research may not be entirely from photocatalytic oxidation, but rather from increased adsorption of a more reactive molecule (i*).

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Synthesis and characterization of a new nanoporous carbon material with a bimodal pore system

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Since two Korean research groups [1,2] independently reported the preparation of mesoporous carbon using mesostructural silica materials as templates in 1999, template synthetic approaches have been extensively applied to synthesize nanoporous carbon materials. These mesoporous carbon materials have numerous application perspectives for the adsorption of bulky organic molecules [3,4], as catalyst supports [5,6] and as electrode materials [7,8]. In general, the template synthetic procedure for producing mesoporous carbon is as follows: (1) preparation of the mesoporous silica, (2) removal of the structure directing agent (surfactant), (3) synthesis of a carbon precursor/silica nanocomposite, (4) carbonization, (5) removal of the silica template. In such a preparation process, the surfactant molecules in the as-synthesized template are completely eliminated by calcination at high temperatures. Moreover, an additional carbon precursor must be introduced into the channels of mesoporous silica template in order to obtain mesoporous carbon.

Recently, nanoporous carbon materials have been synthesized using both the mesostructural template and an organic surfactant as the carbon source [9,10]. Yu and co-workers [9] synthesized mesoporous carbon using an as-synthesized MCM-48 silica/surfactant composite as the template, however, it is not possible to obtain the mesoporous carbon directly by carbonizing the organic surfactant into nanoporous carbon without the introduction of an additional carbon precursor (poly-divinylbenzene) prior to the carbonization. Pinnavaia et al. [10] prepared for carbon nanotubes using non-ionic Pluronic 123 surfactant micelles as carbon precursor. However, the ordered array of nanotubes was not observed during in situ surfactant

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carbonisation because the polyethylene oxide segment of the Pluronic 123 surfactant initially occupies the micropores of the template and cannot be graphitized in the thermal decomposition process. To date, studies on the synthesis of nanoporous carbon with structure network using the surfactant as the carbon precursor are very scarce.

Here we reported the synthesis of nanoporous carbon material using the ordered mesoporous silica molecular sieve SBA-15. The as-synthesized SBA-15 was used as the template and the surfactant occupying its mesopores was used directly as the carbon precursor, without introduction of foreign carbon precursors. A nanoporous carbon material with bimodal pore system was obtained upon the removal of the silica template.

Mesoporous silica SBA-15 was prepared as reported in the literature [11,12]. Briefly, high-quality SBA-15 was prepared using the triblock copolymer, $EO_{20}PO_{70}EO_{20}$ (Pluronic P123, Acros), as the surfactant and tetraethyl orthosilicate (TEOS, 98%) as the silica source. The mixture of 4 g copolymer:0.04 mol TEOS:0.24 mol HCl:6.8 mol H_2O was aged at 353 K overnight, without stirring. The solid product was recovered, washed and air-dried at room temperature. For comparison purposes, some of the as-synthesized SBA-15 was calcined directly at 823 K for 4 h in air to remove the surfactant, and the resulting sample was denoted as CS15. The synthesis of the nanoporous carbon material is depicted briefly as follows [13]: 1 g of as-synthesized silica SBA-15 was impregnated with 6 g 98 wt% concentrated sulphuric acid for 12 h at room temperature, causing the colour of the sample to change from white to brown. The surfactant was partially carbonized or cross-linked during this acid pre-treatment in order to prevent it from changing to volatile matter and evaporating during carbonization at high temperature. The mixture was heated to 823 K in a quartz boat for 3 h under a nitrogen flow (purity 99.999%) in a tubular oven, after which the sample was cooled to room temperature. The resulting black sample was denoted as CS15N. The carbon/silica composite (CS15N), obtained after pyrolysis, was soaked in 10 wt% hydrofluoric acid for 12 h at room temperature to remove the silica template. The template-free carbon product was filtered, washed with the deionized water and dried at 363 K overnight, and the sample was denoted as CS15NS.

Fig. 1 shows transmission electron micrographs (TEM) of as-synthesized SBA-15, CS15N and CS15NS samples viewed along and perpendicular to the direction of the hexagonal pore arrangement. Ordered-channel arrays of parallel lines in the as-synthesized SBA-15 and CS15N are clearly observed along the direction of the pore arrangement, suggesting an ordered mesoporous structure. Furthermore, the structure of CS15NS preserves the hexagonally ordered mesostructure of the silica SBA-15 after removal of the mesoporous silica template. The edges of the pores in CS15NS are smooth hexagons (Fig. 1(c)). The structure of the pore is honeycomb-like, which is similar to the structure of MCM-41 silica [14]. The pore size is approximately 5.0 nm with a thick uniform pore wall. This indicates the structure of CS15NS may stem from the pore structure of SBA-15 silica.

The ordered mesoporous structure of CS15NS carbon was investigated by X-ray diffraction (XRD). Curve a in Fig. 2 is consistent with a characteristic XRD pattern of an as-synthesized SBA-15 mesoporous silica with d-spacing value of 9.88 nm from literature [12]. The CS15N composite shows a similar XRD patterns to that of as-synthesized SBA-15, but the main diffraction peak shifts to a lower 2θ value, resulting a d-spacing value of 19.6 nm. The presence of four diffraction peaks in the CS15N composite (Fig. 2 curve b) confirms that the framework of SBA-15
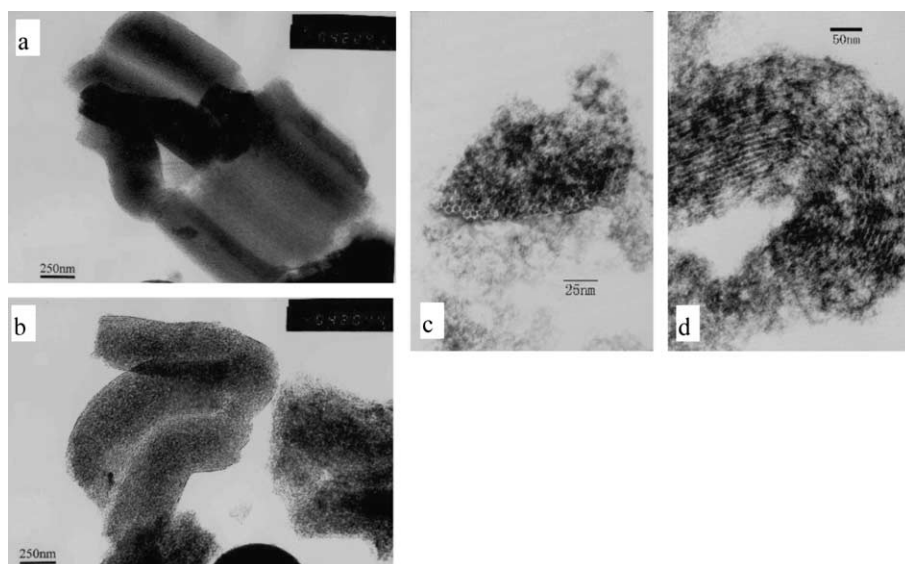

Fig. 1. Typical TEM images of as-synthesized SBA-15 (a), CS15N (b) and the CS15NS carbon (c, d). The carbon was synthesized using the surfactant as a carbon source and as-synthesized SBA-15 as a template. The TEM images were obtained with a JEM 2000EX operated at 100 KV.
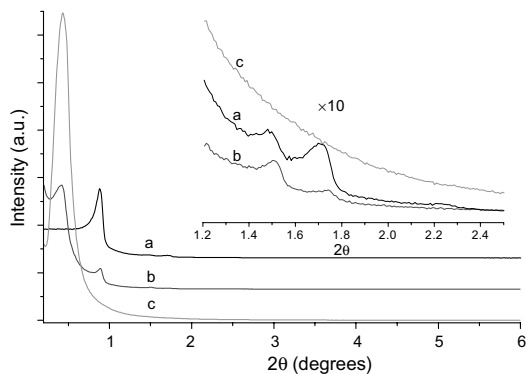
Fig. 2. X-ray diffraction (XRD) patterns of as-synthesized SBA-15 (curve a), CS15N (curve b), CS15NS (curve c).

mesoporous silica is retained after the high temperature carbonization. Interestingly, a strong broad diffraction peak centred at $2\theta = 0.43°$ is clearly observed in the XRD pattern of CS15NS carbon, resulting in a *d*-spacing of 19.0 nm (Fig. 2, curve c), demonstrating that the mesoporous structure framework is still retained even after the removal of the silica by HF etching. An analogous diffraction pattern has been observed for SNU-2 carbon [15]. Fig. 3 shows the thermogravimetric analysis (TGA) of as-synthesized SBA-15 and CS15NS carbon prepared in an oxygen atmosphere.
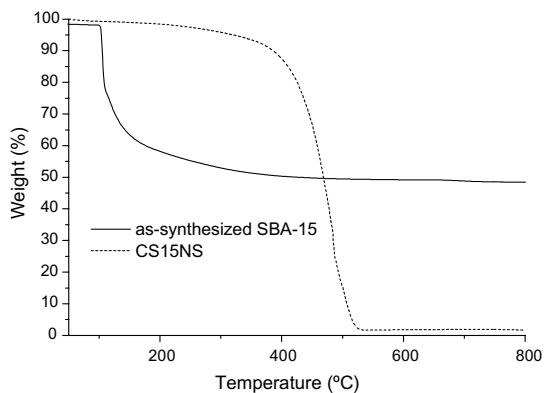

Fig. 3. Weight change curves for as-synthesized SBA-15 and CS15NS.

As-synthesized SBA-15 shows a total weight loss of approximately 50 wt%, which can be attributed to the removal of the surfactant, which is in agreement with the literature results [11,12]. However, the CS15NS carbon shows a residue content after the carbon combustion of about 1.5 wt%. This indicates that silica template dissolution in HF solution is nearly complete [16] and the intense XRD peak does not result from the SBA-15 silica template, but from the carbon material.

Fig. 4 shows the nitrogen adsorption/desorption isotherms and pore size distributions (derived from the desorption branch) of the CS15, CS15N, and CS15NS samples. Structural parameters of the samples are presented in Table 1. The isotherms of all of the samples are type IV and characteristic of mesoporous materials with capillary condensation [17]. For CS15NS, the capillary condensation step is shifted to a lower relative pressure ($0.4p/p_0$), suggesting the smaller pore diameters. The pore size distribution shows two kinds of pores centred at approximately 0.9 nm and 4.3 nm (Fig. 4B, curve c). The appearance of a new micropore can be accredited to the carbonization of the carbon source polymer [1,8,16]. The 4.3 nm mesopores for the CS15NS is smaller than the pore diameter of CS15 (5.7 nm) and CS15N (8.8 nm) samples to a significant extent. The difference can be related to the contraction of framework structure upon the removal of silica template [1,8]. The nanoporous carbon has the highest BET surface area of 782 m^2/g and the pore volume of 0.77 cm^3/g, respectively.

In summary, an ordered nanoporous carbon was synthesized using SBA-15 as the template and the surfactant as the sole carbon source. The surfactant was partially car-

Table 1
Structural properties of three samples

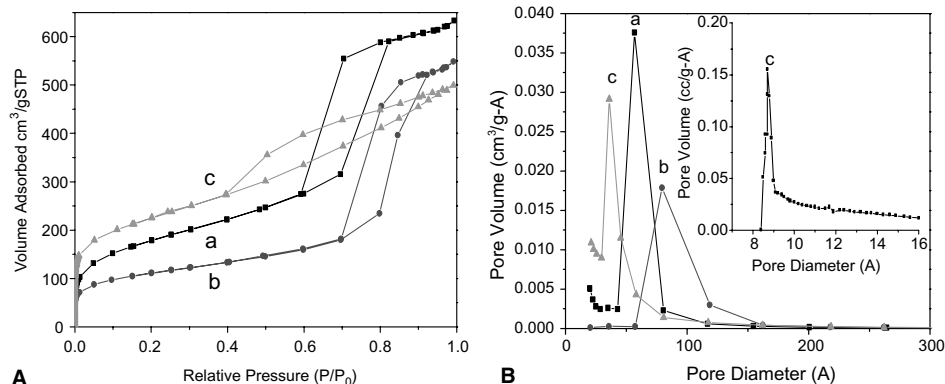| Sample	d (nm)	S_{BET} (m^2/g)	V_{meso} (cm^3/g)	V_{micro} (cm^3/g)	P_{PSD} (nm)
CS15	9.15	639	1.0	0.16	5.7
CS15N	19.6	388	0.86	0.11	8.8
CS15NS	19.0	782	0.77	0.23	4.3

Fig. 4. (A) Nitrogen adsorption isotherms and (B) pore size distribution calculated from desorption branch of the isotherms, micropore diameter calculated by Horvath-Kawazoe (HK) model (inset) for (a) CS15, (b) CS15N and (c) CS15NS.

bonized and immobilized in the pores of as-synthesized mesoporous SBA-15 using concentrated sulphuric acid. The advantages of this method are that the expensive surfactant does not need to be removed and no additional carbon precursors are introduced into the mesoporous silica template. A uniform carbon material can be easily achieved inside the silica mesopores so that the resulting nanoporous carbon material preserves the architecture of mesoporous silica templates. It is expected that this simple direct template synthetic method can be also applied to the synthesis of other types of nanoporous carbon.

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Carbon nanospheres produced in an arc-discharge process

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Spherical carbons with micrometer dimension have been prepared for 20 years due to their uniform packing for high density and homogeneous properties. They are applied as the high density carbon artifacts within electrodic material for lithium ion battery and low pressure-drop adsorbent bed. Recently, nanospherical carbons have been extensively reported since C60 fullerene has been focused although

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