Suspension assisted synthesis of triblock copolymer-templated ordered mesoporous carbon spheres with controlled particle size†

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A general strategy in terms of large-scale and shape-controlled synthesis was used to design highly ordered mesoporous carbon spheres with controlled size from 50 to 500 μm by an evaporation induced organic–organic self-assembly inside ethanol-in-oil emulsions.

Mesoporous carbon materials are widely used in adsorption, catalyst and electrode materials.[1–5] Key to realization of these applications is to synthesize the materials into precise, pre-determined nanostructures that can be preserved in a robust engineering form by a simple and efficient method. However, control over morphology and internal mesostructure of mesoporous carbons remains a challenge,[6] especially when considering scaling laboratory synthesis up to industrial volumes.

Recently, organic–organic self-assembly of triblock copolymers[7–9] has been developed to synthesize ordered mesoporous carbons, which has greatly stimulated the development of mesoporous carbon materials. Zhao's group reported on the use of phenolic resols as carbon precursors and triblock copolymers as templates in an evaporation-induced self-assembly (EISA) route to fabricate ordered mesoporous carbons.[10–12] A series of ordered mesoporous carbons with *Im3m*, *P6mm*, *Ia3d* and *Fd3m* symmetry were directly obtained by varying the type and concentration of triblock copolymers. EISA usually provides mesostructured films with a thickness of several hundred nanometres to micrometres. However, for organic–organic composites, severe mass and volume shrinkage during calcination and pyrolysis makes those films too weak to be used in the engineering field, only the powder form can be obtained. It is widely accepted that spherical particles are very advantageous to handle in a closed packed or slurry bed, due to flow resistance, low fluid resistance and low particle release characteristics.[13] By an aerosol-assisted EISA pathway, ordered mesoporous carbon spheres with much smaller particle diameters from 100 nm to 5 μm can be obtained.[14] However, those fine spherical particles also exhibit some inherent drawbacks in engineering applications. What is more, conventional EISA and aerosol-assisted EISA pathways are both unsuitable for industrial production. If ordered mesoporous carbons could be fabricated by a simple and large-scale synthesis into a spherical shape at the macroscopic diameter scale, their applications should be widely expanded.

Here we report a strategy that is reproducible and fulfils the growing demand for large scale production of ordered mesostructured carbon spheres with relatively larger particle size. This strategy is based on an EISA combined with suspension polymerization to fabricate well-ordered mesoporous carbon spheres. A schematic representation of the preparation is shown in Fig. 1. The precursor ethanol solution, containing triblock copolymers and carbon precursor polymer oligomers, was dispersed into a continuous hot oil phase as primary emulsion droplets by the combined action of steric stabilizer and agitation. As a result of preferential thermal evaporation of ethanol, which progressively increased the concentration of the triblock copolymers and nonvolatile polymer oligomers in the droplets, the spontaneous self-assembly was driven towards the formation of liquid-crystalline mesophase hybrids. The primary droplets underwent continuous breakage and coalescence into larger rigid, spherical polymer particles initiated by thermal polymerization. Upon carbonisation, ordered mesoporous carbon spheres with controlled particle size and mesostructure were generated.

To demonstrate this method, triblock copolymer F127 as templates and resorcinol–furfural oligomers as carbon precursors are reported here. As a typical synthesis, 4.6 g resorcinol were dissolved in 40 g ethanol, followed by adding 6 g furfural and 0.75 g 1 wt% HCl ethanol solution. After stirring at 298 K for 30 min, 0.64 g hexamethylenetetramine and 8 g F127 were added and the mixture was stirred for another 60 min to obtain a clear dark red solution. The mole ratios of the reactants were about 0.015 F127 : 1 resorcinol : 1.5 furfural : 0.005 HCl : 0.1 hexamethylenetetramine : 20 EtOH.

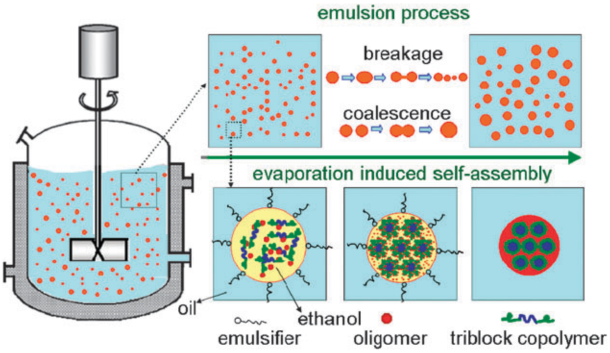

Fig. 1 Schematic representation of the preparation process.

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Then, the solution was placed in a reactor containing a mixture of 500 ml paraffin oil mixed with 1 wt% of the emulsifier sorbitan monooleate Span-80, and the suspension was stirred at 400 rpm at 333 K for about 2 h, followed by stirring at 373 K for 6 h. The spherical polymer particles were separated from the solvent by filtration, washed with ethanol and air-dried at 313 K. Finally, the mesoporous carbon spheres were obtained by pyrolyzing the polymer particles at 1073 K for 3 h with a heating rate of 1 K min^{-1} under purified N_2 flow. The as-made carbon spheres were directly characterized by SEM, N_2 adsorption, TGA and dynamic light scattering (DLS) analysis, and the spheres were ground into powder for the XRD and TEM characterization.

We have found that the sphere-forming process is sensitive to the experimental conditions; hence, attention must be paid to the choice of oil and emulsifier, the polymerization degree of the precursors, the size of the reactor, the type and size of the agitator and the rate of stirring. In this work, paraffin oil is selected as a continuous oil phase, as it is almost immiscible with triblock copolymer, polymer oligomer and ethanol, to ensure a minimal interaction with the triblock copolymer aggregate structure in the ethanol droplets. In the absence of emulsifier, the droplets appear to be unsatisfactory in paraffin oil because of a macro-aggregation problem. Therefore, the addition of an appropriate amount of emulsifier is necessary to stabilize the emulsion droplets. The choice of emulsifier is known to be dependent on the HLB number and the composition of the emulsion. Moreover, in this work, the emulsifier should not significantly interfere with triblock copolymer micelles in droplets. Span 80 is selected as an eligible emulsifier, using which micrometre-size spherical particles are easily formed. The reactor tank and the agitator were fixed at a given dimension. Two key parameters, emulsifier concentration and stirring speed, are varied here for tuning particle size and distribution.

Fig. 2a–c show SEM images of different ordered mesoporous carbon spheres prepared at a stirring speed of 400 rpm for the emulsifier Span 80 concentration of 0.1, 0.5 and 2 wt%, respectively. All samples had the same precursor formulation. The irregularly shaped particles with many pits on the surface were generated when the samples were prepared at a low Span 80 concentration of 0.1 wt%. With the increase of Span 80 concentration, the particles had a smooth surface and their sizes obviously decreased, and few visible defects on the surface were observed. However, little change was observed in the particle size and surface morphology on further increasing the Span 80 concentration. This result was similar to that obtained in the conventional emulsification system.[15] The mean diameters estimated by DLS were about 244, 108 and 101 μm for the spheres prepared at Span 80 concentrations of 0.1, 0.5, 2 wt%, respectively, which are in good agreement with the SEM observations.

Fig. 2d–f show the SEM images of samples prepared at a Span 80 concentration of 0.5 wt% for stirring speeds of 100, 200, and 600 rpm, respectively. The as-produced carbon particles were all finely monodispersed spheres with a smooth surface. The mean diameters were about 341, 185 and 60 μm respectively, according to the results of DLS. The larger spheres with diameters up to 1000 μm could be obtained on further decreasing the stirring speed; however, quite a number of agglomerations were present. The high stirring speed made smaller particles, and the low stirring speed produced large particles. This is apparently because an increased stirring speed causes a high shear rate in the continuous phase, causing stretching of large droplets and eventually splitting of the large drop into smaller ones.

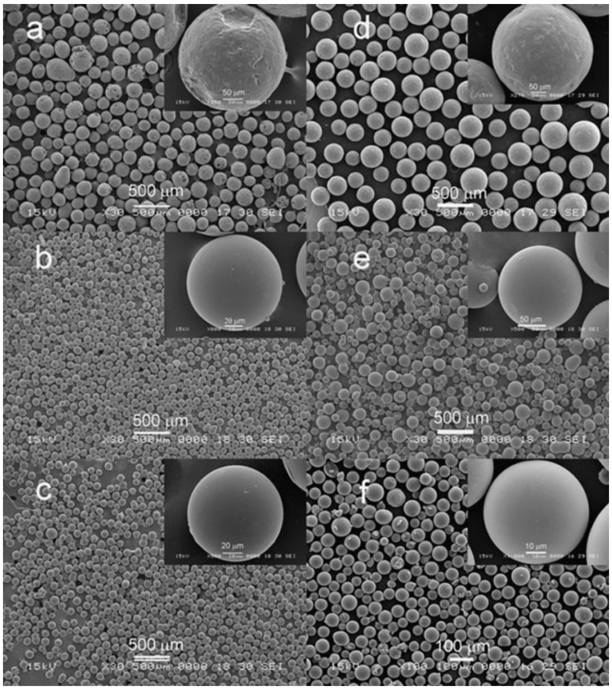

Fig. 2 SEM images of ordered mesoporous carbon spheres synthesized at a fixed stirring speed of 400 rpm for various emulsifier concentrations: (a) 0.1 wt%, (b) 0.5 wt%, (c) 2 wt% and at a fixed emulsifier concentration of 0.5 wt% for various stirring speeds: (d) 100 rpm, (e) 200 rpm and (f) 600 rpm. The insets show a sphere at high magnification. The mole ratios of the reactants were 0.015 F127 : 1 resorcinol : 1.5 furfural : 0.005 HCl : 0.1 hexamethylenetetramine : 20 EtOH.

The ordered hexagonal structure of mesoporous carbon spheres synthesized at the mole ratios of 0.015 F127 : 1 resorcinol : 1.5 furfural : 0.005 HCl : 0.1 hexamethylenetetramine : 20 ethanol was confirmed by XRD, TEM and N_2 adsorption. The XRD pattern of a representative sample is shown in Fig. 3(1a). Three well-resolved XRD peaks with *d*-spacings in the appropriate ratio $1 : (1/\sqrt{3}) : (1/\sqrt{4})$ are observed, which are respectively indexed to be the (10), (11) and (20) reflections of a 2D *P6mm* hexagonal mesostructure. The unit cell size ($a_0 = 2d_{(10)}/\sqrt{3}$) is calculated to be *ca.* 10.8 nm. Fig. 4a and 4b show TEM images of the sample having the typical stripelike and hexagonally arranged structures with larger domain recorded along the (001) and (110) directions, which further confirms a high-quality *P6mm* mesostructure. The unit lattice parameter of the sample estimated from the TEM images is about 9.5 nm, which is a little smaller than the value calculated from the XRD data. N_2 adsorption and desorption isotherms of hexagonal mesoporous carbon spheres in Fig. 3(2a) are type IV with a capillary condensation step at P/P_0 = 0.4–0.6, which implies a uniform pore size. The BJH pore size distribution of

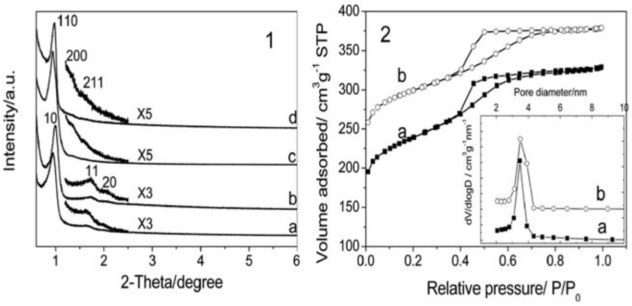

Fig. 3 (1) XRD patterns of ordered hexagonal mesoporous carbon (a–b) and cubic mesoporous carbon (c–d). (a) and (c) were prepared by the EISA combined with suspension polymerization method, while (b) and (d) were prepared by a conventional EISA method for comparison. (2) N_2 adsorption and desorption isotherms of (a) hexagonal mesoporous carbon spheres and (b) cubic mesoporous carbon spheres. The isotherm b is offset vertically by 50 cm^3 g^{-1} for clarity. The inset shows the corresponding BJH pore size distribution curves.

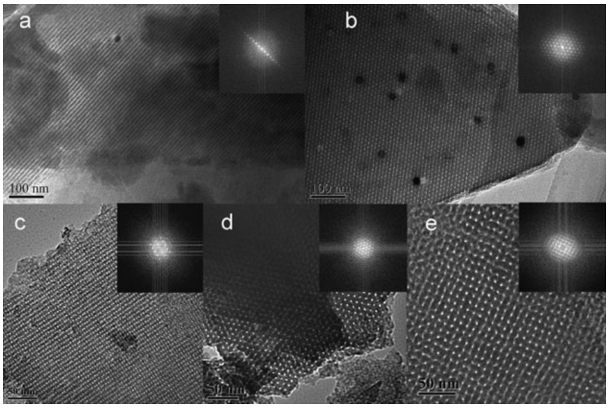

Fig. 4 TEM images of ordered hexagonal mesoporous carbon spheres recorded from (a) [110] and (b) [001] directions and cubic mesoporous carbon spheres recorded from (c) [110], (d) [111] and (e) [100] directions. The insets are the corresponding FFT diffractographs.

the sample exhibits a narrow distribution with a mean size of 3.5 nm. The BET surface area is measured to be 763 m^2 g^{-1} and total pore volume 0.51 cm^3 g^{-1}. The ratio of micropore volume to the total pore volume is about 0.44.

When the molar ratio of the reactants was changed to 0.008 F127 : 1 resorcinol : 1.5 furfural : 0.005 HCl : 0.1 hexamethylenetetramine : 20 ethanol, at the same emulsion conditions, no significant change of the sphere size was found from the DLS results, which suggests the precursor composition has a minor influence on the sphere-forming process and the final particle size. However, the mesostructure with *Im3m* symmetry was obtained as a result of the decreasing volume ratio between oligomers and copolymers, similar to the conventional EISA method.[11] The XRD pattern of this sample in Fig. 3(1c) shows an intense diffraction peak at $2\theta = 0.96^\circ$ and two resolved peaks at the 2θ range of 1 to 2°, which should be indexed to be (110), (200), and (211) reflections of the body-centered cubic structure with *Im3m* space group.[16] The larger domain regularity along the (111), (100) and (110) direction of the *Im3m* mesostructure is visible in TEM images (Fig. 4c–e). The N_2 adsorption and desorption isotherms of this sample in Fig. 3(2b) show typical type-IV curves. The sample has a large BET surface area of 785 m^2 g^{-1}, a total pore volume of 0.50 cm^3 g^{-1} and a ratio of micropore volume to total pore volume of 0.52.

The mesostructure of carbon spheres prepared here has been roughly compared with the ordered mesoporous carbons prepared by a conventional EISA method under the same precursor composition. No significant differences are observed in XRD patterns (Fig. 3(1)) and TGA curves (see ESI†) for both hexagonal and cubic mesostructures. The dispersed emulsion droplets may be considered as micro-systems, with the self-assembly proceeding therein. The droplets are large enough to contain a large number of spherical or rod-like micelles which can be regularly aligned into a liquid crystal phase domain, and this is why the mesostructure of spheres in this procedure is similar to that of those prepared by a conventional EISA method. However, unlike the two interfaces (liquid–solid and liquid–vapor) for a conventional EISA method, evaporation of ethanol takes place at the liquid–liquid interface for the suspension-assisted EISA method, which may cause some discrepancies, especially in the pore channel orientation. Further investigations along this line are underway.

In summary, a general strategy in terms of large-scale and shape-controlled synthesis was used to design ordered mesoporous carbon spheres by an evaporation induced organic–organic self-assembly inside ethanol-in-oil emulsions. The particle size can be controlled by adjusting the emulsion conditions, while the mesostructure can be tuned by varying the precursor composition. These ordered mesoporous carbon spheres with relatively large particle size offer tremendous potential for applications in catalysis, separation and adsorption.

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