



Synthesis of hierarchical porous silicon oxycarbide ceramics from preceramic polymer and wood biomass composites

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Abstract

Hierarchical porous SiOC ceramics were successfully prepared using a polysiloxane preceramic polymer mixed with wood biomass by annealing at different temperatures under Ar atmosphere. These SiOC ceramics display a trimodal pore size distribution in the micro-, meso- (micropores + mesopores, 1.7–14 nm) and macro-size scale (1–15 μm). The mesopores and micropores mainly originate from the formation of large amounts of SiC crystals and nanowires, graphite-like microcrystallites, and nm-scale pores of ray parenchyma cells and pits of the wood biomass. The SiOC sample prepared at a higher temperature processes the specific surface area up to 180.5 m²/g. The specific surface area, pore volume and average pore width of the samples can be controlled by adjusting the pyrolysis temperature.

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1. Introduction

Hierarchical porous materials with pore sizes ranging from nanometers to micrometers scale have attracted considerable attention due to their multiple functions such as low density, low thermal conductivity, high thermal shock resistance, high chemical stability and good mechanical properties.^{1–3} These hierarchical porous systems were found to have specialized applications in diverse fields including catalyst supports, gas adsorbents, industrial hot gas filters, supercapacitors, and porous burners.^{4–7}

Previously, silicon-containing preceramic polymers, such as polysiloxanes, polycarbosilanes and polysilazanes, have been successfully used for preparing hierarchical porous SiOC, SiC, SiCN and SiOCN ceramics possessing a large amount of porosity in the micro-, meso- and macro-size scale.^{8–12} Generally, there are several methods for the preparation of these hierarchical porous materials, including a controlled heat treatment and/or

the addition of suitable fillers, or by coating with a mesoporous film, or by selective etching using acid or chlorine gas.^{10,13–16}

For example, hierarchical porous SiOC materials were prepared by etching Si(B)OC glasses with hydrofluoric acid solution.⁹ Hierarchical porous SiOC ceramics were produced from periodic mesoporous organosilica (PMO) particles embedded into a foamed siloxane preceramic polymer.¹⁷ Furthermore, it is well known that SiC nanowires can be synthesized from polymeric precursors under appropriate conditions.^{18–21} SiC nanowires embedded in the porous materials can lead to an increase in the specific surface area (SSA).²²

It has been shown that a remarkable feature of natural biomass such as wood, cotton, bamboo and diatom etc., is their complex hierarchical pore structure attributed to a long-term genetic evolution and optimization. The biomorphic porous constructions from millimeters down to nanometers were always employed as templates to synthesize hierarchical porous materials such as oxide and carbide ceramics.^{23–26} Additionally, it has been proved that the porous and loose structures can provide the growth space for SiC nanowires.^{22,27} It can be concluded that natural biomass has the potential to prepare hierarchical porous materials with high SSA. Wood biomass, as a renewable resource, processes a hierarchical cellular structure containing hollow vessels, tracheids aligned with the axis of the tree trunk

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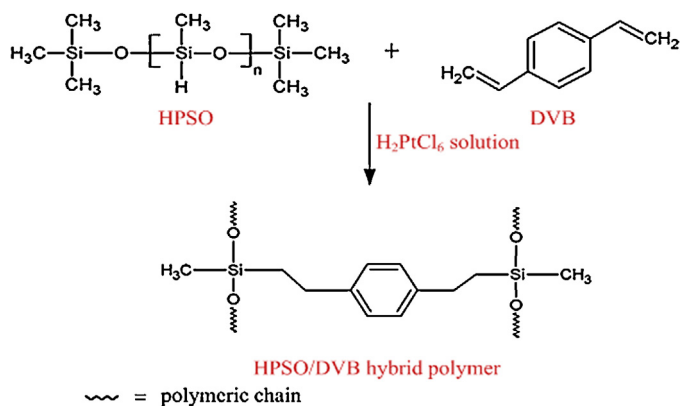


Fig. 1. Reaction between HPSO and DVB giving rise to HPSO/DVB hybrid polymer.

and rays growing in a radial direction. Although porous SiOC systems have been intensively studied in the past few years, the hierarchical porous SiOC systems prepared by addition of natural biomass into preceramic polymer were less addressed. Here, we report on the preparation of hierarchical porous SiOC ceramics (HP-SiOC) using polysiloxane as a preceramic polymer mixed with wood biomass. In this process, the waste wood or woody materials can be utilized effectively in the production of the hierarchical porous materials, and a simple, environmentally benign and cost effective route for preparing the hierarchical porous SiOC ceramics was developed.

2. Experimental procedure

2.1. Preparation of HP-SiOC ceramics

Hydrogen containing silicone oil (HPSO), a colorless transparent liquid containing 1.4 wt.% hydrogen, with a viscosity of 24 mPa s at room temperature (Zhenjiang, Jiangsu, China), divinylbenzene (DVB) (Shanghai, China) and chloroplatinic acid (H_2PtCl_6) (Changshu, Jiangsu, China) were used to produce the hybrid polymeric networks. The mass ratio of the HPSO/DVB/ H_2PtCl_6 hybrid polymer is 60/30/10. Firstly, the H_2PtCl_6 /ethanol solution (11.3 ppm) was mixed into HPSO/DVB solution by ultrasonic vibration. Then the HPSO/DVB/ H_2PtCl_6 solution was cured at 120 °C for 12 h. The polysiloxane precursor was synthesized via hydrosilylation reaction. In this work, the HPSO reacted with DVB as a cross-linking agent to produce the polysiloxane precursor with a three-dimensional network structure. The polysiloxane precursor with a network structure had a higher ceramic yield. Fig. 1 shows the reaction between HPSO and DVB giving rise to HPSO/DVB hybrid polymer. The actual picture of the polysiloxane precursor is shown in Fig. 2a. It can be seen that the polysiloxane is a translucent solid. Fig. 2b shows the FTIR spectrum of the polysiloxane precursor in order to analyze the chemical structures. A weak band at 3304 cm^{-1} assigned to $-\text{OH}$ is observed. The typical band at 2961 cm^{-1} is assigned to the $-\text{CH}_3$ absorption. The band located at 2926 cm^{-1} is attributed to the vibration of the $-\text{CH}_2$ bonds. The band at 2168 cm^{-1} assigned to $\text{Si}-\text{H}$ is also observed due to the incompletely reacted HPSO. The

strong absorption at 1261 cm^{-1} , characteristic of the vibration of $\text{Si}-\text{CH}_3$ bonds, is observed. In addition, the strong absorption bands at 1103 cm^{-1} and 1042 cm^{-1} are assigned to the $\text{Si}-\text{O}$ bonds, corresponding to the mode associated with siloxane chain. The bands from 707 to 894 cm^{-1} are due to the vibration of $\text{C}-\text{H}$ bonds from benzene ring of DVB.

Chinese fir sawdust milled into a powder of about 64 μm was used as the starting material for the synthesis of the HP-SiOC ceramics. Then the wood biomass and as-prepared polysiloxane precursor with a mass ratio of 1:1 were mixed via ball milling at room temperature (P-2, Fritsch, Germany). Green bodies with a size of 30 mm \times 30 mm \times 5 mm were molded using the warm-pressing equipment under a pressure of 40 MPa at 80 °C for 20 min. The pyrolysis of the sample was carried out in a tube furnace under Ar atmosphere. In order to avoid the fast pyrolysis of green bodies resulting in the formation of the microcracks during the sintering process, a multi-step heat treatment was proposed. The green bodies were sintered at a heating rate of 5 °C/min up to 150 °C for 15 min. Then the green bodies were sintered at a lower heating rate of 2 °C/min up to 400 °C for 30 min. At the third stage, the green bodies were heated with 5 °C/min up to the set temperature (1000 °C, 1200 °C, 1300 °C, 1400 °C) for 180 min. Then the furnace was cooled down to room temperature at a cooling rate of 3 °C/min.

2.2. Characterization

The phase composition of the samples was determined by X-ray diffraction (XRD, Max 2550, Japan) using a nickel filtered $\text{CuK}\alpha$ radiation. Raman spectra of the samples were recorded on a Renishaw inVia Reflex spectrometer by using an excitation laser wavelength of 532 nm and laser power of 1 mW at room temperature. The morphology of the samples was observed using field emission scanning electron microscope (FESEM, JSM-7001F, Japan). The elemental composition of wood powders was analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES, Vista-MPX, America). The microstructure of the samples was further characterized by using a field emission transmission electron microscope (TEM, H-800, Japan) and high-resolution TEM (HRTEM, JEOL-2010, Japan). The specific surface areas and pore size distributions (PSDs) of the samples were obtained from nitrogen adsorption-desorption measurements at 77 K using an automatic instrument (NOVA2000, USA). Prior to this measurement, the samples were carried out by degassing at 250 °C for 2 h. The specific surface areas were calculated from the isotherms by the multipoint Brunauer-Emmett-Teller (BET) method. The PSDs and pore volumes were determined using the non-local density functional theory (NLDFT) method.

3. Results and discussion

3.1. XRD analysis

XRD analysis was used to investigate the phase evolution of the HP-SiOC samples. Fig. 3 shows the XRD patterns of

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