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SiBCN-ZrO₂ hybrid ceramic aerogels through the polymer-derived ceramics (PDCs) route

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ABSTRACT

The SiBCN-ZrO₂ hybrid ceramic aerogels were fabricated by pyrolysis of preceramic aerogels prepared from Polyborosilane/Zirconium 5n-butoxide /Divinylbenzene (PSNB/ZBO/DVB) combining a simple hydrosilylation reaction with CO₂ supercritical drying. The micromorphology and pore structure parameters of the preceramic hybrid aerogels were investigated. Structural evolution of the ceramic hybrid aerogels and the crystallization behavior were studied by scanning electron microscope (SEM), X-ray diffraction (XRD) and transmission electron microscopy (TEM). The results showed that all the preceramic hybrid aerogels had a typical mesoporous structure. The neck region between the particles of SiBCN-ZrO₂ ceramic hybrid aerogels was gradually increased when the sintering temperatures increased from 750 °C to 1550 °C. After heat treatment at 1550 °C, the specific surface area and pore volume for the samples were drastically reduced down to 108.85 m² g⁻¹ and 0.49 cm³ g⁻¹, respectively. The ZrO₂ nanocrystals were well-distributed in amorphous SiBCN network backbone, the final crystalline phases were composed of hexagonal BN, β-SiC crystals and monoclinic ZrO₂.

1. Introduction

In past few decades, the aerogels have attracted much attention for various industrial applications, such as gas adsorption, catalysis, water treatment, drug supports and biochemical fields, owing to the high porosity, nanoporous nature, low thermal conductivity (0.015–0.050 W/mK) and high specific surface area (100–1000 m²/g) [1–7]. Since the original silica aerogel was produced in 1931 by Kistler, various functional aerogels and aerogel composites have been explored [8,9]. For example, Liu et al. [10] reported a kind of hybrid organic-inorganic mesostructured aerogels combining properties of thermal super-insulation, mechanical robustness, flexibility and transparency to visible-spectrum light. Li and his coworkers [11] presented a fungal hyphae/graphene oxide aerogel which could be used for radioactive uranium ions (U(VI)) removal. In order to obtain a material with numerous advantages including low cost and remarkable electrochemical behaviors, Chen et al. [12] developed a nitrogen and sulfur co-doped graphene aerogel. However, most aerogels are prone to take place shrinkage and pore structure collapse when the temperature is above 1000 °C [13–16], so the preparation of aerogels which are applied to ultra-high temperature fields is a great challenge.

In recent years, polymer derived ceramic aerogels were widely used in harsh environments (high-temperature and/or highly corrosive

environments) because of its excellent chemical, physical and structural stability [17–21]. Development to date, several kinds of non-oxide ceramic aerogels including SiOC, SiC, SiCN were synthesized [22–24]. Comparing with binary ceramics such as SiC, BN and ternary ceramics such as SiOC, SiCN, etc., SiBCN has a better performance on physical stability, chemical stability, thermal vibration resistance, coefficient of thermal expansion, hardness, etc. [25–27]. So it could be a potential aerogel matrix for high temperature applications. Zirconium dioxide (ZrO₂) is a kind of material with excellent chemical stability, thermal stability, insulativity and light-proofness, besides that, ZrO₂ still has an outstanding ion exchange performance which could be used in catalysts, adsorbents and other applications [28–31]. Therefore, SiBCN-ZrO₂ aerogel not only holds the ion exchange capacity which comes from ZrO₂, but also retains the high thermal stability and good mechanical properties of SiBCN, showing a great potential in these applications such as insulation, adsorption and catalytic. It has been reported that SiC-based composite ceramics can be obtained by pyrolyzing the boron powders doped polycarbosilane (PCS) [32]. However, it is difficult to form a uniform system by this fabrication method as a result of the presence of insoluble solid powder. In order to avoid this situation, the additive component could be liquid phase which can achieve uniform mixing with liquid precursor.

In this study, a simple method was reported to synthesize SiBCN/

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ZrO₂ ceramic aerogels by taking the advantage of PDCs processing. The PSNB/ZBO preceramic hybrid aerogels were first prepared by combining a simple hydrosilylation reaction with CO₂ supercritical drying (SCD). For this step, the PSNB, Zirconium n-butoxide (ZBO) was used as precursors and the divinylbenzene (DVB) was used as crosslinking agent. Then the SiBCN-ZrO₂ ceramic hybrid aerogels were synthesised by pyrolysis in N₂ atmosphere. The obtained PSNB/ZBO preceramic hybrid aerogels and SiBCN-ZrO₂ ceramic hybrid aerogels all exhibited a porous network structure. At the same time, a liquid-liquid dispersion system ensures the components of SiBCN-ZrO₂ ceramic hybrid aerogels distributing uniformly. Furthermore, SiBCN-ZrO₂ hybrid aerogels can be widely used in many fields because of its excellent chemical stability at high temperatures. Take the field of adsorption as an example, ceramic hybrid aerogels which have adsorbed organic dyes could be recycled by calcination in air owing to the outstanding thermostability.

2. Experimental section

2.1. Materials

Polyborosilane precursor (PSNB, MW~1500 g/mol), was provided by the National University of Defense Technology, China. Zirconium n-butoxide (ZBO) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. The crosslinking agent, Divinylbenzene (DVB), was provided by Aladdin Industrial Corporation, China. Tetrahydrofuran (THF) was purchased from Tianjin Qishengyuan Trading Co., Ltd., and used as solvents.

2.2. Preparation of PSNB/ZBO preceramic hybrid aerogels

At first, appropriate amount of PSNB and ZBO (the mass ratio of PSNB/ZBO was 2:1, 3:1, 4:1 respectively) were added into 7.56 g THF and stirred for 5 min at room temperature. Subsequently, 0.6 g of DVB was added to the solution and kept stirring until the reaction mixture became homogeneous and transparent. Then, the solution was transferred into a closed pressure vessel with an internal Teflon liner and kept at 120 °C for 5 h in the vacuum drying oven. After the temperature of pressure vessel was cooled to room temperature, the PSNB/ZBO preceramic hybrid wet gels were obtained. Then, the wet gels were kept in alcohol for 1 week and the alcohol was renewed with a fresh one once per day in order to remove the unreacted precursor. Finally, the PSNB/ZBO preceramic hybrid aerogels were prepared by combining a CO₂ supercritical drying technology.

2.3. Preparation of SiBCN-ZrO₂ ceramic hybrid aerogels

After drying at 65 °C for 24 h in an oven, the prepared PSNB/ZBO preceramic hybrid aerogel blocks were heated to 750 °C, 950 °C, 1150 °C, 1350 °C and 1550 °C under N₂ atmosphere respectively, with a heating rate of 4 °C min⁻¹ and maintained for 1 h at the maximum temperature, then the pyrolysis was completed by cooling the sample to room temperature with a cooling rate of 5 °C min⁻¹. The SiBCN-ZrO₂ ceramic hybrid aerogels were obtained. The process for preparation of the SiBCN-ZrO₂ ceramic hybrid aerogels is summarized in the Scheme 1. In this article, the mass ratio of PSNB: ZBO in preceramic hybrid

aerogel are 2:1, 3:1 and 4:1, and the corresponding samples are denoted as "S2", "S3" and "S4", respectively.

2.4. Characterization

Fourier transform infrared spectrometer (FT-IR, 380 Nicolet) was utilized to analyse the chemical composition of the obtained materials over the range of 400–4000 cm⁻¹ with a spectrum resolution of 4 cm⁻¹. The microstructure of the prepared aerogels were observed by a scanning electron microscopy (SEM, JSM-7800F). The transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns of the prepared ceramic hybrid aerogels were acquired using a FEI Tecnai G2 F20 transmission electron microscope operated at 200 kV. The specific surface area and pore-size distributions of the samples were determined by a N₂ adsorption technique (Beishide, 3H-2000PS1) at 77 K. While the phase transformation of the SiBCN-ZrO₂ ceramic hybrid aerogels was characterized by X-ray diffraction (XRD, D8-ADVANCE) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at a scanning rate of 0.02° s⁻¹ in the 2 θ range from 10° to 80°.

3. Results and discussion

3.1. FT-IR of PSNB/ZBO preceramic hybrid aerogels

Fig. 1 shows the FT-IR spectra of (a) PSNB precursor and (b) PSNB/ZBO preceramic hybrid aerogels. With respect to the unreacted PSNB precursor (Fig. 1a), the bands at 2100 cm⁻¹ and 1265 cm⁻¹ are associated with the Si-H stretching vibration and Si-C stretching vibration, respectively. As for PSNB/ZBO preceramic hybrid aerogels, the Si-H stretching vibration peaks at 2100 cm⁻¹ has a modest decrease, and further more, the new peaks at 1200 cm⁻¹, 1470 m⁻¹ and 1580 cm⁻¹ are assigned to C-C saturable bonds, Zr-O-Zr bonds and aromatic C=C double bonds, respectively. The above results could confirm that the hydrosilylation reaction between the Si-H of PSNB precursor and the -CH=CH₂ of DVB happened.

3.2. Morphology of PSNB/ZBO preceramic hybrid aerogels with different ZBO content

The SEM images of S2, S3 and S4 are shown in Fig. 2. As shown in Fig. 2, all the samples exhibit a porous network structure, which provided guarantee for the PSNB/ZBO preceramic hybrid aerogels having a low density and high porosity. At the same dimension, it could be found the microstructure of three hybrid aerogels exist a slight difference. The porosity and particle size of the prepared hybrid aerogels show a certain increase while the mass ratio of PSNB: ZBO increasing from 2 to 3 (Fig. 2a-b). The reason could be explained that, when the mixed liquid system had a number of ZBO, the polymerization rate would decrease as well as the nucleation rate of the spherical particles. As the nucleation rate reduced, a single particle would continue to grow, resulting in a larger particle size, pore size and a smaller porosity of the aerogel matrix. Meanwhile, comparing the SEM images of S2, S3 and S4, it can be found that the sample of S4 has the lowest pore size and the largest particle size. This could be related to a fewer ZBO existing in total solute system. In such a situation, the agglomeration of PSNB

Scheme 1. Schematic of the fabrication process for SiBCN-ZrO₂ ceramic hybrid aerogels.

Fig. 1. FTIR spectra of (a) PSNB precursor, (b) PSNB/ZBO preceramic hybrid aerogels.

particles would play a more decisive role, finally resulting in the pore structure with a biggish particle scale (Fig. 2c). Moreover, the sample of S3 possesses a highest porosity, but a small number of macropore structure ($d > 50$ nm) still can be found in Fig. 2b. In summary, the particle scale and pore size of the prepared preceramic hybrid aerogels can be moderately controlled by adjusting the ZBO content.

3.3. Nitrogen absorption of PSNB/ZBO preceramic hybrid aerogels with different ZBO content

The N_2 adsorption-desorption isotherms (Fig. 3a) and pore size distribution curves (Fig. 3b) were used to illustrate the influence of ZBO content on the pore properties of the hybrid aerogels. In Fig. 3a, all the curves of hybrid aerogels resemble type IV isotherm with a H3 hysteresis loop according to the IUPAC classification, suggesting the presence of considerable fraction of macropores and large mesopores. This is mainly because that the CO_2 supercritical drying technology is propitious to increasing the specific surface area and porosity of composite aerogels by reducing the capillary force. On the basis of Table 1, it is obvious that the ZBO content of the hybrid aerogels do not significantly affect the pore characteristics of the aerogels when the initial concentration of solvent remains unchanged, which is essentially in agreement with the results obtained by scanning electron microscopy (Fig. 2). The BET surface area, average pore size and pore volume of the prepared PSNB/ZBO preceramic hybrid aerogels are in the range of $516.88\text{--}621.59\text{ m}^2\text{ g}^{-1}$, $10.60\text{--}12.88\text{ nm}$ and $1.89\text{--}2.01\text{ cm}^3\text{ g}^{-1}$, respectively, which indicated that the hybrid aerogels all had a typical mesoporous structure. Because of the facts of a smaller pore volume corresponding to a smaller specific surface area and average pore diameter, it can be summarized that the sample of S3 showed the best

microstructure with the lowest density and the highest average pore size, specific surface area as well as pore volume.

3.4. Formation of the SiBCN-ZrO₂ ceramic hybrid aerogels

According to the above analysis, the sample of S3 was selected as the raw materials for high temperature sintering. Moreover, in order to investigate the morphology evolution process, the micrographs of samples which pyrolyzed at different temperatures were observed by SEM. Fig. 4(a-f) show the microstructures of the hybrid aerogel heat treated at different temperatures (750–1550 °C). It was obvious that the neck region between the particles of SiBCN-ZrO₂ ceramic hybrid aerogels is gradually broadened when the sintering temperatures increased from 750 °C to 1550 °C. Meanwhile, the porosity of hybrid aerogels were gradually decreased, and the network structure of samples became denser. In addition, the obtained SiBCN-ZrO₂ ceramic hybrid aerogels which through a polymer ceramic process had a relatively uniform pore diameter. Thus it can be seen, the mesopores structure of the prepared ceramic hybrid aerogels could be remained after being sintered at the high temperature.

Fig. 5 shows the transmission electron microscopy (TEM) images and the selected area electron diffraction (SAED) patterns of the ceramic hybrid aerogels after pyrolyzing at 1550 °C. As seen in Fig. 5(a,b), transmission electron microscopy images show the ZrO₂ nanocrystals are well-distributed in amorphous SiBCN network backbone. Moreover, the whole aerogel matrix keeps a relatively uniform pore structure, which is basically consistent with the results of SEM and nitrogen adsorption-desorption. The representative HRTEM images of a part of the surface of SiBCN-ZrO₂ ceramic hybrid aerogel are shown in Fig. 5(c,d), where the ZrO₂, β -SiC and a little amount of BN crystalline phase could be seen obviously, and the hybrid aerogel is mostly amorphous with no regular atoms arrangement. As revealed in Fig. 5c, the well-resolved lattice fringes with an interplane distance of 0.25 nm corresponds to the d-spacing of the (311) plane in β -SiC. The lattice fringes shown in Fig. 5d can be related to the (111) crystallographic plane ($d = 0.31$ nm) of monoclinic zirconia and the (002) crystallographic plane ($d = 0.33$ nm) of hexagonal BN, respectively.

The XRD patterns of the ceramic aerogels pyrolyzed at different temperature are recorded and shown in Fig. 6. As shown in Fig. 6, the obtained sintered products are amorphous when the sintering temperature is below 1350 °C. After further heating up to 1550 °C, several strong diffraction peaks can be observed which indicated that crystalline phase appeared in calcined hybrid aerogels at this temperature. The diffraction peaks at 2θ of 31.5° , 51° correspond to lattice planes of (111), (101) of monoclinic zirconia, indicating that the crystallization phase of ZrO₂ was successfully formed after the high temperature calcination. There are two extra diffraction peaks at $2\theta = 26^\circ$, 61° , assigning to the (002) lattice plane of hexagonal BN and (311) lattice plane of β -SiC crystals, respectively. Therefore, the crystalline transformation process occurred in the temperature range of 1350–1550 °C

Fig. 2. SEM images of preceramic hybrid aerogels with various ZBO contents: (a) S2, (b) S3, (c) S4, respectively.

Fig. 3. N₂ adsorption-desorption isotherms (a) and pore-size distribution curves (b) for preceramic hybrid aerogels with different ZBO contents.

Table 1

Nitrogen sorption results of the preceramic aerogels.

Sample	Density (g cm ⁻³)	BET surface area (m ² g ⁻¹)	Average pore diameter (nm)	Pore volume (cm ³ g ⁻¹)
S2	0.31	516.88	10.60	1.89
S3	0.27	621.59	12.88	2.01
S4	0.29	542.45	11.10	1.93

and the final products were composed of hexagonal BN, β-SiC crystals, monoclinic zirconia and the rest of amorphous SiBCN.

The N₂ adsorption/desorption isotherms and corresponding pore size distribution curves for the samples pyrolyzed at different temperature are shown in Fig. 7. All these aerogels show typical type IV isotherms (the samples pyrolyzed in N₂ show a minor adsorption volume at low relative pressures) with a H3 hysteresis loop according to IUPAC nomenclature (Fig. 7a). Fig. 7b reveals a narrow pore size distribution with pore size ranging from 10 nm to 70 nm, and a considerable number of pores locate at around 30 nm. The measured SSA

Fig. 4. SEM micrograph of (a) preceramic aerogel; sample of S3 pyrolyzed at (b) 750 °C; (c) 950 °C; (d) 1150 °C; (e) 1350 °C; (f) 1550 °C.

Fig. 5. TEM images, SAED patterns and HRTEM images of the sample of S3 pyrolyzed at 1550 °C.

Fig. 6. XRD pattern of the sample of S3 pyrolyzed at different temperatures.

values and corresponding pore volumes are given in Table 2. When sintering temperature gradually rises from 750 °C to 1550 °C, the specific surface area and pore volume of the samples are drastically

Table 2

Nitrogen sorption results of of preceramic aerogel after pyrolysis at different temperatures.

Sintering temperature (°C)	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)
750	211.74	1.57
950	168.69	1.18
1150	154.45	0.92
1350	135.89	0.78
1550	108.85	0.49

reduced from $211.74 \text{ m}^2 \text{g}^{-1}$ to $108.85 \text{ m}^2 \text{g}^{-1}$ and $1.57 \text{ cm}^3 \text{g}^{-1}$ to $0.49 \text{ cm}^3 \text{g}^{-1}$, respectively, which was lower than that of the original preceramic hybrid aerogel ($621.59 \text{ cm}^3 \text{g}^{-1}$). These results that a modest shrinkage of the pore structure of samples would arise after being pyrolyzed at high temperature under N_2 atmosphere, which matched the SEM observations (Fig. 4), but the obtained SiBCN-ZrO₂ ceramic aerogels still possessed a basic micropore and mesoporous structure.

Fig. 7. N_2 adsorption-desorption isotherms (a) and pore-size distribution curves (b) of the sample of S3 pyrolyzed at different temperatures.

4. Conclusion

In this paper, the SiBCN-ZrO₂ hybrid ceramic aerogels were fabricated by pyrolysis of preceramic aerogels prepared from Polyborosilane/Zirconium n-butoxide /Divinylbenzene (PSNB/ZBO/DVB) combining a simple hydrosilylation reaction with CO₂ supercritical drying. The particle scale and pore size of the prepared preceramic hybrid aerogels could be moderately controlled by adjusting the ZBO content. The BET surface area, average pore size and pore volume of the prepared PSNB/ZBO preceramic hybrid aerogels were in the range of 516.88 m² g⁻¹–621.59 m² g⁻¹, 10.60–12.88 nm and 1.89 cm³ g⁻¹–2.01 cm³ g⁻¹, respectively, which indicated that the hybrid aerogels all had a typical mesoporous structure. The preceramic hybrid aerogels pyrolyzed at 1550 °C in N₂ atmosphere kept a basic aerogel structure (the specific surface area and pore volume are 108.85 m² g⁻¹ and 0.49 cm³ g⁻¹, respectively), and the ZrO₂ nanocrystals were well-distributed in amorphous SiBCN network backbone. After heat treatment at 1550 °C, the final products were composed of hexagonal BN, β-SiC crystals, monoclinic zirconia and the rest of amorphous SiBCN.

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