Letter to the Editor

Synthesis of ultrahigh-pore-volume carbon aerogels through a "reinforced-concrete" modified sol–gel process

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ABSTRACT

Ultrahigh-pore-volume carbon aerogels were synthesized by adding rigid silica nanoparticles to resorcinol-formaldehyde sols, followed by supercritical drying, pyrolysis and HF leaching. The presence of silica nanoparticles in polymer gels dramatically inhibits volume shrinkage and framework collapse during the supercritical drying and pyrolysis processes, resulting in the obtained carbon aerogels exhibiting very low bulk density and high pore volume. By changing the mass ratio of silica nanoparticles/resorcinol-formaldehyde resin, pore volumes of carbon aerogels can be tuned in the range of 2.8–6.0 cm³/g.

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1. Introduction

Carbon aerogel, a network structure of interconnected nanosized primary particles, has been verified to have unique physiochemical properties [1], controllable mesopore structure [2] and many promising applications, including various electrochemical applications [3], catalyst supports [4], and thermal insulation materials [5]. The carbon aerogel is usually synthesized through polymerization of resorcinol and formaldehyde in dilute solution followed by super-critical drying and pyrolysis [6]. However, the polymerized organic gel is highly flexible, and easily occur huge volume shrinkage during supercritical drying, especially high temperature supercritical drying. Furthermore, serious skeleton collapse during the high-temperature carbonization procedure results in relatively high bulk density and low pore volume of the as-prepared carbon aerogel. Hard template method is one of the promising methods to prepare ultrahigh-pore-volume carbon aerogels, because the introduced template not only produces lots of pores after its removing but also inhibit the volume shrinkage during supercritical drying and pyrolysis [7].

Herein, we propose a modified hard template method, "reinforced-concrete" approach, to prepare ultralow-density and ultrahigh-pore-volume carbon aerogels. A rigid constituent of colloidal silica nanoparticles was incorporated in the resorcinol-formaldehyde solution to obtain polymer gels. The presence of silica nanoparticles in the polymer gels can dramatically inhibit volume shrinkage and framework collapse during the supercritical drying and pyrolysis process, resulting in the obtained carbon aerogels with very low bulk density and high pore volume.

2. Experimental

The ultrahigh-pore-volume carbon aerogel was synthesized through a sol–gel method in the presence of colloidal silica nanoparticles (Ludox SM-30). Silica-polymer gels were prepared by sol–gel polymerization from 100 ml mixture solution, including resorcinol (R), formaldehyde (F), silica nanoparticles, and deionized water. The silica-polymer gels were gelled at 85 °C for 5 days and then dried under supercritical petroleum ether conditions [8] to obtain silica-polymer aerogels. The silica-carbon hybrid aerogels (S-CA) were obtained by pyrolysis of silica-polymer aerogels at 800 °C for 3 h in the nitrogen atmosphere. After silica-carbon aerogels were immersed in 10 wt.% HF solutions for 24 h, silica was removed and carbon aerogels (CA) were left. Calcination of the silica-carbon aerogels at 550 °C for 5 h in air could burn off carbons and generate silica aerogels (SA). The as-prepared carbon aerogels, silica aerogels, and silica-carbon hybrid aerogels are denoted as CA-x/y, SA-x/y, and S-CA-x/y, respectively, where x is the reaction concentration (R+F, g/100 ml) and y is the amount of silica sol (g).

The bulk density (ρ) of the aerogels was determined by measuring the dimensions and mass of each cylindrical sample. The N₂ adsorption/desorption isotherms of the samples were measured using a Micromeritics ASAP 2020 analyzer. The BET surface areas (S_{BET}) were analyzed by the Brunauer–Emmett–Teller method. Micropore surface areas (S_{mic}) and external surface areas (S_{ext}) were obtained by a t-plot method. Total pore volume (V_t) was

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calculated by single point method at the relative pressure of 0.995. The average pore diameters (D_p) and the mesopore size distributions were obtained by the Barrett–Johner–Halendar (BJH) model. The morphologies of aerogels were observed under transmission electron microscopy (TEM, JEOL JEM-1200EXII), and scanning electron microscopy (SEM, JEOL JSM-6360LV).

3. Results

3.1. Volume evolution and bulk density of the aerogels

No obvious volume shrinkages of hybrid gels were observed during high temperature supercritical drying and only about 20% (±3%) volume shrinkages were detected for gels during pyrolysis, which are significantly smaller than those of polymer gels without colloidal silica nanoparticles during drying and pyrolysis [8]. The bulk densities of the prepared carbon aerogels are shown in Table 1. The lowest bulk density of 0.08 g/cm³ was obtained at the initial reactant concentration of 5 g/100 ml and the amount of the silica sol of 40 g. With the decrease of initial reactant concentration or increase of the amount of the silica sol, the bulk density of the carbon aerogels decreased.

3.2. N₂ adsorption measurements

The N₂ adsorption–desorption isotherms and resultant pore size distributions of silica-carbon aerogels, silica aerogels and carbon aerogels are shown in Fig. 1, and the corresponding pore characters are also summarized in Table 1. All aerogels exhibit type-IV curves with a broad capillary condensation step reflecting the mesoporous character of these aerogels. On comparison with their mother carbon-silica aerogels, the pore sizes of silica aerogels and carbon aerogels are both a little larger, and their distributions get wider, suggesting that the removal of silica or carbon phases could generate new free space for the resultant aerogels. The specific surface areas and the pore volumes of silica aerogels are around 147 m²/g and 0.8 cm³/g, respectively, corresponding to the expected values of colloidal silica [9]. The mesoporous carbon aerogels have very high specific surface area of 1121 m²/g and huge pore volume of 4.7 cm³/g, which are much higher than their silica counterparts. The pore volume of silica-carbon aerogels reflects a compromise between pore volumes of their silica and carbon components. For carbon aerogels prepared at constant amount of silica sol used (e.g. 40 g), as the initial reactant concentration decreased from 20 to 5 g/100 ml, and pore volume of carbon aerogels increased from 2.8 to 6.0 cm³/g.

3.3. TEM and SEM observations

Fig. 2 shows the TEM and SEM images of the aerogels. The silica-carbon hybrid aerogel (Fig. 2a) exhibits a disordered and compact mesoporous network, in which carbon and silica frameworks are
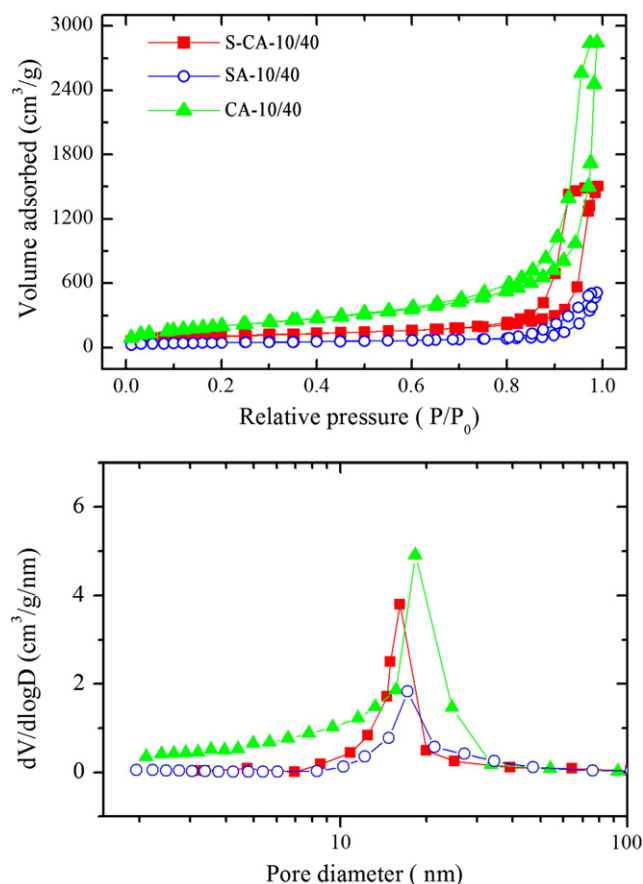

Fig. 1. N₂ sorption isotherms and the resultant pore size distributions of typical silica-carbon aerogels, silica aerogels and carbon aerogels.

separated and "homogeneously" distributed. The silica aerogel has a roughened surfaces arranged in a "pearl necklace" three-dimension structure. And the carbon aerogel consists of highly ramified and fibrous chains with typical amorphous carbon frameworks. These results revealed that the carbon and silica networks are independent and interpenetrated each other inside the network of silica-carbon aerogels. We also have calcined the hybrid silica-polymer gels without passing through the pyrolysis and analysis the structure of this sample by TEM (not shown in this paper). Similar structures were obtained as to that of the pyrolysis one, indicating that the silica network was formed before pyrolysis. The SEM images of carbon aerogels (Fig. 2d) shows that there are also some micrometer-sized macropores in this sample.

4. Discussion

The schematic representation of the preparation of ultrahigh-pore-volume carbon aerogels in the presence of silica nanoparticles is shown in Fig. 3. Colloidal silica is a nanometric particle size solution of silica particles in water. These colloidal solution is stable due to the pH is kept slightly on the alkaline side of neutral, which can prohibit the hydrolysis of Si(OH)₄. However, if the resorcinol and formaldehyde added into the colloidal silica solution, the thermodynamic balance would be broken. The hydrogen ions from the surface of colloidal silica tend to dissociate in aqueous solution, yielding the further polymerization of colloidal silica and then forming the 3-D silica gel. Meanwhile, the resorcinol and formaldehyde can be easily polymerized into branch polymers in the basic solution. After sol–gel transformation, the silica gel and polymer gel interpenetrate each other, forming a 3-D hybrid gel. The obtained hybrid gels have a "reinforced-concrete"-like structure, in which rigid silica gel sever as "reinforcing-steel-bar" and high branch plastic

Table 1
Bulk density and porous parameters of aerogels.

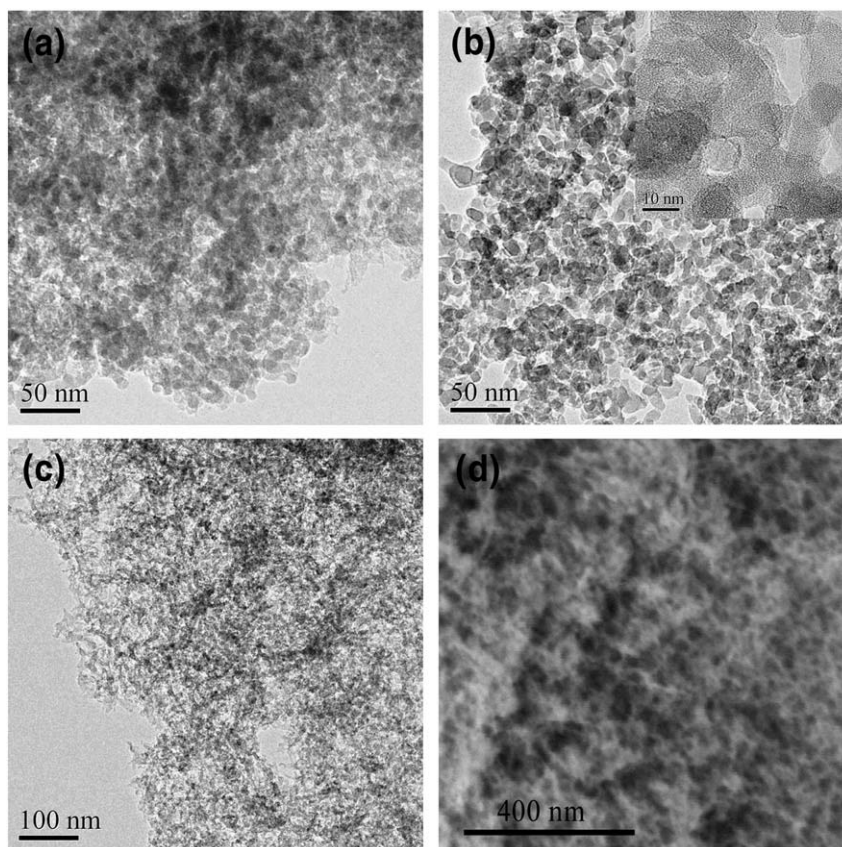| Samples	ρ	S_{BET}	S_{ext}	S_{mic}	V_T	D_p
	g/cm³ ± 0.01	m²/g ± 5	m²/g ± 5	m²/g ± 5	cm³/g ± 0.1	nm ± 0.1
S-CA-10/40	0.31	373	330	43	2.3	16.1
SA-10/40	0.17	156	142	14	0.8	17.2
CA-10/40	0.15	1121	962	159	4.7	19.1
CA-5/40	0.08	911	768	143	6.0	27.8
CA-15/40	0.19	709	578	131	2.9	19.1
CA-20/40	0.22	786	654	132	2.8	18.3
CA-10/30	0.17	934	802	132	3.9	19.3
CA-10/50	0.15	723	525	198	4.1	24.2

Fig. 2. TEM images of silica-carbon aerogels (a), silica aerogels (b), carbon aerogels (c) and SEM image of the carbon aerogel (d).

resorcinol-formaldehyde resins act as "concrete" [10]. After supercritical drying, pyrolysis and silica removal, the obtained carbons inherited the initial 3-D network. The rigid silica networks not only sever as template for producing mesopores after HF leaching, but also inhibit the shrinkage and framework collapse of the carbon aerogels during the supercritical drying and pyrolysis processes, which are the key factors for preparing ultrahigh-pore-volume carbon aerogels. Since the shrinkage of carbon aerogels is small, the density and pore volume are dominated by the concentration of resorcinol and formaldehyde and the amount of silica sol. Therefore, decreasing of the concentration of

resorcinol and formaldehyde or increasing the amount of silica sol, the pore volume of the prepared carbon aerogel increased and the bulk density decreased.

5. Conclusions

A "reinforced-concrete" approach to prepare ultrahigh-pore-volume carbon aerogels is first demonstrated, by adding a rigid constituent of colloidal silica sol in the resorcinol-formaldehyde solution. Because of the presence of rigid silica nanoparticles, the
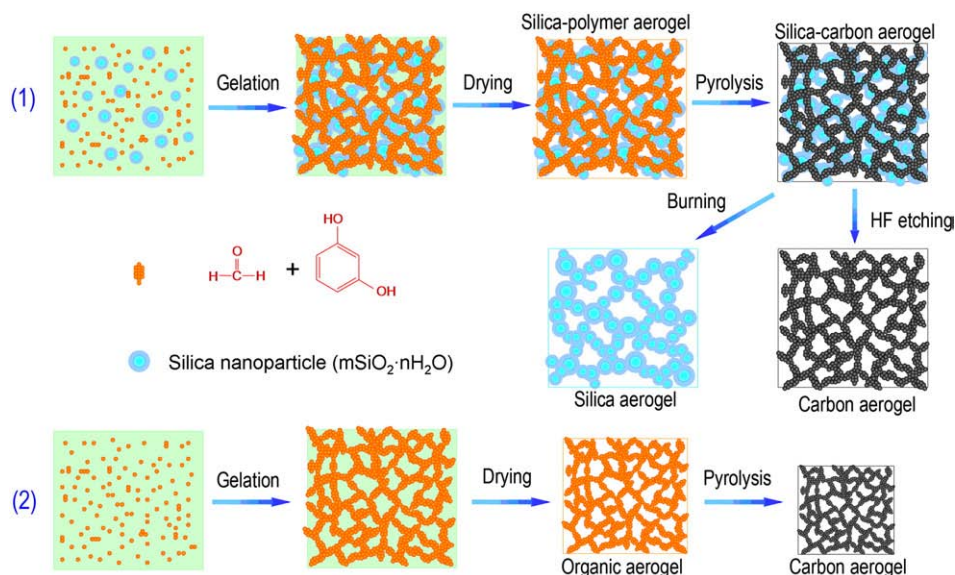

Fig. 3. The schematic representation of preparation of carbon aerogels with (1) or without (2) colloidal silica nanoparticles.

volume shrinkage and framework collapse can be effectively alleviated, resulting in the as-prepared carbon aerogels with very low bulk density and very high pore volume.

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