defined structures. One central challenge lies in avoiding structure collapse during formation of the mesoporous architecture and removal of the organic templates, due to the high lattice energy in most metal oxides.

While only few functional materials self-assemble into optimal nanostructures, template-assisted precision replication utilizing a self-assembled template is very versatile. In particular, block copolymers have been extensively developed to self-assemble into arrays of various well-defined one-, two- and three-dimensional structures [14,15]. The morphology and period length-scale of block copolymer can be adjusted by tuning its composition and molecular weight. After adoption of an appropriate morphology during phase separation, nanoporous matrices can be derived by partially or entirely removing one block through ozonolysis [16], UV degradation [17], base or acid treatment [18–20] and reactive ion etching [21]. In particular materials with gyroid morphology have drawn much attention due to the 3D inter-connected framework of such a morphology. Block copolymer self-assembly

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provides an effective, straightforward and economic way to produce mesoporous templates with gyroid morphology.

Metals and metal oxides can be filled into the gyroid porosity by many techniques, for example, electro-deposition [1,22–24], electroless plating [25,26], solution impregnation [27], seed growth [28], and atomic layer deposition [29]. However, nanocasting by melt infiltration, as a rather straightforward method, has become one of the rapidly expanding methods to design and fabricate functional materials for advanced nanoscience and technology [30]. It's based on the infiltration of a porous template with an active phase or precursor to form a nanocomposite, which is subjected to further post-treatment to remove the template and give the final product.

We have successfully developed a series of cross-linked 1, 2-polybutadiene-PDMS block copolymers, which yield nanoporous 1, 2-polybutadiene templates by selectively and quantitatively etching PDMS with tetrabutyl ammonium fluoride (TBAF) [31]. It features controllable morphology, pore size, high porosity and facile surface modification [32], making it a versatile material in many applications like membrane ultrafiltration [33,34], and liquid-core waveguides [35]. Traditionally templates can be categorized into two groups: "hard" templates like mesoporous silica and alumina, and "soft" templates like mesoporous polymers. Cross-linked nanoporous polybutadiene provides certain merits in the melt filtration process. Firstly, it can be easily processed into free-standing thin film that can be easily separated from the precursor, which is difficult to achieve from "hard" particle templates. Although anodized aluminum oxide films are commercially available [36], their cylinder pore system do not provide 3D interconnectivity. Secondly, cross-linking imparts stability and chemical inertness to the template, which is essential for maintaining the structure integrity in the melt infiltration process since chemical and physical (dissolving) reaction of the template with the precursor is generally undesired.

This work explores the use of block copolymer self-assembly for the manufacture of metal oxides thin films of micrometer thickness with well-defined periodic morphology, high surface area and structure connectivity. The nanocasting procedure by melt filtration is shown in Scheme 1: first, the block copolymer self-assemble into gyroid morphology and the PDMS domain in the polymer template is removed. Then the template is immersed into the liquid inorganic precursor. After proper post infiltration treatment, the nanocomposite materials are calcined to burn away the polymer template and simultaneously crystallize the metal oxides with the desired crystal phase. As the pore size of the 1, 2 - PB polymer template is approximately 10 nm the adjective "nanoporous" means "mesoporous" in the present study; following tradition [24,31–35,37] the term is mainly used in relation to the porous polymer template.

2. Experimental

2.1. Polymer template preparation

The 1,2-PB-*b*-PDMS copolymer was synthesized by living anionic polymerization as described in ref 29. The 1,2-PB-*b*-PDMS block copolymer was dissolved in tetrahydrofuran (THF, Sigma–Aldrich) containing 0.01 mol of dicumyl peroxide cross-linker (DCP, Sigma–Aldrich) per mole of 1,2-PB repeating units. The nanoporous membrane made from 1,2-PB-*b*-PDMS was fabricated by sandwiching the polymer between two microscope glass slides. Porosity was generated by etching the PDMS block [34] and the thickness was controlled by means of a spacer.

2.2. Synthesis of gyroid TiO_2 thin film

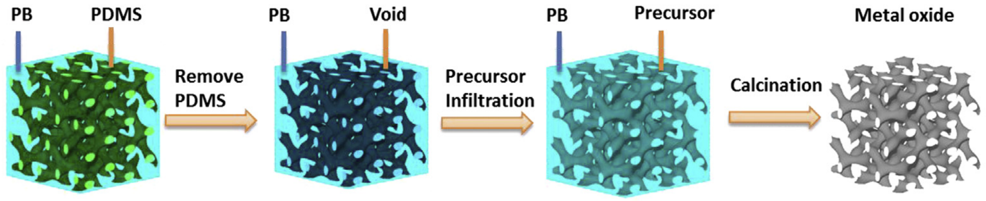
The mesoporous TiO_2 material was synthesized by the nanocasting method using the above cross-linked nanoporous PB as template. Typically, the dried PB template was dropped into a glass bottle containing 5 ml of titanium tetraisopropoxide ($Ti[OCH(CH_3)_2]_4$, Aldrich, 97%, m.p. 287–290 K) at room temperature. The bottle containing the mixture was sealed and ultrasonicated for 1 h to mix the precursor and PB template. Subsequently, the film was taken out and immersed into isopropanol for several seconds with shaking to remove excess precursor hanging on the outer template surface. The composite material was transferred to a chamber at 353 K under saturated water vapor for 2 h to fully hydrolyze the precursor. The resulting material was subjected to the same precursor filling and hydrolysis loop, and this step was performed three times in order to achieve a high degree of pore-filling. Finally, the PB template was removed and the titania precursor crystallized by heating in an oven at 723 K under static air conditions for 2 h with a rate of 1 K/min for both heating and cooling.

2.3. PB surface modification

After cross-linking of the PB domain, 30–50% of the original double bonds in 1,2-PB typically survives the cross-linking reaction [37] and are preferred loci for coupling of thiols by thiol-ene chemistry [35]. Sodium 2-mercaptoethanesulfonate (MESNA, Sigma–Aldrich) was grafted onto the pendent vinyl groups of nanoporous 1,2-PB. Briefly, 500 mM thiol (MESNA) and 10 mM of the photo initiator (2,2-dimethoxy-2-phenylacetophenone, DMPA) were prepared in a 25/75 v/v mixture of water and methanol. Then the nanoporous PB was immersed in this solution for 1–2 h. Subsequently, the whole system was subjected to photo-activation under UV light at 365 nm for 30 min [35]. After exposure the template was ultrasonicated in the same solvents three times to remove non-reacted compounds and dried for 8 h under vacuum.

2.4. Synthesis of gyroid SnO_2 thin film

The mesoporous SnO_2 material was prepared by the nanocasting method using the above surface-modified nanoporous PB as template. Typically, the dried PB template was dropped into a glass bottle containing 6 g of tin chloride dihydrate ($SnCl_2 \cdot 2H_2O$, Aldrich, 98%, m.p. 310–311 K) that was melted to liquid phase at 333 K. The



Scheme 1. Schematic illustration of creation of ordered gyroid TiO_2 and SnO_2 from cross-linked nanoporous PB.