

Synthesis of an ordered macroporous carbon with 62 nm spherical pores that exhibit unique gas adsorption properties

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An ordered macroporous carbon with 62 nm spherical pores was synthesized using colloidal-crystal templating and found to exhibit unique gas adsorption properties that have been so far attributed to adsorption in mesopores (size below 50 nm).

Recently, remarkable progress has been made in the synthesis of carbons with periodic porous structures. This progress was achieved using templates, such as zeolites,¹ ordered mesoporous silicas^{2,3} and silica colloidal crystals^{4–6} for the synthesis of ordered microporous (pore size <2 nm), mesoporous (2–50 nm) and macroporous (>50 nm) carbons, respectively. However, the pore sizes currently attainable for ordered carbons span over only certain intervals of micropore, mesopore and macropore ranges. For instance, the pore diameters for ordered mesoporous carbons reported to date were well below 10 nm^{2,3} and the pore size achievable for colloidal-crystal templated carbons was usually above 100 nm,^{4–6} which results in a gap in pore sizes between 10 and 100 nm. A recently proposed colloid-imprinting approach allows one to synthesize carbons with very uniform pores of size from about 7 to at least 25 nm, but these carbons do not exhibit periodic structures.⁷ Pore dimensions up to about 30 nm can be achieved for carbon mesocellular foams,⁸ which are also not well-ordered. Therefore, there is an interest in extending the colloidal-crystal templating approach for ordered carbon synthesis on pore sizes from 100 nm to as low as possible. This requires the synthesis of colloidal-crystal templates that would consist of uniform spherical particles of size below 100 nm. Such particles can be obtained using the method proposed by Osseo-Asare and Arriagada.⁹ This method was successfully used as an initial step for the preparation of colloidal-crystal templates for the synthesis of ordered mesoporous polymers of tunable pore dimensions (15–35 nm)¹⁰ and ordered platinum with pore dimensions on the borderline between mesopore and macropore ranges.¹¹ More recently, colloidal-crystal silica templates with particles synthesized using this method⁹ were used as templates in the synthesis of ordered carbons with repeating distances of 50–70 nm,^{12,13} as seen from transmission electron microscopy (TEM). However, the reported N₂ adsorption data¹² did not indicate the presence of uniform pores of a size on the borderline between the mesopore and macropore ranges, probably because of the presence of defects in an otherwise periodic and uniform porous structure. Herein, a novel method for the formation of the carbon framework is reported, which allowed us to obtain an ordered carbon with macropores (62 nm) of remarkable size uniformity, as seen from a very sharp capillary condensation step and a well-defined H1 type hysteresis loop. This work is a major advancement in the preparation of ordered carbons with a pore size on the borderline between the mesopore and macropore ranges, which are prospective adsorbents, catalyst supports, immobilization media, and model adsorbents for fundamental studies of gas adsorption in porous media.

Monodisperse silica particles of a diameter in the range of 40–90 nm were synthesized using a modification of the procedure described in ref. 9. Typical molar composition used for the synthesis was 1.0 tetraethyl orthosilicate (TEOS):31.0

cyclohexane:1.1 n-hexanol:0.6–0.8 Tergitol NP-9:0.9–1.0 NH₄OH (28 wt.%):6.0–9.0 H₂O. The resulting colloidal silica spheres were washed with ethanol several times to remove surfactants and then dispersed in water–ethanol solution (70/30 vol.%). The particles were allowed to settle down slowly and were dried at about 343 K to create the silica template. The dried crystalline particle array was then sintered slightly at its points of contact by heating at a rate of 5 K min^{–1} to 1073 K for 1 h in order to provide pore connectivity in the carbon replica. Carbon precursor solution of 1.0 phenol (99 wt.%):0.8 formaldehyde (37 wt.%) was added into the void space of the silica template by centrifuging at 1000 rpm for 1 h. Excess precursor and moisture were removed by brief evacuation. Then, 1 M sulfuric acid (catalyst; phenol/sulfuric acid molar ratio of 0.1) was allowed to penetrate into the precursor composite by centrifugation for 1 h. The composite was evacuated to remove dissolved oxygen and moisture, and heated to 398 K for ca. 12 h to get an *in situ* cross-linked polymer. The polymer was then carbonized by heating at a rate of 5 K min^{–1} at 1073 K for 7 h in dry Ar flow to obtain a carbon–silica composite. The silica template was dissolved using 48% aqueous HF for 10 h (the dissolution of silica was checked using TGA) and the resulting carbon was filtered, washed and dried at 323 K.

Fig. 1 shows a TEM image of the silica particles that formed the colloidal-crystal template. The particles were monodisperse spheres with diameter ~70 nm. Fig. 2 and 3 show scanning EM (SEM) and TEM images of the silica-free ordered macroporous carbon framework with close-packed uniform spherical pores ~62 nm in diameter, as determined using high-resolution TEM. The ordering is very good for a material templated with arrays of spheres of such small size. N₂ adsorption isotherms for the silica colloidal-crystal and the templated carbon are shown in Fig. 4. The silica exhibited a type IV isotherm characteristic of mesoporous solids and an H1 hysteresis loop that indicates a facile pore connectivity. The capillary condensation step was not particularly narrow for the silica. The pore space between uniform spheres has such a shape that the distance between pore walls varies in different pore parts. The silica colloidal-crystal exhibited a BET specific surface area of 190 m² g^{–1}, but the mesopore surface area was only ~60 m² g^{–1}, whereas the

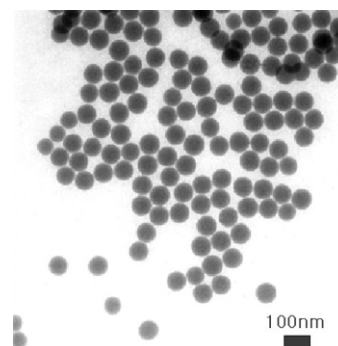


Fig. 1 Colloidal silica particles of diameter about 70 nm.

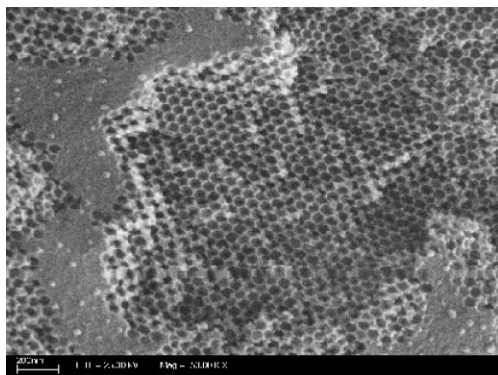


Fig. 2 SEM image of the ordered macroporous carbon with 62 nm pores.

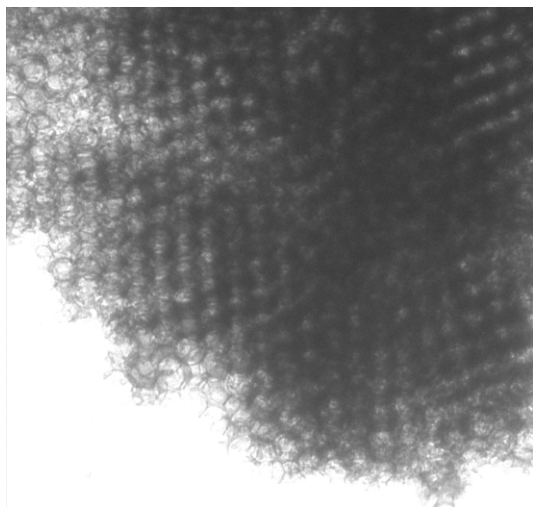


Fig. 3 TEM image of the ordered macroporous carbon with 62 nm pores.

remaining surface area is related to the presence of micropores (micropore volume was $0.06 \text{ cm}^3 \text{ g}^{-1}$).

The ordered carbon exhibited a type IV adsorption isotherm with an H1 adsorption–desorption hysteresis loop. This adsorption characteristic was usually attributed to adsorption in mesopores, which were classified by IUPAC as pores of diameter 2–50 nm.¹⁴ A 62 nm pore size falls into the macropore range and thus would be expected to result in type II adsorption behavior,¹⁴ which is not observed. This clearly shows that the adsorption behaviour typical of mesopores can be observed for macroporous solids (according to the IUPAC classification) with uniform pores of size close to the upper limit of the mesopore range. Thus, the borderline between mesopore and macropore ranges at 50 nm should be treated as an approximate one.

To our best knowledge, this is the first case of a colloidal-crystal templated carbon that exhibits a clear type IV adsorption behavior. A previous report⁵ of carbons with larger macropores showed a predominantly type I behavior with low-pressure hysteresis, which can be related to adsorption in framework micropores (this kind of hysteresis indicates poor transport properties) and low macropore area. Another study, which employed the same kind of template as used herein, reported an ordered carbon with 50 nm pores that exhibited an adsorption isotherm, which did not level off at pressures close to saturation,¹² thus being intermediate between types II and IV. The present results strongly suggest that the pores of the latter carbon were not well separated by the walls, and thus the structure had an appreciable amount of defects. It is clear that the carbon reported herein exhibits a gas adsorption behaviour unprecedented for macroporous materials, which is likely to arise from the remarkable uniformity of size of its 62 nm macropores.

The carbon exhibited a total pore volume of $1.68 \text{ cm}^3 \text{ g}^{-1}$ and a BET specific surface area of $750 \text{ m}^2 \text{ g}^{-1}$, out of which 130 m^2

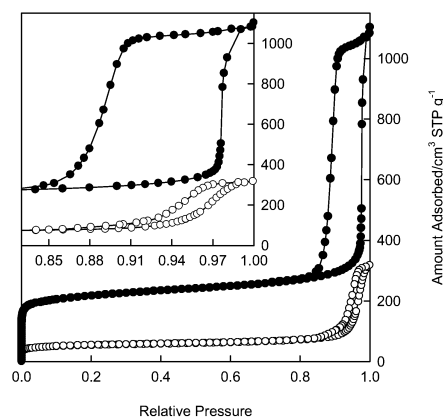


Fig. 4 N_2 adsorption isotherms for the silica colloidal crystal (hollow circles) and the templated carbon with 62 nm macropores (filled circles).

g^{-1} is attributable to the surface of macropores and the rest arises from the presence of a considerable amount of micropores ($0.29 \text{ cm}^3 \text{ g}^{-1}$) located in the ordered carbon framework. The micropore nature of frameworks is typical for ordered mesoporous and macroporous carbons.^{2,3,5,6}

The colloidal-crystal templated carbon with 62 nm pores exhibited an extremely sharp capillary condensation step centered at a relative pressure of 0.977 (see Fig. 4). The capillary evaporation took place at much lower relative pressures (0.89), which indicates that connections between the pores are much more narrow than the pores themselves. Another carbon synthesized using the same template exhibited the capillary condensation at about 0.973. This shows that the capillary condensation in uniform 62 nm spherical pores takes place at a relative pressure of about 0.975. This experimental result is in a striking disagreement with the predictions of Broekhoff and de Boer¹⁵ who indicate that these capillary condensation pressures should be observed for spherical pores 97–116 nm in diameter. Predictions based on the Kelvin equation for open cylindrical pores¹⁵ are somewhat more consistent with the experimental data. Clearly, much work is required to understand and adequately describe adsorption behavior in large pores, and this endeavor is greatly facilitated by the availability of ordered carbons reported herein.

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