One-step synthesis of ordered mesoporous carbonaceous spheres by an aerosol-assisted self-assembly†

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Ordered mesoporous carbonaceous spheres with variable structures have been successfully prepared by using phenolic oligomers as a carbon precursor and amphiphilic triblock copolymers as a template *via* a one-step aerosol-assisted organic–organic self-assembly method.

Mesoporous carbons with high surface areas and large uniform pores are of great interest due to their potential applications in separation, catalysis, electrochemical double layer capacitor (EDLC) and hydrogen storage systems.[1–5] Especially, the synthesis of spherical mesoporous carbons has particularly received much attention for column packing, fillers or catalyst supports.[6–8] The nanocasting strategy using mesoporous silica particles as scaffolds has been intensively engaged in the replication of carbon spheres because it allows controlling the pore structure and particle size simultaneously.[9–11] Nevertheless, some drawbacks are present. First, the nanocasting is a tedious, high-cost, and thus industrially unfeasible method which involves pre-synthesis of the solid scaffolds, pyrolysis of carbon precursors within the pore channels of silica hard templates, followed by the selective removal of the silica template. Second, both the fidelity and structural integrity of the mesoporous carbon replicas are degenerated in the harsh carbonization and template removal process. This leads to morphology/structure defects of mesoporous carbon spheres.

More recently, alternative methods have been reported for the synthesis of mesoporous polymer/carbon materials *via* direct organic–organic self-assembly.[12–15] Highly ordered mesoporous polymer and carbon frameworks with large uniform pores and high surface areas have been successfully synthesized by using amphiphilic triblock copolymers (PEO-PPO-PEO) as a template *via* the evaporation induced self-assembly (EISA) method. Compared with the synthesis of mesoporous silica particles, the aerosol-assisted co-assembly has been regarded as an efficient and productive route in simultaneously controlling the morphology and mesostructures.[16–18] However, studies on morphology, especially the spherical morphology of the ordered mesoporous polymer/carbon materials have been seldom reported by using such an approach.[19]

Herein we report a one-step synthesis of ordered mesoporous carbonaceous spheres *via* aerosol-assisted organic–organic assembly in which amphiphilic triblock copolymers were used as templates and soluble phenol resols with low-molecular weight as carbon precursors. Ordered mesostructured carbonaceous particles exhibit polydispersed spherical morphology with diameters from 100 nm to 5 μm. The block copolymer plays an important role in the organization of the organic–organic mesostructures. The pore size and mesostructures can be varied by changing the amphiphilic surfactant and phenol polymer oligomer assembly process. To the best of our knowledge, mesoporous carbonaceous spheres with ordered structures are directly derived for the first time *via* a one-step aerosol-assisted self-assembly method.

The aerosol-assisted self-assembly method was carried out with an ethanol precursor solution containing low-molecular-weight phenolic resols and triblock copolymers. In one vessel, the aerosols underwent a solvent EISA of phenolic resins and triblock copolymers by drying, the thermopolymerization of the frameworks and the partial removal of the triblock copolymer templates by heating at 250 °C. Finally, the templates were fully removed by calcination in N_2 at 350 °C for 3 h. The resol oligomers were prepared from phenol and formaldehyde in a base-catalyzed process according to the procedure reported previously.[12] A typical sol was prepared by adding 6.27 g of resol precursors containing 1.22 g (0.013 mol) of phenol, 0.78 g (0.026 mol) of formaldehyde and 4.27 g of ethanol to the mixture of 0.5–2.0 g of triblock copolymer Pluronic F127 ($EO_{106}PO_{70}EO_{106}$) or P123 ($EO_{20}PO_{70}EO_{20}$) and 14 g of ethanol. Using N_2 (0.1 MPa) as a carrier gas, the sol solution was passed through the atomizer (TSI 3076) to generate aerosol droplets at concentrations $>10^7$ cm^{-3} and nominal aerosol flow rate of 3.0 L min^{-1}. The droplets passed through a quartz glass tube with length of 1.50 m and diameter of 4.4 cm. The samples were characterized using scanning electron microscopy (SEM, Philips XL-30), transmission electron microscopy (TEM, JEOL2011 operated at 200 kV), X-ray diffraction (XRD, Bruker D4 ENDEAVOR diffractometer using Ni-filtered Cu-Kα radiation, λ = 0.15418 nm) and N_2 sorption techniques (Micromeritics Tristar 3000 analyzer at 77 K). Before the measurements of the sorption isotherms, the samples were outgassed at 200 °C in vacuum for 6 h.

SEM images of mesoporous carbonaceous spheres prepared from F127, phenol, formaldehyde and ethanol show polydisperse particles with diameters from 100 nm to 5 μm (Fig. 1(a)). These particles have a smooth surface, even after calcination in N_2 at 350 °C, few visible defects on the surface are observed. TEM images show a unique hexagonal mesostructure (Fig. 1(b)). The ordered hexagonal mesopore arrays can be clearly observed at the edge of the particles with an average pore-to-pore distance of 14.5 nm. The XRD pattern of the mesoporous polymer spheres

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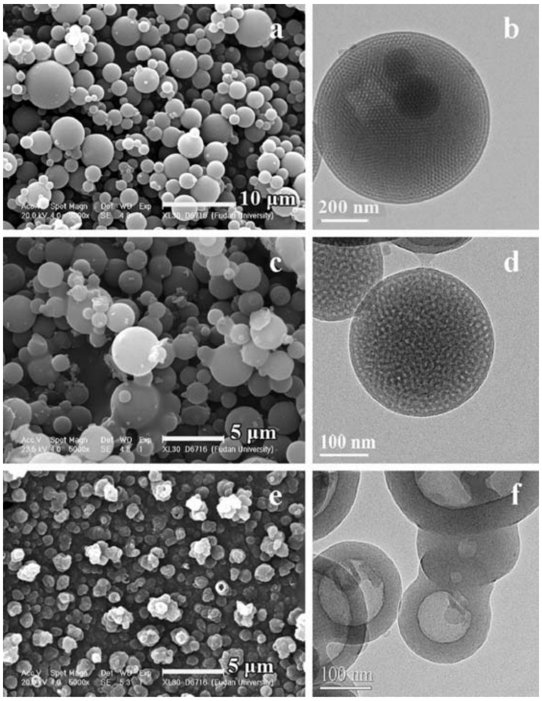

Fig. 1 Representative SEM (left) and TEM (right) images of mesoporous carbonaceous spheres *via* an aerosol-assisted organic–organic assembly by using triblock copolymer F127 as template. Molar ratios: (a) and (b): F127 : phenol : formaldehyde : ethanol = 6.11×10^{-3} : 1 : 2 : 30.54; (c) and (d): F127 : phenol : formaldehyde : ethanol = 1.22×10^{-2} : 1 : 2 : 30.54; (e) and (f): F127 : phenol : formaldehyde : ethanol = 4.58×10^{-3} : 1 : 2 : 30.54.

synthesized by using triblock copolymer F127 as a template shows an intense reflection peak at a *d*-spacing of 13.9 nm accompanied by the second diffraction peak at 7.9 nm, suggesting the formation of two-dimensional hexagonal mesostructures (Fig. 3(a-1)). After the template removal, the XRD pattern shows a broad reflection peak with a *d*-spacing of 12.3 nm (Fig. 3(b-1)). The calculated unit cell parameter is 14.2 nm in agreement with TEM observations. The broad XRD peak suggests a much less ordered domain caused by non-uniform spheres. The N_2 sorption isotherms of the mesoporous carbonaceous spheres prepared by using F127 as a template show representative type-IV curves with an obvious H_1-type hysteresis loop and a clear condensation step at P/P_0 = 0.6–0.7, implying uniform mesopores (Fig. 4(a)). The spheres have a narrow pore size distribution centered at around 5.5 nm as calculated based on the BJH model (Fig. 4(a), inset), while the calculated BET surface areas and the pore volume are 427 $m^2 g^{-1}$ and 0.42 $cm^3 g^{-1}$, respectively. The elemental analysis shows that the C : H : O molar ratio of the particles calcined at 350 °C is 5.0 : 2.1 : 1.0, implying relatively high H and O contents in the frameworks. Thermogravimetric analyses (TGA) show that the copolymer templates can be removed after calcination at 350 °C for 3 h (see ESI†).

Moreover, mesostructures of the carbonaceous spheres can be tuned by varying the concentration of F127. When the molar ratio of F127 : phenol : formaldehyde : ethanol is changed to 1.22×10^{-2} : 1 : 2 : 30.54, no significant change of the polymer sphere size is observed from SEM images (Fig. 1(c)). TEM images (Fig. 1(d)) show that the carbonaceous spheres after the removal of templates have a worm-like mesostructure. XRD patterns reveal a broad reflection with *d*-spacings of 13.0 and 11.7 nm before and after template removal, respectively (Fig. 3(a-2), 3(b-2)), implying that the shrinkage of frameworks is around 10%. N_2 sorption isotherms show typical type-IV curves, suggesting uniform mesopores. The calculated BET surface area and pore volume are 530 $m^2 g^{-1}$ and 0.44 $cm^3 g^{-1}$, respectively. The BJH pore size distributions of the samples are centered at 4.5 nm (Fig. 4(b), inset). However, when the molar ratio of F127 : phenol : formaldehyde : ethanol is 4.58×10^{-3} : 1 : 2 : 30.54, hollow spheres can be obtained. SEM images (Fig. 1(e)) clearly show non-uniform spherical particles with diameters from 100 nm to 2 µm. TEM images (Fig. 1(f)) show that the hollow spheres have a shell with widths of tens of nanometers.

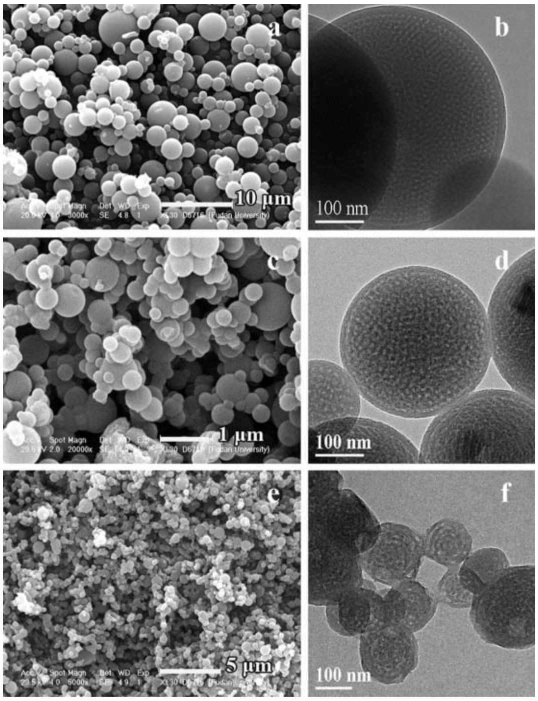

Fig. 2 SEM (left) and TEM (right) images of mesoporous carbonaceous samples prepared by using copolymer P123 as template. Molar ratios: (a) and (b): P123 : phenol : formaldehyde : ethanol = 1.33×10^{-2} : 1 : 2 : 30.54; (c) and (d): P123 : phenol : formaldehyde : ethanol = 1.99×10^{-2} : 1 : 2 : 30.54; (e) and (f): P123 : phenol : formaldehyde : ethanol = 2.65×10^{-2} : 1 : 2 : 30.54.

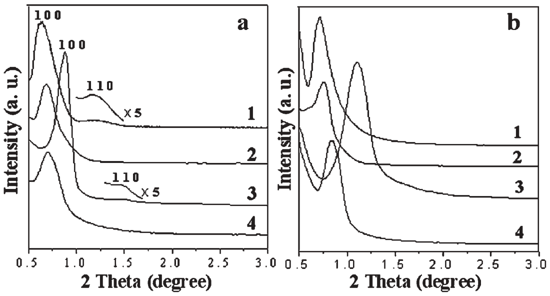

Fig. 3 XRD patterns of the spherical carbonaceous particles prepared by using F127 (1), (2), or P123 (3), (4) as templates before (a) and after (b) calcination. Molar ratio of triblock copolymer : phenol : formaldehyde : ethanol = x : 1 : 2 : 30.54, where $x = 6.11 \times 10^{-3}$ (1); 1.22×10^{-2} (2); 1.33×10^{-2} (3); 1.99×10^{-2} (4).

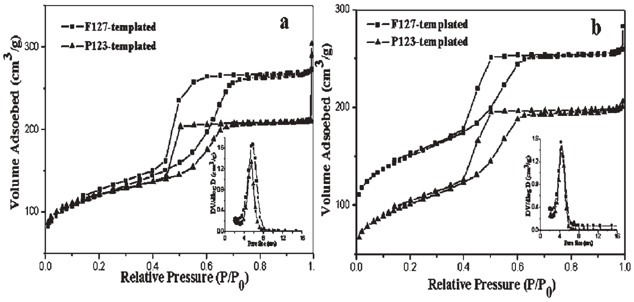

Fig. 4 N_2 adsorption/desorption isotherms and pore size distribution (inset) of the (a) hexagonal and (b) worm-like mesostructured carbonaceous particles obtained by using triblock copolymers F127 and P123 as templates, respectively.

No diffraction peaks can be observed from the XRD patterns, implying no ordered domains were formed in the shells.

When triblock copolymer P123 is used as a template, carbonaceous particles show a perfect spherical morphology with a wide size dispersion at the micrometric scale. When the used amount of P123 is low (molar ratio of P123 : phenol : formaldehyde : ethanol = 1.33×10^{-2} : 1 : 2 : 30.54), spherical particles with diameters from hundreds of nanometers to around 5 μm are obtained (Fig. 2(a)). TEM images (Fig. 2(b)) reveal hexagonal mesopore arrays in some domains, suggesting the formation of a mesostructure with cylindrical pore geometry. XRD patterns of the sample before template removal show two reflections with *d*-spacings of 10.0, 5.9 nm, similar to that for spheres synthesized with F127. The diffraction peaks can be indexed as 100 and 110 reflections of a hexagonal mesostructure (Fig. 3(a-3)). After the removal of the template, the *d*(100) value calculated from the broadened XRD peak decreases to 8.0 nm (Fig. 3(b-3)), implying a distinct shrinkage (20%). The N_2 sorption isotherms show type-IV curves similar to that of the spheres prepared by F127 (Fig. 4(a)). The pore size distribution is centered at around 5.3 nm (Fig. 4(a), inset) while the surface area and pore volume are 427 $m^2\ g^{-1}$ and 0.47 $cm^3\ g^{-1}$, respectively. The C : H : O molar ratio of the particles calcined at 350 °C is measured to be 5.1 : 2.3 : 1.0, which is similar to that of the F127-templated particles.

When the molar ratio of P123 : phenol : formaldehyde : ethanol is changed to 1.99×10^{-2} : 1 : 2 : 30.54, SEM images show that the obtained particles possess similar spherical morphology with diameters from 100 nm to 2 μm (Fig. 2(c)). The XRD pattern reveals only a single broad diffraction peak with *d*-spacings of 12.6 and 10.5 nm before and after template removal, respectively, suggesting a disordered mesostructure (Fig. 3(a-4) and (b-4)). The TEM image (Fig. 2(d)) shows the worm-like mesostructure. N_2 sorption isotherms reveal that the particles possess a BET surface area of 360 $m^2\ g^{-1}$, pore volume of 0.32 $cm^3\ g^{-1}$, and BJH pore size of around 4.4 nm (Fig. 4(b)). When the ratio was changed to P123 : phenol : formaldehyde : ethanol = 2.65×10^{-2} : 1 : 2 : 30.54, TEM images show that the spherical carbonaceous particles have concentric lamellar mesostructure with inter-layer distances around 15 nm (Fig. 2(e), (f)). This agrees with the phase behaviors of the block copolymers, due to lowered curvature energy for the surfactant aggregation. XRD patterns of the particles show a weak diffraction with a *d*-spacing of 11.6 nm before template removal. The absence of diffraction peaks for the carbonaceous spheres after the template removal suggests the absence of a long-range ordered mesostructure, which may be due to the collapse of the frameworks during calcination.

In summary, ordered mesoporous carbonaceous spheres have been prepared *via* a one-step aerosol-assisted organic–organic self-assembly. The polydisperse spherical carbonaceous particles exhibit variable pore size and pore structures by controlling the block copolymer templates and amount of resin oligomers. To the best of our knowledge, mesoporous carbonaceous spheres with ordered structures are directly derived, for the first time, in one-step by using phenolic resols as a carbon precursor and triblock copolymer as a template. This approach provides an efficient route to synthesize mesoporous carbon particles with variable particle size and pore structures which would be promising in many potential applications.

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