



Synthesis of hierarchical porous carbon particles by hollow polymer microsphere template

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ABSTRACT

Carbon particles with hierarchical pore structure are prepared from resol-type phenol–formaldehyde resin using hollow polymer microspheres as template. The template microspheres have a polystyrene shell with transverse hydrophilic channels connecting to the interior cavity. They are stable and permeable, so a crosslinking catalyst can be previously loaded into the cavity reservoir. Following the incorporation of resol phenol–formaldehyde resin, the aggregates of resin and hollow microspheres have been achieved. Porous carbon particles are derived from carbonization of the composite particles. The structures of carbon materials can be tuned from open wall to closed wall by varying the resol/template weight ratio. The carbon particles are comprised of a series of pores with broad size distribution: from micropore, mesopore to macropore. The porosity development in the carbon materials has been investigated by electron micrograph and N₂ adsorption.

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1. Introduction

Porous carbons are widely used in gas separation, catalyst supports, electrode materials, water purification, gas storage and other applications [1,2]. A variety of templates, such as organic small molecules, surfactant, colloidal spheres, colloidal opal, silica xerogels and mesoporous silica has been utilized for the fabrication of porous carbons [1–5]. Various templates result in different pore sizes ranging from micropores, mesopores to macropores. Recently, carbon foams with hierarchical pore structures have earned growing interest because of their potential use in catalysis, fuel cells, and hydrogen storage [6–9]. Porous silica foams or colloidal silica have been employed as templates by filling the carbon precursor into the pores or interstitial voids of the template. Carbonizing the precursor and subsequently removing of the template yield the multiporous carbon [10–17]. Apart from inorganic templates, many organic templates such as polymer nanosphere or polymer opal have also been used. Use of organic template makes the process more rapid by obviating the need for removal of the template, since the template becomes decompose during carbonization [18,19]. But the macroporous carbons are generally found to be in the form of large inverse opal monolith and necessitate an array of monodisperse microsphere as template [16,19,20].

Herein, we report the synthesis of carbon particles with hierarchical pore structures by utilizing the hollow polymer microspheres

as template. We have previously reported the synthesis of phenolic resin and derived hollow carbon microspheres with double-shelled structure by utilizing partially sulfonated polystyrene hollow microspheres as template [21]. It is the key that the derived sulfonic acid ($-\text{SO}_3^- \text{H}^+$) can expeditiously absorb resol phenol–formaldehyde resin (PF) and hence catalyze crosslinking of the resin therein at room temperature. In this report, the parent polystyrene hollow microspheres without sulfonation are preloaded with oxalic acid as a catalyst inside the interior cavities. The oxalic acid containing hollow polystyrene microsphere can efficiently absorb resol prepolymer and hence catalyze the crosslinking reactions for PF composite particles. The porous carbon particles are obtained by carbonization of the PF composite aggregate.

2. Experimental

2.1. Synthesis of samples

- (1) *Phenol–formaldehyde (PF) resin solution.* The resol precursor was synthesized by alkaline (MgOH) catalytic reaction between phenol and formaldehyde at a molar ratio 1/1.3 [21]. The PF resol was dissolved in ethanol with a solid content 60 wt.%. The concentrated solution was further diluted with ethanol to a solid content 20 wt.% for use.
- (2) *PF composite particles.* 0.1 g freeze-dried hollow microsphere template (purchased from Rohm & Haas Company) was immersed in 5 ml 1 M oxalic acid ethanol solution for 24 h to allow an equilibrium uptake. The hollow microspheres loaded with oxalic acid solution had been separated by centrifugation

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and washed with ethanol to remove the residual oxalic acid outside of the microspheres. Then the hollow microspheres loaded with oxalic acid solution were dispersed into 5 ml ethanol. A designed amount of PF resin solution was dropped into the dispersion under continuous stirring at ambient temperature for 4 h forming PF composite particles. The morphology of the composite particles was controlled by varying the PF/template weight ratio. Three representative samples S1, S2 and S3 were prepared from adjusting the PF/template weight ratio (R) 1/1, 2/1, 10/1, respectively. The PF composite particles were further crosslinked at 150 °C for 2 h.

- (3) *Porous carbon particles.* Porous carbon particles were prepared by carbonization of the PF composite particles at 800 °C for 2 h in nitrogen with a heating rate of 5 °C min⁻¹. The porosity development in the carbon materials was investigated by carbonized S2 at 450 °C, 600 °C and 800 °C for 2 h under nitrogen gas denoted as N450, N600 and N800, respectively. Some samples were prepared by pre-treating S2 with oxygen gas at 250 °C for 0.5 h and subsequently carbonizing at 450 °C and 800 °C for 2 h in nitrogen gas denoted by O450 and O800, respectively.

2.2. Characterization

Transmission electron microscopy (TEM) was performed using a JEOL 100CX microscope operating at 100 kV. Very dilute dispersion of the particles in ethanol was spread on the carbon-coated copper grids for observation. Scanning electron microscopy (SEM) was performed with a HITACHI S-4300 instrument operating at 15 kV. Samples were deposited from ethanol dispersion on silicon wafers and vacuum sputtered with Pt.

FT-IR spectra were recorded by BRUKER EQUINOX 55 using KBr pellet samples. Powder X-ray diffractometer (Rigaku D/max-2500) was used to characterize the materials. Raman spectroscopy was performed with a RM2000 Microscopic Confocal Raman Spectrometer with a 514.5 nm Ar-ion laser operating at 4.7 mW. Elemental analysis was carried out using a Flash EA-1112 apparatus. Nitrogen adsorption was performed on a Micromeritics ASAP 2020 M Porosity Analyzer. Conductivity was measured on compressed pieces of dry powders using a standard four-probe method at room temperature. The size of compressed piece was 1.5 cm in diameter and the pressure was 10 MPa.

3. Results and discussion

The template microspheres are mainly composed of a polystyrene shell containing transverse hydrophilic channels [22] and their polymers have been characterized by FT-IR (Fig. 1a). They are stable and permeable enough to spur the preloading of catalyst oxalic acid solution into the cavity reservoir. Subsequently, the hollow microspheres preloaded with catalyst solution are dispersed into resol ethanol solution. The diffusion of the catalyst oxalic acid through the channel has been observed on account of the fact that the diffusibility of resol precursor is slower than that of the oxalic acid. Outward diffusion of the catalyst aids in depositing and crosslinking of the PF precursor. Hence, the deposition of PF resin predominately takes place on the outer surface of the template, which is similar the Kirkendall-like process in which the material products grow in the direction of the faster-moving species [23,24]. Fig. 1b shows the FT-IR spectrum of as-synthesized PF composite particles S2. Two bands around 3397 cm⁻¹ and 1235 cm⁻¹ correspond to the O–H stretch and the O–H bending, respectively. These two bands are assigned to resol precursor. The band of 1074 cm⁻¹ is the symmetric C–O–C stretch, indicating that the composite particles are partly crosslinked [25]. Treatment at 150 °C for 2 h (Fig. 1, curve c) results in the weaker O–H stretch and Ar–OH

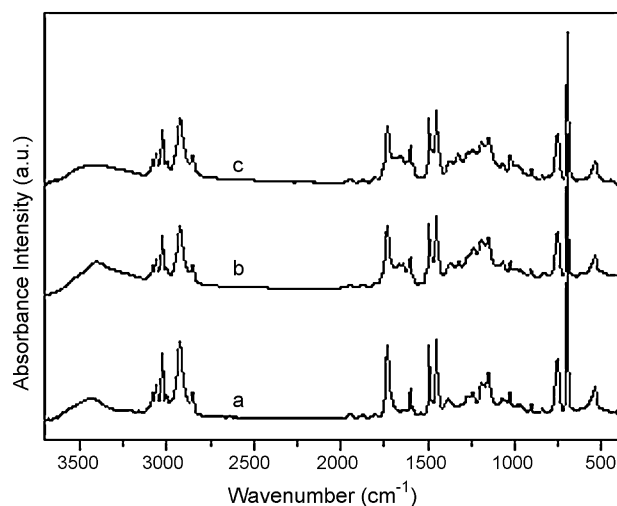


Fig. 1. FT-IR spectra of (a) the hollow polystyrene microspheres template; (b and c) the as-synthesized PF composite particles S2 using hollow polymer microspheres before and after being treated at 150 °C for 2 h in nitrogen.

stretch at 3397 cm⁻¹ and at 1200 cm⁻¹, respectively, further facilitating the crosslinking of PF resin. The asymmetric C–O–C stretch at 1148 cm⁻¹ and the symmetric C–O–C stretch at 1074 cm⁻¹ depict that PF is crosslinked mainly through ether linkage.

The carbonization of PF resin under high temperature transforms it into carbon and subsequently, the template is removed. The morphologies of the composite particles and corresponding carbon materials can be controlled by varying the PF/template weight ratio R . By adjusting the R ratio of 1/1, the synthesized composite particles are individual microspheres and these microspheres exhibit smooth outer surface along with excellent dispersion (Fig. 2a), indicating that a small amount of phenolic resin begets single composite microspheres. But Fig. 2b shows that the corresponding carbon exhibits a macroporous structure after carbonized at 800 °C for 2 h under nitrogen, revealing that the catalytic crosslinking of the PF resin is not yet accomplished and the carbonization procedure results in an aggregate of microspheres. When the weight ratio R is increased to 2/1, the template microspheres and these microspheres exhibit smooth outer surface along with excellent dispersion (Fig. 2c), indicating that a small amount of phenolic resin begets single composite microspheres. But Fig. 2b shows that the corresponding carbon exhibits a macroporous structure after carbonized at 800 °C for 2 h under nitrogen, revealing that the catalytic crosslinking of the PF resin is not yet accomplished and the carbonization procedure results in an aggregate of microspheres. When the weight ratio R is increased to 2/1, the template microspheres become adhere to each other by PF resin and form cluster (Fig. 2c), which results in the formation of macroporous carbon particles with open wall structures after carbonization (Fig. 2d). The aggregates become even larger by a further increase in the PF resin amount (the ratio increases upto 10/1). Fig. 2e indicates that some hollow microspheres are broken when the PF composite particles have been treated with tetrahydrofuran, further testifying the fact that PF is partly crosslinked. Accordingly the carbon particles possess closed macroporous structures with thicker wall (Fig. 2f).

Elemental analysis of the open macroporous carbon particles (Fig. 2d, sample N800) shows a composition of 93.6 wt.% C, 1.0 wt.% H and 5.3 wt.% O. XRD results and selective area electron diffraction (not shown) indicate that the nature of carbon material is glassy. The Raman spectrum of N800 (Fig. 3) depicts the presence of two broad bands at 1360 cm⁻¹ and 1591 cm⁻¹, which is consistent with the previously reported results [26]. Although the carbon particles are porous, their walls are well connected in three dimensions. The carbon foam has an appreciable electrical conductivity of $1.5 \times 10^{-2} \text{ S cm}^{-1}$.

The porosity development of the composite particles S2 during the carbonization step and the structural effect of oxygen pre-treatment have been investigated by electron micrograph and N₂ adsorption. Fig. 4 shows typical EM images of carbons prepared from composite particles at various carbonization conditions. The macropore structures are evolved following a treatment at 450 °C

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