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Carbons with Extremely Large Volume of Uniform Mesopores Synthesized by Carbonization of Phenolic Resin Film Formed on Colloidal Silica Template

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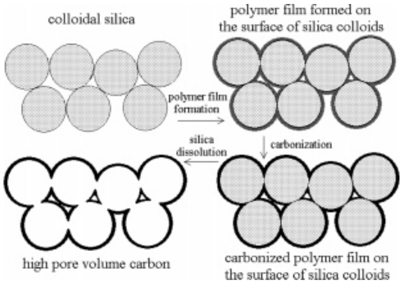
Since the pioneering work by Knox et al.[1] on the use of porous silica spheres as hard templates to prepare uniform carbon beads for chromatographic separations, mesoporous carbons have attracted a lot of attention. Especially, the idea to employ ordered mesoporous silicas (OMSs, such as MCM-41 and SBA-15)[2] as templates, instead of conventional silica particles that have disordered porosity, led to the discovery of ordered mesoporous carbons (OMCs) in 1999,[3] which turned out to be a breakthrough in the area of nanomaterials. This synthesis route involves impregnation of a silica template with a carbon precursor followed by carbonization of the resulting composite and the template removal. So far, the so-called "hard template" synthesis has been significantly developed and brought a variety of novel OMCs obtained by using different carbon precursors (see reviews[4] and references therein). Recently, the "soft template" strategy used in the synthesis of OMSs[2] was adapted to the development of OMCs;[5] this approach seems to be very promising, but further research is needed to make it feasible to tailor OMCs over a wide range of pore sizes and structures.

While the use of OMSs[2] as hard templates is advantageous because a variety of OMC structures can be created,[3,4] this approach has some disadvantages too; namely, it affords OMCs with relatively small mesopores and moderate pore volumes, which is due to a limited possibility of tailoring the thickness of pore walls in OMSs. The use of silica colloidal crystals (SCCs) and colloidal silica aggregates as hard templates eliminates the aforementioned disadvantages.[6] The availability of silica colloids over a wide range of sizes allows one to tailor the pore size of the resulting carbons over the entire range of mesopores and above as well as to design carbon materials with very large pore volumes (LPV). The former feature is especially important for applications of these carbons for adsorption, catalysis, and separations of large molecules, while the latter can be utilized for the fabrication of very light materials. Note that carbon foams and aerogels have large pore volumes (often more than 2−3 cm^3/g),[7] but their pore size distributions are broad. Also, the LPV carbons can be prepared by a nonuniform filling of silica templates with some carbon precursors to create irregular large pores due to the merge of neighboring pores after template removal;[8] however, the aforementioned methods do not permit one to control precisely the pore geometry, size, and connectivity in the resulting carbons. The formation of a uniform carbon film of the controlled thickness on the pore walls of a proper hard template is probably the only way to produce the LPV carbons with uniform pores.

Scheme 1. Illustration of the Proposed Recipe for the Synthesis of Carbons with Extremely Large Volume of Uniform Mesopores



Here we propose the synthesis of carbons with extremely large pore volume (~6 cm^3/g for 24 nm silica colloids) and narrow bimodal pore size distribution. This synthesis involves the formation of a uniform polymeric film on the silica pore walls of SCCs or colloidal aggregates and its carbonization and template removal as illustrated in Scheme 1. After proper pretreatment of the silica template and under controlled experimental conditions, the mixture of resorcinol and crotonaldehyde copolymerize on the silica surface and form a uniform film. To the best of our knowledge, this is the first report on the synthesis of mesoporous carbons that allows one to tailor the size of uniform mesopores and simultaneously to achieve an extremely large pore volume by selecting the size of silica colloids in the template and controlling the film thickness of deposited carbon.

The carbon synthesis was carried out by using aggregates of 24 nm spherical silica colloids, which were impregnated with oxalic acid (catalyst) to reach the catalyst/silica ratio of 4 wt %. The pretreated silica template was filled with a solution of resorcinol and crotonaldehyde (2-butenal) of the 1:1.2 molar ratio using an incipient wetness method. Next, the composite sample in an open container was held at a temperature of 60 °C for 0.5 h. An initial pre-polymerization was carried out at 120 °C for ~10 h and continued by further thermal treatment at 200 °C for 5 h. The resulting sample was transferred into a tube furnace for carbonization under nitrogen at 900 °C for 2 h using the heating rate of 2 °C/min. The removal of silica template was done by using diluted HF acid. The resulting carbon was rinsed with butanol and hexane and dried in a vacuum oven at 80 °C for ~10 h.

The template pretreatment with oxalic acid used as a catalyst and a temperature-controlled polymerization assured the formation of a uniform polymeric film on the silica surface. The polycondensation reaction occurs via electrophilic substitution, resulting in linking the resorcinol rings through 2-butenal bridges. In an acidic environment (oxalic acid), 2-butenal favors substitution at the para-position of resorcinol. An increase of the temperature from 120 to 200 °C was used to increase the reaction rate, decompose the organic catalyst to CO, CO_2, and H_2O, and remove those species prior to carbonization. The dissolution of silica from the silica−carbon composite caused the creation of uniform spherical pores having the diameter of the silica colloids used, which in addition to the pores reflecting unfilled space between silica colloids in the template gave a bimodal pore size distribution in the resulting carbons.

Adsorption analysis of the 24 nm colloidal silica template revealed its total pore volume of 0.2 cm^3/g, the BET surface area of 132 m^2/g, and no detectable microporosity. The pore size distribution (PSD) calculated by using the modified BJH method[9] is bimodal with the pore widths of 6.6 and 9.6 nm (Figure 1S in

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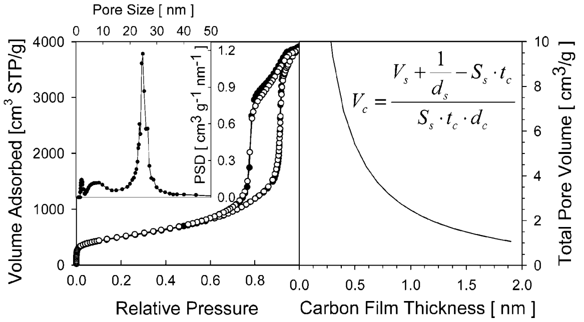

Figure 1. Nitrogen adsorption isotherms at −196 °C and the corresponding pore size distribution (left panel) and the theoretical dependence of the total pore volume on the carbon film thickness (right panel) for the mesoporous carbons synthesized by using a 24 nm colloidal silica template.

Supporting Information). The SAXS and XRD patterns for this sample (Figures 2S and 3S in Supporting Information) show one high-intensity peak and some low-intensity peaks, suggesting a partial structural ordering; however, an exact analysis of these patterns did not provide justification for assigning any specific structure. Adsorption and SAXS data indicate a dense packing of silica colloids in the template, making it suitable for the synthesis of carbon replicas.

Shown in Figure 1 (left panel) are nitrogen adsorption isotherms for two carbons obtained by using a 24 nm colloidal silica template at the same conditions. These isotherms show an extremely high nitrogen uptake (~4000 cm^3 STP/g), which corresponds to ~6.0 cm^3/g total pore volume and ~93% porosity.

The resulting carbons exhibited high specific surface area of ~1800 m^2/g and relatively low microporosity of 0.14 cm^3/g; the latter reflected by the first small peak on PSD located at ~2 nm (see inset in the left panel of Figure 1). A main feature of this PSD is the presence of two kinds of mesopores indicated by the peak maxima at 8.5 and 24.8 nm. The large spherical mesopores reflect the size and shape of the dissolved colloids (~24 nm), while the others represent unfilled space between colloids during process of the film formation; their size (~8.5 nm) is close to the average size of pores in the silica−carbon composite (Figure 1S in Supporting Information). These data indicate that the resulting LPV carbon is a faithful film-type replica of the colloidal silica template having amorphous pore walls as evidenced by the Raman spectrum shown in Supporting Information Figure 4S.

Since the total pore volume is obtained by converting the maximum amount of adsorbed nitrogen per gram of a porous material to the volume of liquid nitrogen, its value can be enlarged by increasing porosity (volumetric factor) and/or by reducing true (skeletal) density (mass factor). Thus, the total volume of pores per gram of a carbon replica can be increased by reducing the thickness of the carbon layer on the template surface and reducing the porosity of the template. This effect is illustrated in Figure 1 (right panel), which presents the theoretical dependence between the carbon pore volume (V_C) and the carbon film thickness (t_C) calculated according to the inserted expression for the 24 nm colloidal silica template under study using the surface area (S_S) and pore volume (V_S) of the template as well as the silica (d_S) and carbon (d_C) densities. This dependence starts at the point reflecting a full filling of the template, for which $V_C = \sim 1.08$ cm^3/g. The aforementioned formula (see derivation in Supporting Information) can be applied to any kind of geometry of templates and their replicas. It is very useful for the estimation of the carbon film (wall) thickness (after subtracting the volumes of micropores and secondary pores from the experimental total pore volume of the carbon studied). For the system studied, this formula predicts the carbon film thickness of ~0.5 nm, which is comparable to ~0.6 nm obtained on the basis of thermogravimetric data for the carbon−silica composites shown in Figure 5S (Supporting Information). Theoretically, one can make a carbon with much higher pore volume than 6 cm^3/g, but the mechanical strength of the carbon walls with a thickness below ~0.5 nm seems to be insufficient to support the structure.

In conclusion, this work shows that carbons with extremely large volume of uniform mesopores and narrow size distribution can be fabricated by formation of a thin carbon film on the pore walls of colloidal silica templates followed by template dissolution. Their pore volume and pore size can be tailored by selecting the carbon film thickness and the size of silica colloids used. Also, the LPV OMCs can be obtained by using SCCs as hard templates.

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Supporting Information Available: Synthesis recipe, theoretical relations, and figures with nitrogen adsorption isotherms and the corresponding PSD curves, as well as SAXS, XRD, Raman, and TGA data. This material is available free of charge via the Internet at http://pubs.acs.org.

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