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A novel route for preparing mesoporous carbon aerogels using inorganic templates under ambient drying



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ABSTRACT

A low-cost approach for mesoporous carbon aerogel synthesis using calcium carbonate particles as templates and ambient pressure drying is reported in this paper. The removal of templates by acid treatment produced additional mesopores that mimic the template particles. The resulting carbon aerogels showed higher mesopore ratio and a significantly larger pore volume compared with those without templates. This study provides a low-cost and easy-to-scale-up method for producing mesoporous carbon aerogels with large pore volumes.

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1. Introduction

To achieve high theoretical specific capacity and energy density of lithium–sulfur [1], lithium–air [2], and lithium–silicon batteries [3], mesoporous materials as cathode support were developed to specifically address volume expansion/shrinkage and poor electrical conductivity [4]. However, the main problem is the lack of a material with porosity and pore size distribution that could be readily tailored.

Carbon aerogels (CAs) have been recently recognized as novel support materials because of their interconnected microstructure, high specific surface area, controllable pore structures, and high electrical conductivity [5]. However, its production usually involves tedious and costly supercritical fluid drying, which is essential to maintain the mesoporosity after solvent removal [6]. Although a solvent-exchange technique has been developed to prepare CAs by ambient pressure drying, the as-obtained CAs usually have poor mesoporosity and relatively high mass density [7]. Much effort has been focused on seeking a simple, low-cost, and scalable method to prepare CAs with controlled mesoporosity and high pore volume.

A novel approach to synthesize CAs using calcium carbonate particles as template during organic aerogel (OA) synthesis followed by ambient pressure drying is reported in this paper.

The prepared CAs showed well-controlled mesoporosity with higher mesopore ratio and a significantly larger pore volume than those of CAs without templates. This process has the potential to reduce production costs compared with the traditional supercritical fluid-based approach.

2. Experimental

In a typical synthesis, 8 mg of calcium carbonate (CaCO₃, Aldrich) was added to 100 mL of 0.8 mmol/L cetyl trimethylammonium bromide (CTAB, Aldrich) aqueous solution and sonicated for 2 h. The dimension of the calcium carbonate in the solution is determined to be about 12 nm from a dynamic light scattering technique (see Fig. S1 in the Supporting material). Resorcinol (0.059 mol, Aldrich), formaldehyde (11.0 mL, 37% aqueous solution, Aldrich), and the reaction catalyst (sodium carbonate, 0.035 g, Aldrich) were then added to the solution, and the reaction mixture was cured at elevated temperatures of 50, 85, and 95 °C each for 1 d. Brown monolithic gels were formed. These wet gels were subjected to solvent-exchange three times with petroleum ether every 24 h and then dried at 80 °C at ambient pressure for 1 d. The product was carbonized to obtain the CaCO₃–CA composites and then etched with hydrogen chloride to remove the templates in the composites, thereby producing the mesoporous CAs.

The specific surface area and pore structure parameters of the aerogels were determined from the adsorption isotherm of nitrogen at 77 K (ASAP2010, Micromeritic, USA). The Brunauer–Emmett–Teller (BET) equation was used to calculate specific surface

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area [8]. The Barrett–Joyner–Halenda (BJH) method [9] was used to calculate mesopore distribution. Micropore volume and mesopore specific surface area were obtained using the *t*-plot method [10]. Total pore volume was obtained by converting the amount of nitrogen adsorption at a relative pressure of 0.95 to the liquid nitrogen volume. The mesopore volume was calculated by subtracting the micropore volume from the total pore volume. High-resolution transmission electron microscopy (TEM) was used to analyze the morphology of the prepared CAs.

3. Results and discussion

Table 1 lists the BET surface area and pore structure parameters of the prepared OAs and CAs. The addition of CaCO₃ particles resulted in a significant increase in pore size relative to that of the pristine CAs. The CAs with templates (CA-3 and -4) had a significantly higher pore volume (up to 1.33 cm³/g) and a significantly larger mesopore diameter (up to 16.11 nm) than those without templates (pore volume, 0.56 cm³/g; mesopore diameter,

Table 1
Pore structure parameters of organic and carbon aerogels in this study.

Sample	S_{BET}^a (m ² /g)	V_{meso}^b (cm ³ /g)	V_{total}^c (cm ³ /g)	D_p^d (nm)	Remarks
OA-1	2	0.01	0.01	34.11	No template, no solvent exchange
OA-2	337	0.60	0.54	6.66	No template, solvent-exchanged
CA-2	556	0.51	0.56	6.44	
CA-3	600	0.93	0.97	10.75	Templated, no solvent-exchange
OA-4	233	0.90	0.84	14.55	Templated, solvent-exchanged
CA-4	610	1.26	1.33	16.11	

Note:

^a S_{BET} : BET surface area.

^b V_{meso} : BJH desorption cumulative pore.

^c V_{total} : total pore volume of pores between 17 and 3000 Å diameter.

^d D_p : mesopore diameter.

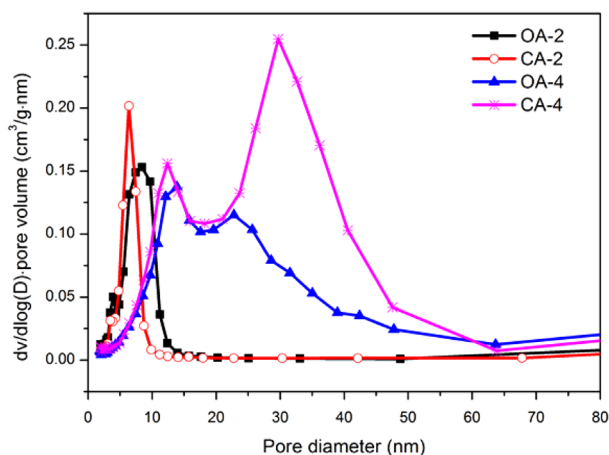


Fig. 1. Pore size distribution of organic aerogels and carbon aerogels derived from the BJH method.

6.44 nm for CA-2). These results are favorable to the electrochemical properties of a cathode support.

Fig. 1 shows the pore size distribution of OAs and CAs derived from the BJH method. For pores with diameters smaller than 20 nm, the pore size profiles of OAs are highly consistent with those of their corresponding carbonized counterparts. The major difference between CA-2 and CA-4 is that CA-2 has only a single pore pattern at 9 nm, whereas CA-4 has both the 12 and 30 nm pores. The 30 nm-sized pores of CA-4 were related to the textural pores constituted by the surrounding carbon species that were transformed from organic gels. Notably, both size and amount of the 30 nm-sized pores of CA-4 were greatly enhanced compared with OA-4 after carbonization. This result is due to the slight shrinkage of textural pores in OAs after the loss of support materials.

The mesopores in CA particles were examined by TEM, and the results are shown in Fig. 2. The images reveal that CA-2, without templates, was composed of small 8 nm-sized pores formed by an enclosure of carbon species. Except for the small pores, CA-2 and -3 displayed several pores with diameters of 30 nm. Closer examination of CA-4 in Fig. 2c reveals an obvious “textural” pore surrounded by several circular pores (indicated by A–D). This result indicates that the textural pores were formed by gels containing templates, which is due to the templating mechanism of the microemulsion in sol–gel polymerization. In this process, the CaCO₃ spheres emulsified by CTAB acted as the “nuclei” to synthesize CAs, as shown in the proposed mechanism in Fig. 2d.

A templating mechanism that is consistent with the experimental observation and the test data is shown in Fig. 3. In this mechanism, the RF polymerizes in organic phase (carbon chains of CTAB) around CaCO₃ particles and forms insoluble agglomerates with the CaCO₃ microspheres. As the polymerization proceeds, the dispersed intermediate composites grow and coat around the particles until they are aggregated together by collision and ultimately cross-link into a three-dimensional nano-network. The mechanism is very similar to that described for the early stages of the formation of RF gels. Because no template was present during the synthesis of the pristine RF sol, the particles are able to grow only much smaller than in the other syntheses with templates in the case of similar frequency of particle collision. Addition of the CaCO₃ templates produces an organic/inorganic composite material, which is larger than the RF intermediates without templates. Consequently, the resulting carbon aerogels have a much better “textural mesoporosity” consisting of the space between the large RF sol particle.

To simplify the production method, we attempted to bypass the solvent-exchange step and directly dried the organic gels under ambient pressure. As a result, the organic RF gels without templates turned black after air-drying, and the pores of the gels almost completely collapsed, with a very small BET surface area of 2 m²/g (OA-1). However, the pores of the organic gels containing CaCO₃ only slightly collapsed, and the major pore structures were retained. Thus, the corresponding CAs still produced a relatively high surface area of 600 m²/g (CA-2), as shown in Table 1. Fig. 4 shows that after solvent exchange, CA-3 exhibited significantly more mesopores with diameters of 12 nm than those in CA-4 but almost no significant pores with 30 nm diameter. This result is due to the collapse of larger mesopores (or some macropores) into smaller mesopores because of the absence of solvent exchange. However, the mesostructures were still large enough to load cathode materials for lithium batteries. The results imply that, by our method, the duration for forming CAs can be considerably shortened by directly drying wet organic wet gels at ambient pressure even without a solvent-exchange step, which will significantly reduce the production cost. Notably, no calcium was left in the CAs after acid washing, as detected by energy-dispersive X-ray spectroscopy, which is important for energy storage applications.

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