



Synthesis of ordered mesoporous silicon oxycarbide monoliths via preceramic polymer nanocasting

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ABSTRACT

Highly ordered mesoporous silicon oxycarbide (SiOC) monoliths have been synthesized using liquid poly(hydridomethylsiloxane) (PHMS) as starting preceramic polymer and mesoporous carbon CMK-3 as direct template. Monolithic SiOC-carbon composites were generated via nanocasting of PHMS into CMK-3, pressing without any additive, cross-linking at 150 °C under humid air and subsequent thermolysis at 1000 or 1200 °C under argon atmosphere. The carbon template was finally removed by the thermal treatment at 1000 °C in an ammonia atmosphere, as a result of the generation of monolithic SiOC ceramics with ordered mesoporous structures. The products were characterized by scanning electron and transmission electron microscopes, X-ray diffraction, Fourier transformation infrared spectrometer, X-ray photoelectron spectroscopy and nitrogen absorption-desorption analyzer. The as-prepared SiOC monoliths exhibited crack-free, ordered 2-dimensional hexagonal *p6mm* symmetry with high specific surface areas. With increasing the calcination temperature, the ordered mesoporous structure was still remained and the specific surface area just had a slight reduction from 616 to 602 m² g⁻¹. Moreover, the porous SiOC monoliths possessed good compression strengths and anti-oxidation properties.

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1. Introduction

Porous monolithic materials have become very popular due to the good combination of the compact integral structures and the porous microstructures. Large surface areas and multimodal porosities are great advantages in many fields, such as electrochemistry, energy storage, separation, chromatography and catalysis [1–4]. For instance, porous monoliths can be used in flow through catalytic or separation systems and give better performance and higher permeability compared with packed columns [4,5]. Among the various porous monolithic materials, silicon carbide (SiC) monoliths have attracted great attention because of their excellent mechanical strength, thermal stability and functional semiconductor characteristics [6–8]. These characteristics make them hold many potential applications in high-temperature catalysis [4,9], separation [5,10] and semiconductors [7]. However, the drawback of dissatisfactory oxidation resistance of SiC materials limits their aerobic high-temperature environment applications.

It has been reported that, after introducing a third component into SiC matrix, such as oxygen, nitrogen, boron or aluminum, as-obtained SiC-based ceramics exhibit much better oxidation resistance compared with pure SiC ceramic [11–14]. This reinforcement

is fundamentally due to the existence of the complex-covalent bonding configuration in these SiC-based ceramics [11]. Among the ternary SiC-based ceramics, silicon oxycarbide (SiOC) ceramics have been the most promising materials with the consideration of low cost, simplicity of the set-up and environment safety [11,15–17]. Accordingly, much effort has been paid to the design and synthesis of SiOC monoliths that have high surface area, tailored porosity and pore interconnectivity. For example, Ye et al. synthesized monolithic silica/resorcinol-formaldehyde aerogels and then converted them into porous monolithic SiOC materials [18]. Biasetto et al. prepared microcellular SiOC foams by means of a commercially available preceramic polymer as precursor and poly(methyl methacrylate) microbeads as sacrificial fillers [19]. However, the porous SiOC monoliths, prepared by the aerogel- and foam-templating methods, displayed relatively weak mechanical strengths. Vakifahmetoglu et al. prepared monolithic SiOC glass with hierarchical porosity by a one-pot processing method, but the monolith had a low specific surface area of 137 m² g⁻¹ and a weak compression strength of about 1.7 MPa [20]. In addition, the above porous SiOC monoliths were disordered in the mesostructure.

Polymer-derived ceramics is a good road to prepare mesoporous ceramic materials [21,22]. PHMS, poly(hydridomethylsiloxane), as a commercially available polymer, is known as a good polymer precursor for preparing SiOC ceramics through crosslinking and pyrolysis [23,24]. Because it is liquid at room temperature,

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PHMS has good ability to fill into nano-scale channels of porous templates by casting without the aid of any solvent or heating process.

In this study, we describe a facile synthesis of mesoporous SiOC monoliths with ordered hexagonal $p6mm$ symmetry using PHMS as the preceramic polymer. In our synthesis process, highly ordered mesoporous silica SBA-15 was employed as the starting template to prepare its negative replica carbon CMK-3 template. The CMK-3 template was subsequently casted with a THF solution of PHMS using a liquid-phase impregnation, via pressing the gel-like polymer-carbon composites into tablet-like monoliths, cross-linking in humid air, pyrolyzing under argon atmosphere and removing carbon template in ammonia, ordered mesoporous SiOC monoliths with high specific surface areas were obtained. Moreover, the samples possessed high compression strengths and good anti-oxidation properties, which make them be potential candidates for various high-temperature applications.

2. Experimental

2.1. Chemicals

Triblock poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) copolymer Pluronic P123 ($M_w = 5800$, EO₂₀PO₇₀EO₂₀) and Poly(hydridomethylsiloxane) (PHMS) were purchased from Sigma–Aldrich. Tetraethyl orthosilicate (TEOS, analytical reagent, AR) was purchased from Tianjin Chemical Reagents Company. Others chemicals were purchased from Shanghai Chemical Company. All chemicals were used as received state without any further purification. Deionized water was used in all experiments. High-purity argon and ammonia (99.99%) were used in their as-received state during the ceramic preparation.

2.2. Synthesis of hard templates

Mesoporous silica SBA-15 template was prepared by hydrothermal synthesis method according to established procedures [25]. That was to using P123 as structure directing agent and TEOS as a precursor. The SBA-15 template exhibited two-dimensional $P6mm$ hexagonal symmetry with a specific surface area of 527 m² g⁻¹ and an average pore diameter of 8.92 nm. Mesoporous carbon CMK-3 template was synthesized by the nanocasting method using sucrose as a precursor and mesoporous silica SBA-15 as a hard template according to the literature [26]. The CMK-3 template displayed a highly ordered 2D hexagonal mesostructure with a specific surface area of 1530 m² g⁻¹ and an average pore diameter of 4.03 nm.

2.3. Preparation of mesoporous SiOC monoliths

The mesoporous SiOC monoliths were synthesized by replica technique using PHMS as the ceramic precursor and mesoporous CMK-3 as the hard template. For a typical synthesis, 1.0 g of CMK-3 was placed in a flask, dried at 150 °C under a vacuum for 4 h and cooled down to room temperature (RT), and then added in a solution of 3.0 g of PHMS and 10 ml of THF. The mixture was stirred at RT for one day. After that, THF solvent was removed under vacuum to obtain gel-like mixture of PHMS and CMK-3. The gel-like mixture was divided into four parts (1.0 g for each) and each part was pressed into a cylindrical monolith using a cylindrical mould ($\varnothing = 15$ mm) at RT under a low pressure of 5 MPa. All composite monoliths were cross-linked at 150 °C for 20 h under a humid air in a muffle furnace. According to the above procedure, the PHMS–CMK-3 composite monoliths were prepared with the same mass and shape. After that, as-prepared monoliths were

transferred into a horizontal ceramic tube furnace and subjected to the thermal treatment in an argon atmosphere at 1000 or 1200 °C (at heating rate of 1 °C min⁻¹) for 2 h respectively, to generate SiOC-carbon composite monoliths. Finally, the ceramic-carbon composite monoliths were underwent a final thermal treatment in an ammonia atmosphere at 1000 °C (a heating rate of 2 °C min⁻¹) for 10 h, to remove the carbon template and generate ordered mesoporous SiOC monoliths. The monolithic samples prepared at different temperatures were denoted as M–SiOC–T, where M marked as monolith and T marked as temperature.

2.4. Characterization

The morphology of the final products was observed on a field emission scanning electron microscope (FE-SEM, JSM 6701F). Transmission electron microscopy (TEM) measurements were conducted on a JEM-2010 microscope operated at 200 kV, to reveal the ordered structure of the samples. Powdery samples were first dispersed in ethanol with the aid of sonication and then collected using carbon-film-covered copper grids for TEM analyses. Powder small-angle X-ray diffraction (SA-XRD) and wide-angle X-ray diffraction (WA-XRD) patterns were achieved using a Philipps X'Pert PRO X-ray diffraction system (Cu K α radiation, 0.15406 nm). The chemical compositions of the samples were analyzed by Fourier transformation infrared spectroscopy (FTIR) using a Bruker IFS66 V FTIR spectrometer and X-ray photoelectron spectroscopy (XPS) performed on an X-ray photoelectron spectroscopy (ESCALAB 210VG Scientific). The XPS measurements used Al–K α radiation (photon energy 1476.6 eV) as the excitation source and the binding energy of Au (Au 4f_{7/2}: 84.00 eV) as the reference. Before the XPS scanning, the samples were etching using Ar ions for 30 s. Nitrogen absorption–desorption isotherm measurements were performed on a Micrometitics ASAP 2020 volumetric absorption analyzer at –196 °C. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area of each sample, and the pore-size distribution was derived from the absorption branch of the corresponding isotherm using the Barrett–Joyner–Halenda (BJH) method. The total pore volume was estimated from the amount adsorbed at a relative pressure of $P/P_0 = 0.99$. The mechanical compressive strength of the mesoporous SiOC monoliths was evaluated using a universal tensile testing machine (SHIMADZU Universal Testing Machine AGS-X 5kN) at RT. The oxidation stability was evaluated by thermogravimetric analysis (TGA) from RT to 1000 °C under air atmosphere with a heating rate of 10 °C min⁻¹.

3. Results and discussion

The synthetic approach for preparing mesoporous SiOC monoliths is shown in Scheme 1. Herein, the choice of CMK-3 as the hard template is justified by the connection of its hexagonal array of mesopores by micropores in the walls, which permits the replication process [27]. The main advantage of CMK-3 is that the carbon framework can be removed completely under ammonia at a high temperature of 1000 °C [13]. Because this NH₃ etching process is relatively slow, the ordered mesoporous structure can be remained to greatest possible degree [13]. The choice of PHMS as the precursor is due to that it has high ceramic yield (>85%), chemical inertness under ambient conditions and complete conversion into ceramic at temperature less than 800 °C. In our synthesis, THF solution of PHMS was easily filled into the nano-scale channels of CMK-3 template by nanocasting because the CMK-3 has high specific surface area and large pore volume. After removing THF solvent slowly, the resulting mixture consisted of PHMS and CMK-3 became a plasticene-like gel, which was easily pressing into monolith. Furthermore, the presence of Si–H groups in PHMS, hu-

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