

# Three-dimensionally ordered macroporous carbons having walls composed of hollow mesosized spheres†

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Three-dimensionally ordered macroporous carbons were prepared from bimodal polymer–silica colloidal crystals; the resulting carbons had interconnected macropores, and the walls of the macropores were composed of hollow mesosized spheres.

Three-dimensionally ordered macroporous (3DOM) materials have been paid much attention in various application fields, such as photonic crystals, catalysts, and sensors.<sup>1</sup> So far, various kinds of 3DOM materials such as ceramics,<sup>2</sup> metals,<sup>3</sup> polymers,<sup>4</sup> and carbon<sup>5</sup> have been prepared. 3DOM materials can be prepared by the colloidal crystal templating method. Colloidal crystals consisting of monodisperse particles of silica or polymers are used as templates. The template method relies on filling the void space between close-packed spheres with precursors such as liquid metal alkoxide and resin.<sup>1–5</sup> After appropriate processes, 3DOM materials can be obtained by the removal of the templates. Among the series of 3DOM materials, macroporous carbons are attractive as absorbents, catalyst supports, and electrode materials.<sup>6,7</sup> However, the specific surface areas of macroporous carbons are smaller than mesoporous and microporous carbons.<sup>8–10</sup> Larger specific surface area is favorable for uses as catalyst supports and electrode materials of electric double-layer capacitors. Recently, remarkable progress has been achieved in the preparations of macroporous materials with mesoporous structures.<sup>11–13</sup> Of particular interest, 3DOM carbon with mesoporous walls has been prepared by replication of 3DOM silica.<sup>13</sup> The use of 3DOM silica consisting of small silica particles as the template resulted in the mesoporous walls. Another interesting method is the colloidal imprinting reported by Li and Jaroniec.<sup>14</sup> They have successfully made mesoporous carbons from mesophase pitch particles by imprinting colloidal silica particles. These reports stimulated us to fabricate 3-D ordered porous carbons with mesoporous structures using colloidal imprinting.

We report here a novel synthesis of hierarchical carbon structures, namely 3-D ordered macroporous carbons having walls composed of hollow mesosized spheres. Macropores were created by using poly[styrene-(*co*-2-hydroxyethyl methacrylate)] (PSHEMA) polymeric colloids as hard templates and hollow

mesosized spheres were templated by smaller silica colloids. Thus, two types of colloids of significantly different sizes were used to create a macrosized polymeric colloidal crystal with voids filled with mesosized small silica colloids. The obtained carbon has a 3-D ordered macroporous structure as well as uniform spherical mesopores.

Monodisperse PSHEMA latex was prepared in absence of emulsifier using potassium persulfate as initiator. The latex was prepared by batch surfactant-free emulsion copolymerization of styrene and 2-hydroxyethyl methacrylate following the procedure reported by Reese and Asher.<sup>15</sup> The amounts of reagent used are as follows: 70 g styrene, 2 g 2-hydroxyethyl methacrylate, 210 mL water, and 0.11 g potassium persulfate. The diameter of the prepared PSHEMA particle was 450 nm confirmed by scanning electron microscope observation. Three kinds of silica colloids CS10, CS50, and CS100, which had average diameters of 10 ~ 20 nm, 40 ~ 50 nm, and 70 ~ 100 nm, respectively (Snowtex<sup>®</sup>, supplied from Nissan Chemical Industry), were used as received. The monodisperse PSHEMA latex and the silica colloids were uniformly mixed in deionized water by an ultrasonic treatment. The mixed suspension was simply evaporated in a Petri dish at 333 K for 24 hours, and the PSHEMA–silica composite accumulated on the bottom of the petri dish. During the evaporation, the monodisperse polymer particles self-assemble into an ordered lattice where the silica particles are forced to pack closely at the interstices between polymer particles. The volume ratio of PSHEMA and silica in the composite was controlled to be 74 : 26, which allowed the polymer particles to form close-packed lattice in the composite. The obtained PSHEMA–silica composite was treated at high temperatures in a horizontal furnace under dry argon atmosphere (30 mL min<sup>-1</sup> flow rate). The temperature was increased from room temperature to 1273 K at a heating rate of 5 K min<sup>-1</sup> and cooled to room temperature. After the carbonization, the silica particles were removed with 10% aqueous hydrofluoric acid, and the resulting porous carbons were washed with ultrapure water and dried in a vacuum oven at 383 K.

The PSHEMA particles were interconnected during the heat-treatment at higher than the glass transition temperature (~373 K) as shown in Fig. 1.<sup>16</sup> PSHEMA is a thermally degradable polymer, and it decomposes by a depolymerization mechanism.<sup>17,18</sup> Indeed, thermogravimetric (TG) analysis under nitrogen atmosphere revealed a clean decomposition of PSHEMA at about 673 K with <2% formation of residual material (see Supplementary Information†). However, several groups reported preparation of carbonaceous materials from polystyrene-based resins.<sup>19–21</sup> Although PSHEMA decomposed at around 673 K into monomers, dimers, trimers *etc.*,<sup>18</sup> some of the decomposed materials

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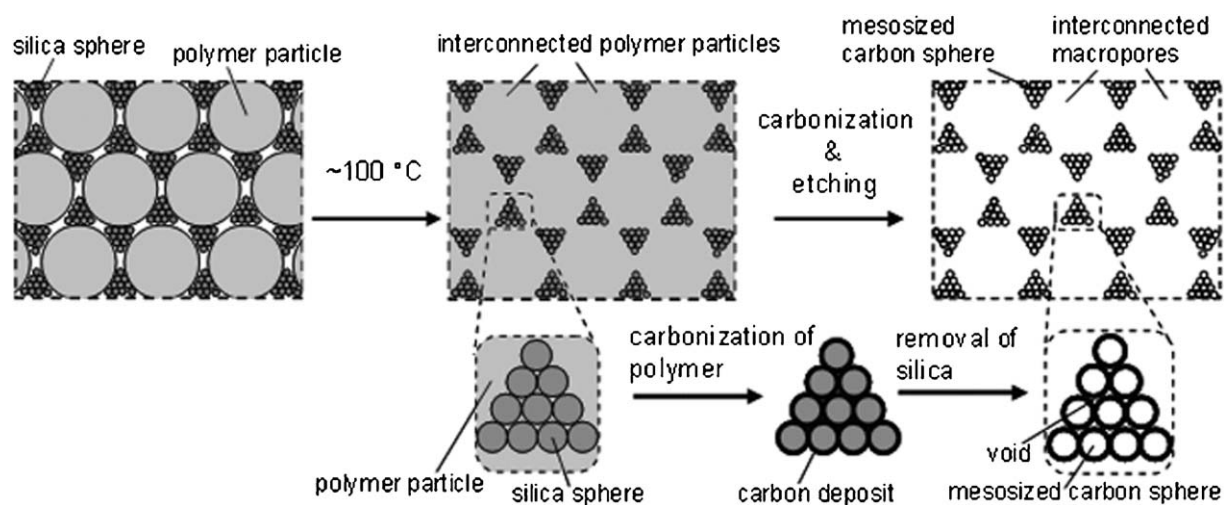


Fig. 1 Schematic illustration of synthesis of 3-D ordered porous carbon having walls composed of hollow mesosized spheres.

were carbonized at the surface of the silica. During the carbonization of the bimodal polymer–silica colloidal crystal, the removal of polymer template creates ordered macropores and simultaneously the escaping fragments of decomposing polymer deposit around silica colloids in the form a carbon layer; after removing silica colloids the uniform hollow mesosized spheres are formed (Fig. 1). TG measurement revealed that the yield of the carbonized product was *ca.* 20% for each sample (see Supplementary Information†).

Fig. 2 displays field-emission scanning electron microscope (FE-SEM, JSM-6100, JEOL) images of the prepared porous carbons. The prepared carbons have large interconnected macropores (350–390 nm). The size of large macropore was slightly smaller than a PSHEMA particle (450 nm), because shrinkage of the macropore took place during the carbonization process. The walls of the large macropores were composed of small spherical pores, which were formed by removing the silica colloids. The wall of the small spherical pore was very thin. Unfortunately, the spherical mesopores could not be observed clearly in Fig. 2c, because the pore size was in the range of 10–20 nm and difficult to observe using SEM. The degree of ordering of the large macropores increased as the size of the silica sphere decreased, because it became facile for the polymer particles to form close-packed structure in the composite as reducing the size of silica sphere. In the case of the carbon prepared from the composite of

PSHEMA-SC10 (Fig. 2c), the inverse opal structure was clearly observed. The obtained materials were, of course, disordered carbon, which was confirmed by X-ray diffraction and Raman spectroscopy (see Supplementary Information†)—a temperature of 1273 K being too low for graphitization. TG analysis of the porous carbons in air revealed less than 1% formation of residue (see Supplementary Information†), indicating that almost all the silica particles were dissolved. Therefore, the walls of mesosized spheres have some pores.

Fig. 3 shows nitrogen adsorption–desorption isotherms of the porous carbons at 77 K measured on a Micromeritics TriStar3000 adsorption analyzer. The nitrogen isotherm patterns of the porous carbons are classified as Type-IV isotherms with H2-type hysteresis (IUPAC classification).<sup>22</sup> The amount of adsorbed N<sub>2</sub> of each sample gradually increased in the region of middle  $P/P_0$  and markedly increased again in the region of high  $P/P_0$ , such as  $>0.7 P/P_0$ . This adsorption behavior can be attributed to the capillary condensation of N<sub>2</sub> in the mesopores (and/or macropores) and multilayer adsorption on the mesopores and macropores. The pore size distributions (PSD) of mesopores for the porous carbons were calculated by BJH (Barret–Joyner–Halenda) method from the adsorption branches (Fig. 4).<sup>23</sup> The porous carbon prepared from PSHEMA–CS10 composite has a peak centered at 15 nm in the PSD curve, which is in good agreement with the size of silica sphere used as the template for the mesosized

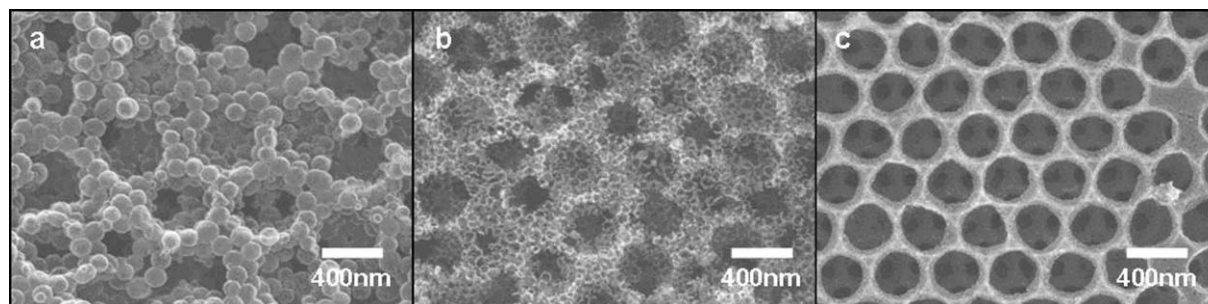
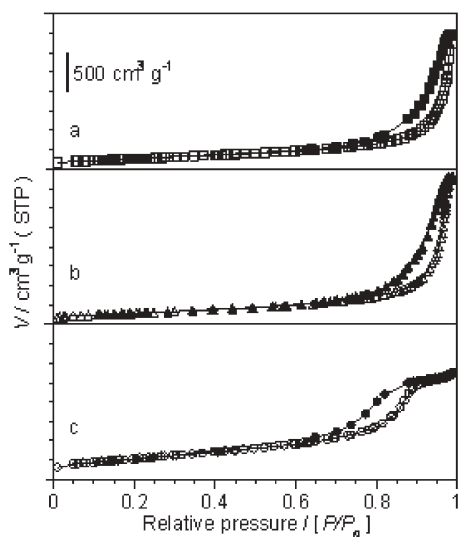
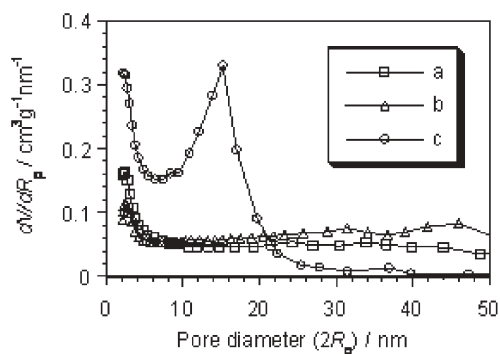


Fig. 2 FE-SEM images of the porous carbons prepared using an organized hard template consisting of large polymer colloids (450 nm diameter) and small silica colloids. The particle sizes of silica colloids used as templates of the small spherical pores were 70 ~ 100 nm (a), 40 ~ 50 nm (b), and 10 ~ 20 nm (c), respectively.



**Fig. 3** Nitrogen adsorption-desorption isotherms of the porous carbons prepared using an organized hard template consisting of large polymer colloids (450 nm diameter) and small silica colloids. The particle sizes of silica colloids used as templates of the small spherical pores were 70 ~ 100 nm (a), 40 ~ 50 nm (b), and 10 ~ 20 nm (c), respectively. The open and solid dots represent adsorption and desorption branches, respectively.



**Fig. 4** PSDs of the porous carbons calculated from the adsorption branch of the isotherms by BJH method. The particle sizes of silica colloids used as templates of the small spherical pores were 70 ~ 100 nm (a), 40 ~ 50 nm (b), and 10 ~ 20 nm (c), respectively.

carbon sphere. Two other samples have meso/macrosized carbon spheres larger than 40 nm as observed by SEM (Fig. 2), however, they showed monotonous PSD features in the whole mesopore region ( $2 \text{ nm} < 2R_p < 50 \text{ nm}$ ). It was considered that the distribution of mesopores in the wide range was due to the interstices between hollow carbon spheres. The specific surface areas of the porous carbons prepared using three kinds of colloidal silica CS100, CS50, CS10 were found to be  $492 \text{ m}^2 \text{ g}^{-1}$ ,  $523 \text{ m}^2 \text{ g}^{-1}$ , and  $974 \text{ m}^2 \text{ g}^{-1}$ , respectively, from nitrogen BET (Brunauer-Emmett-Teller) adsorption measurements. The specific surface area of the porous carbon remarkably increased with decreasing the particle size of the silica used as template of the small spherical pores.

In summary, novel 3-D ordered porous carbons were prepared in a simple way from bimodal polymer-silica colloidal crystal. The porous carbons included bimodal pores, which were large macropore and small spherical pore corresponding to the sizes of polymer and silica particles, respectively. The large macropores were interconnected and three-dimensionally ordered, and the walls of large macropores were composed of small hollow carbon spheres. The macropore size and the hollow carbon sphere size can be controlled facily by choosing the sizes of polymer and silica particles, respectively. Further efforts to fabricate multimodal porous carbons with higher specific surface area are currently underway in our group. This kind of porous carbon may be applicable to catalyst supports and electrode materials of supercapacitors.

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