# Mesoporous carbon nanomaterial prepared directly by the second-side modified cyclodextrin through silica as template

**Yu Liu*, Dong-Sheng Guo, Heng-Yi Zhang and Yan-Li Zhao**

*Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P. R. China*

A mesoporous carbon nanomaterial possessing high BET surface area (*ca* 785 $m^2/g$) and unique pore size (6–7 nm with narrow PSD) has been prepared directly by modified cyclodextrin-silica nanocasting, a simple, one-step preparative route to mesoporous carbon with the pore size controlled by a silica template.

**Keywords**: carbon, cyclodextrin, mesoporous materials, nanocasting, silica template

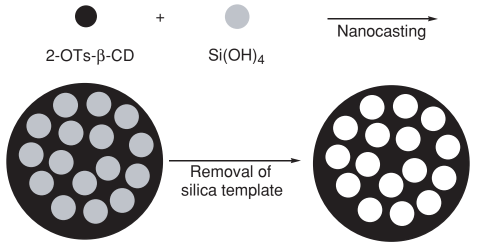
Investigations on mesoporous materials possessing particular structures have gained extensive attention in recent years because of their potential in several areas of catalysis, adsorption, synthesis, conduction, *etc*.[1-4] Therefore, a lot of effort has been devoted to develop novel nanoporous materials containing corresponding pore morphology, pore size, and wall material which can be extended over a broad range of science and technology.[5-8] Among them, the fabrication of mesoporous carbons is extremely important for their applications in separation of bulky organic materials and electrode materials as compared with the usual microporous carbons. Ryoo *et al*.[9,10] developed a templating method to prepare ordered mesoporous carbon molecular sieves, via carbonisation of sucrose-filled ordered mesoporous silica using sulfuric acid as catalyst. Employing phenol-formaldehyde resins instead of sucrose as carbon precursor, Hyeon *et al*.[11] obtained the carbon replica of inorganic templates such as surfactant-stabilised silica sol and mesoporous MCM-48. Jaroniec *et al*.[12] reported a novel approach to the synthesis of mesoporous carbons by colloidal imprinting. It is noted that the nanocasting technique shows the main advantage of solidifying inorganic compounds by replicating the original phase structure,[13-19] making it possible to analyse a delicate and fragile, not cuttable and badly contrasted complex fluid by its solidified, permanent, well-contrasted and cuttable "hardcopy". However, to the best of our knowledge, there are no studies on the fabrication of mesoporous carbon materials by one-step nanocasting so far, although microporous carbon was prepared directly by cyclodextrin-based nanocasting.[20] In the present paper, we report our investigation of the fabrication of mesoporous carbon nanomaterial utilising a nanocasting technique. The nanomaterial obtained was characterised by scanning electron microscopy (SEM), X-ray diffraction (XRD), nitrogen sorption measurement and transmission electron microscopy (TEM).

Cyclodextrins (CDs), a class of cyclic oligosaccharides with six to eight D-glucose units linked by α-1,4-glucose bonds,[21-23] have been taken as porogens and templates to afford worm-like nanoporous silica materials during the silica nanocasting procedure,[24] because CDs can be dispersed in a silica gel matrix at the nanometre level for the hydrogen-bonding interactions between hydroxyl moieties of CDs and residual silanol groups of silica gel. More recently, Sayari *et al*.[20] reported the direct preparation of microporous carbon with narrow pore size distribution (PSD) resembling the diameter of β-CD by similar nanocasting to that mentioned above, which made CDs further act as the precursor of porous carbon nanomaterials. The chemically modified CDs are known to show significant difference in aspects of both recognition and assembly in comparison with native CDs.[25-27] We now examine the character of porous carbon material obtained by nanocasting based on the simplest modified β-CD at the second side.

The organic/inorganic hybrid prepared by the modified β-cyclodextrin-silica nanocasting was calcined under vacuum, and then the silica template was removed by HF solution. Scheme 1 presents the one-step preparation procedure of the carbon nanomaterial. The surface morphology of the obtained carbon material is shown by the SEM image in Fig. 1, which gives macrostructure information of the homogeneous granule with size up to the micron scale.

To confirm the formation of amorphous materials, we characterised the modified CD, organic/inorganic hybrid material, and porous carbon nanomaterial respectively by XRD as presented in Fig. 2. The characteristic broad peak around 20–25° resulting from the amorphous state of silica is shown in Fig. 2b, which indicates that the crystalline CD is dispersed in the silica gel matrix. Moreover, the X-ray pattern of the highly disordered, nongraphitic carbon is shown in Fig. 2c.

Furthermore, the carbon nanomaterial was verified by nitrogen sorption measurement. As can be seen from the sorption isotherm displayed in Fig. 3, the current carbon nanomaterial is a mesoporous adsorbent, because it shows typical features of Type IV isotherm[28] with an increase in the slopes of the isotherms and a clear hysteresis loop in the pressure range of 0.6–0.9. In the mean time, the sorption data show that the porous carbon nanomaterial possesses a high BET surface area (*ca* 785 $m^2/g$) and an especially large pore volume (*ca* 1.6 $cm^3/g$), while the corresponding BET surface area, before removing silica template, is only 0.1968 $m^2/g$. As confirmed by calculation using the Barrett–Joyner–Halenda (BJH) method on



**Scheme 1** Preparation procedure of cyclodextrin-based mesoporous carbon.

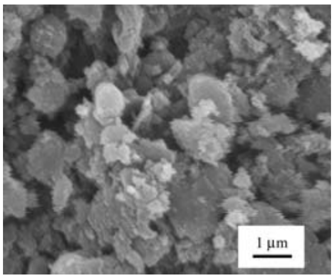


**Fig. 1** The SEM image of the carbon nanomaterial.

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* Correspondence. E-mail: yuliu@public.tpt.tj.cn

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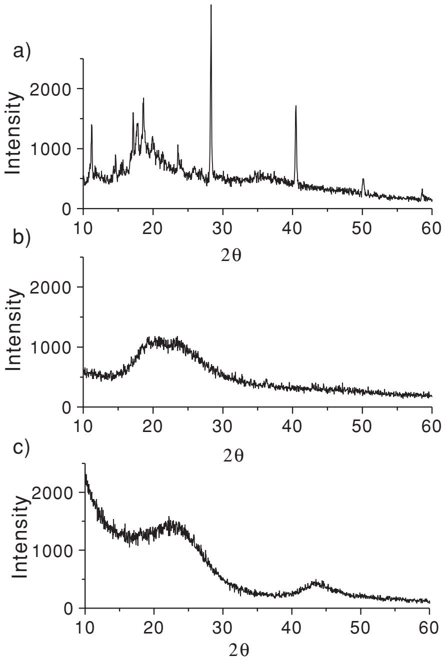

**Fig. 2** XRD patterns for (a) the modified CD; (b) the organic/inorganic hybrid material, and (c) the porous carbon nanomaterial. θ = diffraction angle.

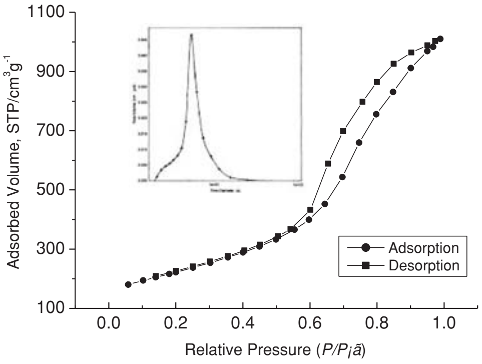

**Fig. 3** Nitrogen BET adsorption isotherm of the porous carbon nanomaterial. Inset: the corresponding pore size distribution curve calculated from the desorption branch by the BJH theory.

the basis of desorption data,[29] the current carbon exhibits a narrow PSD with an average diameter of 6.3 nm (Fig. 3 inset), which is about 4 times larger than the β-CD diameter (1.53 nm).

Nevertheless, with the nitrogen sorption measurement in mind, it is difficult to characterise the pore structure solely on this evidence. To obtain further structure evidence for the porous carbon, we observed its optical impression by TEM. As shown in Fig. 4, the current carbon nanomaterial is homogeneous and nanoporous. From the enlarged picture, we can see clearly that the light area corresponding to the pores possesses a size of around 6 nm, which accords well with the result of the nitrogen sorption measurement. The TEM image, together with the data of the nitrogen sorption measurement, indicates that the carbon material is homogenous and mesoporous.

The results obtained show that the pore size of 2-OTs-β-CD-based carbon nanomaterial is larger than that of the corresponding β-methylcyclodextrin (β-MCD) system reported so far,[20] although the used nanocasting methods are similar. One reasonable explanation for the mesoporous character is that, 2-OTs-β-CD could not be self-assembled to the hollow nanotubes causing the worm-type micropores as compared with β-MCD, because the aromatic substituting group in 2-OTs-β-CD could be shallowly self-included into the cavity,[30] and thus 2-OTs-β-CD could not be taken as porogen during the present nanocasting procedure of carbon material. For the formation of the mesopores with average pore size of 6.3 nm, it can be concluded that the pores are exactly generated by the removal of silica template while CD just acts as the material of the wall via carbonisation, which was confirmed well by the nitrogen sorption measurement of the material before removing the silica template. That is, the pore size and morphology represent simply the structure of the silica matrix. Moreover, it should be noted that the conformation of the modified CD influenced the silica structure via soft chemistry to some extent, which in turn affected the carbon mesopore structure. Therefore, the modified CD, tethered by its functional group, was taken as not only the precursor of wall material but also as one controlling factor of pore morphology.

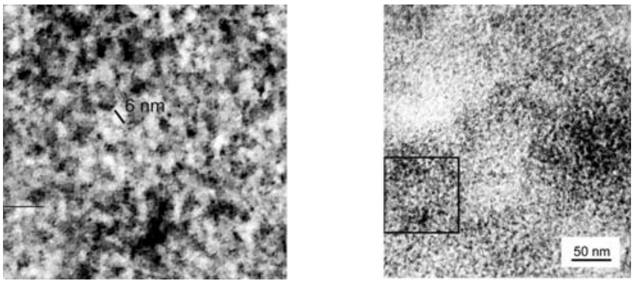

**Fig. 4** TEM image of the mesoporous carbon nanomaterial. The left picture is the enlarged TEM image (right) to illuminate the pore structure more clearly.

In summary, a novel mesoporous carbon nanomaterial was prepared directly by one-step nanocasting based on the simple modified cyclodextrin through silica as template. Possessing high BET surface area (*ca* 785 m$^2$/g) and unique pore size (6–7 nm with narrow PSD), the resulting mesoporous carbon is of potential use in such applications as adsorbents, catalyst supports, and electrode materials.

## Experimental

The modified cyclodextrin, mono[2-(*p*-toluenesulfonyl)]-β-cyclodextrin (2-OTs-β-CD), was prepared as reported previously.[31] Tetraethoxysilane (TEOS > 97%) was distilled before use. 2-OTs-β-CD (2.0 g) was dissolved in distilled water (3.0 ml) to form a solution of concentration 40 wt%. Sulfuric acid was added to adjust the pH to 2.5. Next, a double amount (weight) of TEOS (4.0 g) with respect to CD was added under vigorous stirring. The mixture was stirred continuously at room temperature until complete homogenisation. The ethanol formed during hydrolysis was removed under reduced pressure at 30–40 °C, and a transparent gel was obtained. After aging naturally for several days, the hybrid material was calcined at 900 °C under vacuum. The temperature was raised to 500 °C in 4 h, kept for 10h, and then was raised to 900 °C in 7 h and kept for 8 h. After carbonization, the silica template was removed by ultrasonically agitating the black carbon–silica composite in HF solution (3 mol/l). As a result, the nanoporous carbon was obtained after filtration and drying.

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