



Facile synthesis of resorcinol–formaldehyde/silica composite aerogels and their transformation to monolithic carbon/silica and carbon/silicon carbide composite aerogels

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ABSTRACT

Resorcinol–formaldehyde/silica composite (RF/SiO₂) gels were synthesized in one pot by simply mixing the monomers and dried under supercritical carbon dioxide to form RF/SiO₂ aerogels. Carbon/silica composite (C/SiO₂) and carbon/silicon carbide composite (C/SiC) aerogels were formed from the RF/SiO₂ aerogels after carbonization and carbothermal reduction. The as-prepared C/SiC products exhibited a preserved monolithic morphology similar to the original templates and were composed of carbon particles and α -SiC nanocrystals. The C/SiC specimen possessed a BET surface area of 892 m²/g and a porosity of 94.8%, both of which were significantly higher than the BET surface area and porosity of C/SiO₂ and RF/SiO₂ aerogels. The resulting C/SiC monolith was stable up to temperatures near 550 °C, which is almost 150 °C higher than what C/SiO₂ aerogels can tolerate.

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1. Introduction

Aerogels are unique porous materials with a distinctive microstructure consisting of pores and particles in the nanometer size range. Recently, increased attention has been given to monolithic aerogels due to their combined compact integral structure and porous microstructure that exhibits low density, good mechanical behavior, large internal void space and high specific surface area in a material [1–6]. Among these, carbon/silicon carbide composite (C/SiC) aerogels have excellent properties, including chemical and thermal stability, high conductivity, high surface area and high porosity [4], and can potentially be used as adsorbents, thermal insulators or electrode materials [7–10]. In the past, binary carbonaceous silica aerogels were used as precursors of carbon/silica composite (C/SiO₂) aerogels for the synthesis of porous SiC by carbothermal reduction [2–4,11–13]. However, the sol–gel processes employed to form hybrid gels were complicated and time-consuming. In these techniques, tetraethylorthosilicate (TEOS) and tetramethylorthosilicate (TMOS) were usually used as a silicon source, and acid and alkali were involved as catalysts. If catalysts are not involved, neither the polycondensation of resorcinol and formaldehyde nor the hydrolysis and polymerization of Si(OR)₄ can take place. Anhydrous sodium carbonate was frequently used in the preparation of RF gels, and silica gels could be prepared using acid–base catalyzed two-step or base catalyzed single-step

methods. Therefore, the conflict of catalysts is a considerable problem in the process of forming hybrid gels. Moreover, there is a very different gelation time between RF gels and silica gels. Therefore, to form carbon–silica hybrid gels, the silica sol and carbonaceous sol had to be prepared separately, and the processing goes through a multiple-step sol–gel process. As a matter of fact, a structurally uniform monolithic hybrid gel is hard to prepare if resorcinol, formaldehyde and Si(OR)₄ are only used as reactants. Ke Chen et al. [2] proposed a way to synthesize RF/SiO₂ gels by introducing acetonitrile to the system. RF sol was first prepared using hydrochloric acid as a catalyst, and then the TEOS solution was added into the RF sol, and lastly HF was added to obtain the hybrid gels. Nicholas Leventis et al. [3] used acrylonitrile instead of resorcinol and formaldehyde as a carbon source to synthesize hybrid gels, which is more complicated than the method that was reported by Ke Chen et al.

3-(Aminopropyl)triethoxysilane (APTES) and (3-aminopropyl)trimethoxysilane (APTMS) were commonly used as amino-functionalized modifiers in the synthesis of porous silica [14–20], but have never been used solely as silica sources. Recently, we have reported a method of preparing nanoporous amine-based sorbent using only APTES as a silica source [21], but the process was still complex and time-consuming. Therefore, according to the modified technology process, we propose a facile synthesis of resorcinol–formaldehyde/silica composite (RF/SiO₂) aerogels. Without mixing two sols (silica sol and RF sol), RF/SiO₂ gels were synthesized in one pot by simply mixing the monomers. Only three reactants (APTES, resorcinol and formaldehyde) and a solvent (anhydrous alcohol) were involved in the sol–gel process, and no catalysts were required. C/SiO₂ and C/SiC aerogels were formed after thermal treatment at different temperatures.

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2. Experimental

2.1. Chemicals

APTES, resorcinol (R), formaldehyde (F, 37% w/w aqueous solution) and anhydrous alcohol (C_2H_5OH) were used as raw materials. All of the reagents and solvents were of analytical grade and used as received without further purification.

2.2. Preparation of RF/SiO₂ aerogels

Scheme 1 shows the synthesis route of RF/SiO₂ aerogels and their conversion to C/SiO₂ and C/SiC aerogels. Resorcinol, formaldehyde, APTES and alcohol were mixed in a pot at room temperature, with R:F:APTES: C_2H_5OH prepared at a molar ratio of 1:2:1:60. Subsequently, the compound was transferred into polypropylene molds (48 mm in inner diameter) and placed into an air oven at 60 ± 0.1 °C. The liquid gelled within 70 min. After gelation, the wet gel was demolded, aged at 75 ± 0.1 °C for 24 h and simultaneously washed with ethanol every 8 h to remove water and residual chemicals. After solvent exchange, the alcohol gels were dried in an autoclave (HELIX 1.1 system, Applied Separations, Inc., Allentown, PA) with supercritical fluid CO₂ to form RF/SiO₂ aerogels.

2.3. Formation of C/SiO₂ and C/SiC aerogels

The thermal treatment was performed in a tube furnace (72 and 80 mm inner and outer diameters of tube, respectively, 120 mm heating zone). RF/SiO₂ aerogels were initially carbonized to form C/SiO₂ aerogels

under flowing argon (150 ± 10 ml/min) at 800 °C for 3 h. Subsequently, the flow rate of argon was reduced to 60 ± 10 ml/min, and the temperature was increased (1500 °C) for the carbothermal reaction and maintained for 5 h. Samples for analysis were removed at 800 °C and 1500 °C, by interrupting heating and by letting the tube furnace cool down to room temperature under flowing argon.

2.4. Measurement and characterization

Bulk densities (ρ_b) were calculated from the weight and the physical dimensions of the samples. Skeletal densities (ρ_s) were determined by helium pycnometry using a Micromeritics AccuPyc II 1340 instrument. Porosity was determined from the ρ_b and ρ_s values, porosity = $1 - \rho_b/\rho_s$. The microstructure and energy spectrum of the specimens were surveyed by LEO-1530VP scanning electron microscopy (SEM). The phase composition of the sample was evaluated by ARL ARLXTRA X-ray diffraction (XRD) using a Cu-K α radiation. Transmission electron microscopy (TEM) was conducted using a JEOL JEM-2010 electron microscope. Surface areas, average pore diameter, pore volume and pore size distribution were measured by nitrogen adsorption/desorption porosimetry using a Micromeritics ASAP2020 surface area and pore distribution analyzer after the samples were degassed in a vacuum at 200 °C for 6 h. The specific surface area (σ) was calculated using Brunaur–Emmett–Teller (BET) and t-plot (for micropores) methods. By using the non-local density functional theory (NLDFT) model, the pore size distribution was derived from the desorption branch of isotherms, and the total pore volume was estimated from the adsorbed amount at a relative pressure p/p_0 of 0.986. Thermogravimetric analysis (TGA) was performed using a NETZSCH STA449C thermogravimetric analyzer to determine the thermal stability under a constant air flow of 30 ml/min at a heating rate of 10 °C/min. The SiO₂ and SiC contents were also determined by thermogravimetric analysis. The weight fraction of the remaining material was assumed to be pure stoichiometric SiO₂ and SiC.

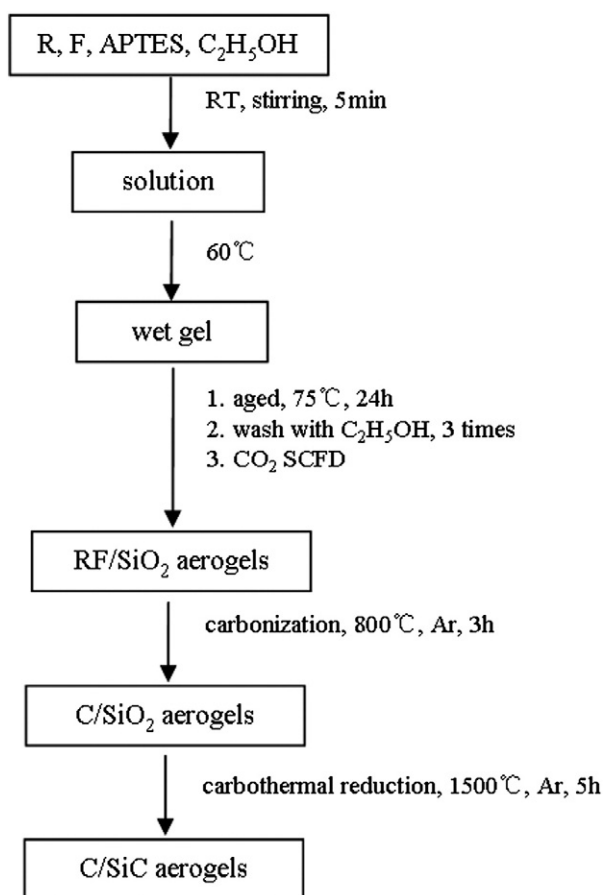
3. Results

Fig. 1 shows the photographs of RF/SiO₂, C/SiO₂ and C/SiC aerogels. The selected characterization data of samples are summarized in Table 1.

Fig. 2 shows the XRD patterns of samples at different stages. The XRD spectra of RF/SiO₂ and C/SiO₂ aerogels are similar and have no visible diffraction peak that corresponds to the presence of amorphous silica and carbon. For the C/SiC aerogel, the peaks with 2θ values of 34° , 35.7° , 38.2° , 41.4° , 60° , 65.6° , 71.8° , 73.6° , and 75.5° correspond to the crystal planes of 101, 102, 103, 104, 110, 109, 116, 203 and 0012, respectively, for moissanite (6H of α -SiC) (PDF# 29-1131). No other crystalline phases of silica, carbon or other impurities were detected. Analysis of the peaks using the Scherrer equation indicates that the average crystallite size of SiC is approximately 15 nm.

Fig. 3(a)–(c) shows the SEM images of RF/SiO₂, C/SiO₂ and C/SiC aerogels. The SEM photographs at higher magnification have been incorporated as insets. RF/SiO₂ and C/SiO₂ aerogels exhibit the disordered, porous structures of a typical colloidal gel. The particles of RF/SiO₂ and C/SiO₂ aerogels are spherical. On the contrary, the particles of C/SiC aerogels are non-spherical and indistinguishable, which are similar to the staghorn coral. The EDX spectrum (Fig. 3(d)–(e)) demonstrates that the oxygen decreased after carbothermal reduction processes, indicating that the SiO₂ was deoxidized and transformed to SiC.

Transmission electron microscopy (TEM) was performed to further understand the crystal structure and microstructure of C/SiC aerogels. From the TEM image (Fig. 4(a)), we can see that the SiC nanoparticles and carbon particles have been composited. As observed from the high-resolution transmission electron image (HRTEM, Fig. 4(b)), the lattice fringe, with a spacing of approximately 0.235 nm, corresponds



Scheme 1. The synthesis of RF/SiO₂ aerogels and their conversion to C/SiO₂ and C/SiC aerogels.

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