Facile Synthesis of Hierarchically Porous Carbons from Dual Colloidal Crystal/Block Copolymer Template Approach

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A facile dual-templating approach is demonstrated to prepare hierarchically ordered macro-/mesoporous carbons. Monodispersed silica colloidal crystals are used as a hard template, amphiphilic triblock copolymer PEO−PPO−PEO as a soft template, and soluble resols as a carbon source. The procedure involves packing and aging of silica microspheres, evaporation-induced organic−organic assembly of mesostructures in the void of microspheres, thermosetting and carbonization of phenolic formaldehyde (PF), and removal of silica scaffolds by HF. The obtained porous carbons have a highly ordered face-centered cubic macrostructure with tunable pore sizes of 230−430 nm and interconnected windows with a size of 30−65 nm. The rigid silica hard templates can prevent the shrinkage of the mesostructure during the thermosetting and carbonization process, resulting in large cell parameters (∼18 nm) and pore sizes (∼11 nm). The bimodal porous carbon materials have large BET surface areas (up to 760 m^2/g), large pore volumes (∼1.25 cm^3/g), and partially graphitized frameworks. With the increase in the silica sphere diameter, the BET surface areas and the window sizes increase. The hierarchically ordered carbon structures show strong diffraction at wavelengths of 500−690 nm depending on the treatment used.

Introduction

Ordered porous carbons with tunable pore sizes and adjustable functionalities and pore structures are appealing for catalyst supports, biological and chemical sensors, separation and filtration, electrodes for electrochemical double layer capacitors (EDLC), fuel cells, photonic waveguides, and many other applications.[1−4] Recently, a variety of approaches have been developed for the preparation of ordered porous carbons with a wide range of pore sizes as reviewed by Ryoo and Lee *et al*.[5,6] By using zeolites as hard templates, they synthesized ordered microporous carbons with uniform pores smaller than 1 nm using various carbon sources via infiltration and chemical vapor deposition (CVD).[7−10] Ordered mesoporous carbons with different pore sizes (usually less than 5 nm) and structures have been successfully synthesized via a nanocasting approach by using various ordered mesoporous silicas as hard templates.[11−14] More recently, an approach based on the organic−organic assembly between amphiphilic block copolymers and phenolic resin precursors has been developed for direct templating synthesis of ordered mesoporous carbons with various pore structures. Block copolymers containing hydrophilic blocks of poly(ethylene oxide) (PEO) or poly(4-vinylpyridine) (P4VP) can be employed as templates.[15−21] By using

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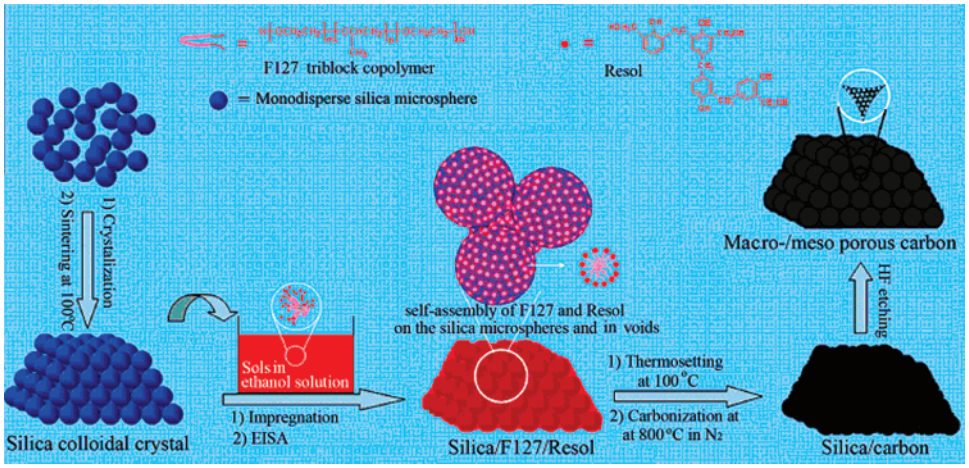
Scheme 1. Synthesis Scheme Used for the Preparation of the Ordered Macro-/Mesoporous Carbons Using Monodisperse Silica Colloidal Crystals and Triblock Copolymer F127 as Dual Templates and Phenolic Resols as Sol Precursors



colloidal crystals of polystyrene (PS) polymers or silica microspheres as templates, researchers have successfully synthesized ordered macroporous carbons with three-dimensional (3-D) faced-centered cubic (fcc) packing. Using the sintered colloidal crystals of silica spheres as templates, Zakhidov *et al*. fabricated 3D ordered macroporous glassy carbon and graphitized carbon through infiltration with phenolic resin and CVD of propylene gas, respectively.[21] Up to now, various approaches, including the infiltration, CVD, and plasma-enhanced CVD methods, have been employed to synthesize ordered macroporous carbon using colloidal crystals of silica or polymer spheres.[23−25] Because the size of the colloidal microspheres is on the order of submicrometers or micrometers, the macropore size is tunable from hundreds of nanometers to several micrometers.

In the past few years, hierarchically ordered porous carbons, especially those possessing well-defined macropores and interconnected meso- and/or micropores, have attracted much attention because they combine the excellent performance of mass transport from macropores and the advantages of high surface areas from micro-/mesopores.[26] This research interest is aroused by the universal existence of hierarchically ordered pore structures in nature (*e.g.*, diatoms, lumbar vertebra, and lungs), which offer efficient transport of fluids and gases.[27] Although it is well-known that the main biophysicochemical processes are principally controlled at a molecular scale, the easy accessibility of cells, small capillaries, or the building blocks, *i.e.*, an efficient link between micro- and macrostructures, is equally important.[28] Similarly, for applications in electrodes, catalysis, and photovoltaic cells, the hierarchically porous carbons with ramified structures can provide better accessibility and chemical activities. So far, great success has been achieved in the synthesis of hierarchically ordered materials with macropore and mesopore walls by using colloidal microspheres and surfactants.[27−37] However, the synthesis is mainly successful in silicate components.[27−33] Although various strategies such as impregnation and nanocasting of mesoporous silica or silica monolith hard templates were explored,[38−45] hierarchically ordered porous carbons have rarely been obtained. Recently, Stein and co-workers[46] prepared ordered bimodal porous carbon structures with

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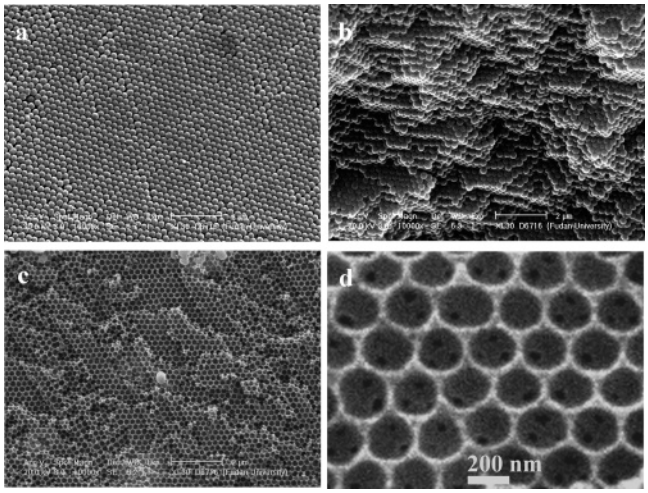

Figure 1. SEM images of (a) as-fabricated silica colloidal crystals, (b) silica colloidal crystals after impregnation with resol/F127 solution and further thermosetting treatment, (c) the ordered macro-/mesoporous carbons after the removal of silica microspheres, and (d) image of (c) with larger magnification. These samples were prepared on the basis of 240 nm silica microspheres.

macropores of 200−400 nm and mesopores of 2.8 nm by a multistep templating method. The procedure involves (a) the preparation of three-dimensional (3D) ordered macro-/mesoporous silicas (3DOM/mSiO_2) by the infiltration of poly(methyl methacrylate) (PMMA) colloidal crystals with a sol of nonionic oligomer surfactant (Brij56, $C_{16}H_{33}EO_{10}$) and silicate precursor of tetramethyl orthosilicate (TMOS); (b) the removal of surfactants and PMMA microspheres by calcination; (c) using the obtained 3DOM/mSiO_2 as a hard template again, phenol resin precursors are used as a carbon source to impregnate the hard template; and (d) pyrolysis of the composite sample and subsequent removal of the silica scaffolds by hydrofluoric acid (HF). However, the procedure is very painstaking and time-consuming. Furthermore, because of the replication from mesoporous silica, the mesopores of the obtained carbon materials are too small in size, which may limit their practical applications involving larger molecules, such as protein enrichment and virus separation.

The successful synthesis of highly ordered carbons via an organic−organic self-assembly approach[15−21] provides us with the possibility of fabricating hierarchically ordered porous carbon structures by combining the surfactant-templating organic resol self-assembly with a colloidal-crystal templating approach. In this paper, we report, for the first time, an approach for the direct synthesis of ordered macro-/mesoporous carbons by using a facile dual-templating approach. Silica colloidal crystals are used as a hard template for the generation of ordered fcc macropore arrays and amphiphilic triblock copolymer PEO_{127}−PPO_{70}−PEO_{127} (Pluronic F127) as a soft template for the mesoporosity. This simple approach allows the organic−organic self-assembly of phenolic resins and triblock copolymers in the confined voids of silica colloidal crystals. The obtained porous carbons have small interconnected windows, large mesopores, high surface areas, and large pore volume.

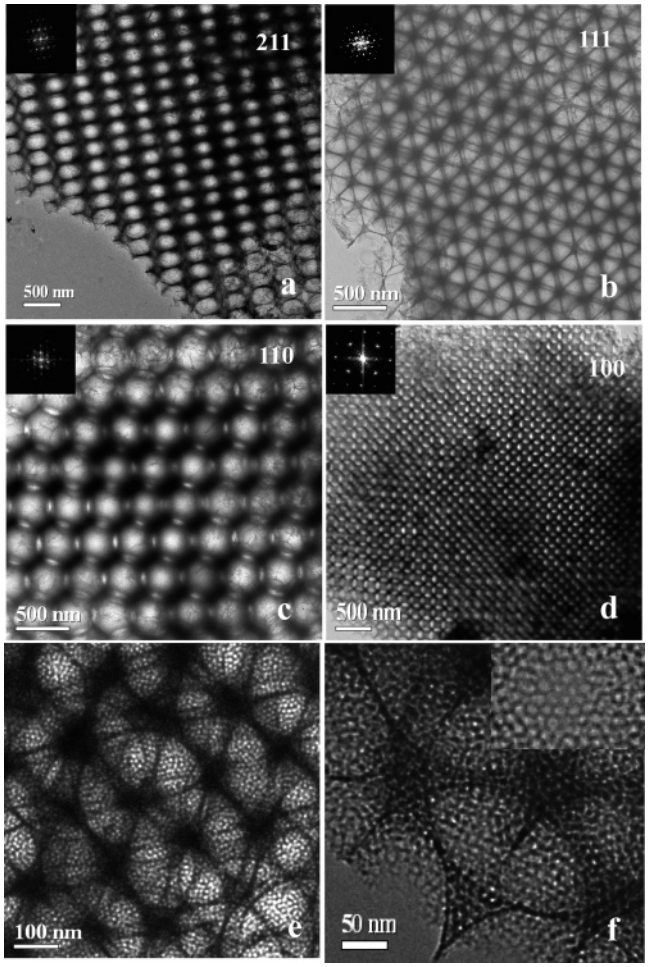

Figure 2. TEM images of ordered macro-/mesoporous carbons with macropore arrays viewed from (a) (211), (b) (111), (c) (110), and (d) (100) planes, respectively. (e ,f) High-magnification TEM images, showing the carbon mesostructure.

Experimental Section

(1) Chemicals. Tetraethyl orthosilicate (TEOS), ethanol, aqueous ammonia (28 wt %), phenol, formalin solution (37 wt %), NaOH, and HCl were analytical reagents and purchased from Shanghai Chemical Company. All chemicals were used as received without further purification. Deionized water was used in all experiments.

(2) Fabrication of Silica Colloidal Crystals. Monodisperse silica microspheres with different diameters (240, 320, and 450 nm) were synthesized according to Stöber's method.[47] All of the spheres were uniform in size with deviations of less than 5%. To obtain high-quality silica colloidal crystals, we first washed the as-made silica microspheres with six cycles of centrifugation/redispersion using 5.0 mL of an ethanol/water mixture (50/50 volume ratio). The purified silica microspheres were then redispersed in an ethanol/water mixture (50/50 volume ratio) and allowed to sediment to form colloidal crystals. After sedimentation at 25 °C for 4 days, the colorful colloidal silica crystal monoliths were formed at the bottom of the container. After the supernatant was removed by careful pumping, the remaining solvent was further evaporated for 12 h at 25 °C and the monoliths were then heated at 100 °C for 24 h for further use.

(3) Preparation of Hierarchically Ordered Porous Carbons. The hierarchically ordered porous carbons were prepared through a dual-templating approach by impregnation of an ethanol solution

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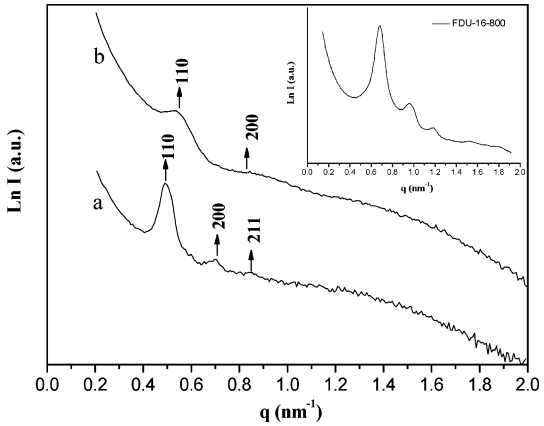

Figure 3. SAXS patterns of (a) the silica/PF/F127 composites obtained by impregnating colloidal crystals of silica microspheres (240 nm in diameter) and further thermosetting, (b) the ordered macro-/mesoporous carbons by further pyrolysis and removal of silica microspheres. The insert is the SAXS pattern of mesoporous carbon FDU-16-800.

of resols and F127. For a typical procedure, 1.0 g of colloidal crystal monoliths of 240 nm silica microspheres was immersed in 5.0 g of a homogeneous ethanol solution containing 1.0 g of resol and 0.5 g of triblock copolymer F127. After impregnation for 24 h at 25 °C, the impregnated composite monoliths were carefully taken out to evaporate ethanol at 25 °C for 12 h, followed by further heating at 100 °C for 24 h. The resulting silica/PF/F127 composites were then pyrolyzed in N_2 at 800 °C for 4 h at a heating rate of 1 °C/min below 450 °C and 5 °C/min above 600 °C. During this process, triblock copolymer F127 was removed. The obtained silica/carbon composites were treated with HF solution (10 wt %) to remove silica, followed by washing with deionized water and drying in a vacuum to give hierarchically ordered porous carbons.

(4) Characterization and Measurements. Scanning electron microscopy (SEM) images were recorded on a Philips XL30 electron microscope (Netherlands) operating at 20 kV. A thin gold film was sputtered on the sample before characterization. Transmission electron microscopy (TEM) images were taken with a JEOL 2011 microscope (Japan) operating at 200 kV. For the TEM measurements, the samples were dispersed in ethanol and then dried on a holey carbon film Cu grid. Small-angle X-ray scattering (SAXS) measurements were taken on a Nanostar U small-angle X-ray scattering system (Bruker, Germany) using Cu Kα radiation (40 kV, 35 mA). The *d*-spacing values were calculated by the formula $d = 2\pi/q$. Nitrogen sorption isotherms were measured at 77 K with a Micromeritics Tristar 3000 analyzer (USA). Before measurements, the samples were degassed in a vacuum at 200 °C for at least 6 h. The Brunauer−Emmett−Teller (BET) method was utilized to calculate the specific surface areas. By using the BJH model, the pore volumes and pore size distributions were derived from the adsorption branches of isotherms, and the total pore volumes (V_t) were estimated from the adsorbed amount at a relative pressure P/P_0 of 0.992. Raman spectra were obtained with a Dilor LabRam-1B microscopic Raman spectrometer (France), using a He−Ne laser with an excitation wavelength of 632.8 nm. The reflection spectra were taken with the light propagating along the normal to the (111) plane by using a Shimadzu UV-31000 spectrophotometer. The photographs were taken with an Olympus BX51 microscope.

Results and Discussion

The hierarchically ordered macro-/mesoporous carbons can be synthesized by the simple dual-template approach combining colloidal hard templating with the solvent-evaporation-induced surfactant assembly (EISA) process. Three-dimensional ordered silica colloidal crystals are used as hard templates, amphiphilic triblock copolymer F127 as a soft template, and soluble phenolic resin (resols) as the carbon source (Scheme 1). First, monodisperse silica microspheres prepared according to Stöber method[44] are packed into a 3D fcc colloidal crystal array by sedimentation followed by heating at 100 °C. A sol containing triblock copolymer F127 and phenolic resol precursors in ethanol solution is then soaked into the voids of the colloidal silica monoliths, and the organic−organic self-assembly of the resins and triblock copolymer F127 occurs during the evaporation of ethanol, resulting in the formation of the ordered mesostructure in the interstitial voids. Further heating at 100 °C for thermosetting of phenolic formaldehyde (PF) results in the formation of silica/PF/F127 composites. Subsequently, the composites are subjected to pyrolysis in nitrogen at 800 °C, during which the triblock copolymer F127 was decomposited and the phenolic resin framework was carbonized,[16a,16b,17a] leading to silica/carbon composites. Finally, hierarchically ordered porous carbons are obtained after the removal of the silica spheres by HF solution.

SEM images show that the silica microspheres have a uniform size with a deviation less than 5%, and the resulting colloidal crystals possess a typically ordered hexagonal array on the top of the monoliths, corresponding to the 111 plane of an fcc structure (Figure 1a). The cross-section SEM images further reveal the 100 plane, confirming an fcc ordered macrostructure. After impregnation with the sol solution of resol precursors and F127, and further thermosetting treatment, the interstitial voids were fully filled and the borderlines silica spheres became indistinct, indicative of the presidence of phenolic resin/F127 composite on the silica spheres (Figure 1b). The SEM image also reveals that the 3D ordered macrostructure of the colloidal crystals is well retained after the impregnation and thermosetting treatment. After further pyrolysis and the removal of silica microspheres, the highly ordered macropores can be clearly observed in the SEM images (Figure 1c), indicating that the ordered macrostructure of silica colloidal crystals is faithfully replicated. The 3D interconnection of the ordered macropore arrays is verified by the arrangement of the macropore windows as shown in the SEM image with high magnification (Figure 1d). The window size of the macropores estimated from SEM images is about 30 nm. It is worth noting that the heating treatment of the colloidal silica crystals at 100 °C is necessary and plays a critical role for successful preparation of hierarchically ordered porous carbon structures. Our results show that, without the treatment, the macropore arrays could collapse after impregnation and carbonization. It suggests that the heating treatment can make the silica microspheres arrays rigid, which prevents the collapse of the macrostructure. Furthermore, it offers the basis for the formation of interconnected windows of macropores by increasing the contact area between neighboring silica microspheres.

TEM images (Figure 2) show the hierarchical pore feature of the obtained porous carbons by the dual-templating approach. The highly periodic ordering morphologies of the

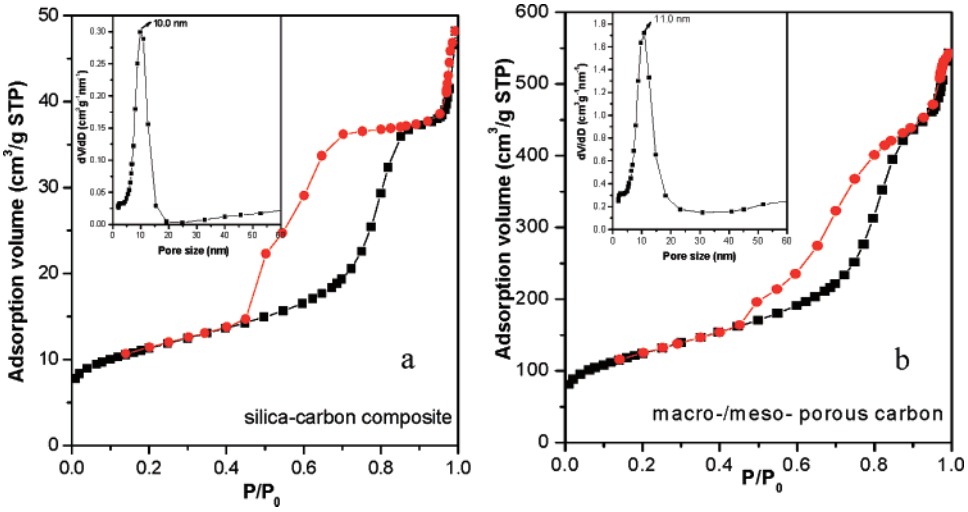

Figure 4. N_2 sorption isotherms and pore size distribution (inset) of (a) silica/carbon composite monoliths and the ordered macro-/mesoporous carbon templated from 240 nm silica microspheres and triblock copolymer F127.

Table 1. Textual Parameters of the Silica/Carbon Composite and Hierarchically Ordered Porous Carbons

sample	macropore size (nm)[a]	macropore window size (nm)[a]	mesopore size (nm)[b]	BET surface area ($m^2\,g^{-1}$)	total pore volume ($cm^3\,g^{-1}$)	*t*-plot ($cm^3\,g^{-1}$)
silica−carbon composite[c]			10.0	40	0.075	0.049
PC-240[d]	234	30	11.0	441	0.84	0.035
PC-320[e]	312	47	12.4	566	1.25	0.043
PC-450[f]	438	65	12.5	763	0.96	0.087

[a] Roughly determined from TEM images. [b] Determined from the adsorption branch on the basis of the BJH model. [c] Templated by 240 nm silica microspheres [d] Where PC represents porous carbon, templated by 240 nm silica microspheres [e] Templated by 320 nm silica microspheres [f] Templated by 450 nm silica microspheres.

macropores and the corresponding Fourier diffractogram further confirm the fcc macrostructure, suggesting the successful replication of colloidal crystal structures (Figure 2a−d). The diameter of the macropores measured from TEM images is about 234 nm, suggesting a small shrinkage (7.3%).

The SAXS pattern of silica/PF/F127 composites shows three resolved diffraction peaks with *q*-values of 0.49, 0.70, and 0.85 nm^{-1} (Figure 3a), corresponding to 110, 200, and 211 reflections of cubic mesostructure with space group of $Im\bar{3}m$. It suggests that an ordered resin mesostructure can be formed within the voids of the silica colloidal crystals. The cell parameter (a_0) is calculated to be 18.1 nm. After carbonization at 800 °C and removal of the silica microspheres, the SAXS pattern of the obtained porous carbon products shows two broad diffraction peaks, suggesting that the cubic ordered mesostructure is retained in small domains. The calculated cell parameter is 16.3 nm, reflecting a minor shrinkage (9.9%) (Figure 3b), in agreement with the TEM observations. Compared with conventional mesoporous carbon FDU-16 prepared with the same F127 template, the mesoporous carbons obtained in the confined voids of silica microspheres possess larger cell parameters.[16] This is due to the rigid silica microspheres functioning as supports to prevent the structure from shrinking.

The large mesopores with a uniform diameter of about 10.5 nm are clearly visible in the TEM image with large magnification (Figure 2f, inset). Because the carbonaceous polymer mesopore frameworks are formed at the spherical surface of the silica microspheres and the limited space of the interstices in the colloidal crystals, many short stripelike patterns can be observed, indicative of the short-range ordering of the mesopore arrays in agreement with the results from SAXS. This phenomenon implies the spherical packing of soft template F127 on the spherical surface during the EISA process (images e and f of Figure 2). The cell parameter estimated from TEM images is about 17.0 nm, which is consistent with the value from the SAXS data.

Nitrogen adsorption−desorption isotherms of the silica/carbon composite monoliths obtained by the pyrolysis of PF/F127/silica composites show representative type IV curves with a pronounced hysteresis at high relative pressure of 0.45−0.85, indicating a narrow mesopore opening (Figure 4a). The sharp capillary condensation at a relative pressure of 0.75−0.83 is clearly observed, suggesting a uniform large mesopore. The pore size calculated from the adsorption branch by the BJH model is 10.0 nm (Figure 4a, inset). The uptake at high relative pressure ($P/P_0 = 0.95-1.00$) suggests the presence of macropores. It may arise from incomplete filling of the precursor within the interstitial spaces of the silica colloidal crystals. The silica/carbon composite monolith possesses BET surface areas as low as 40 m^2/g and a total pore volume of about 0.075 cm^3/g (Table 1). After the removal of silica microspheres by HF etching, the resultant porous carbon monoliths show quasi-type IV isotherms with a sharp adsorption branch similar with that of the silica/carbon composite. An abnormal hysteresis is observed, suggesting the presence of some blocked mesopores or irregular pore windows (Figure 4b). This may be due to the irregular tangency between spherical mesopores and silica microspheres, which results in nonuniform window sizes. The mesopore size (mean value of 11.0 nm) calculated from the adsorption branch is a little larger than that of silica/

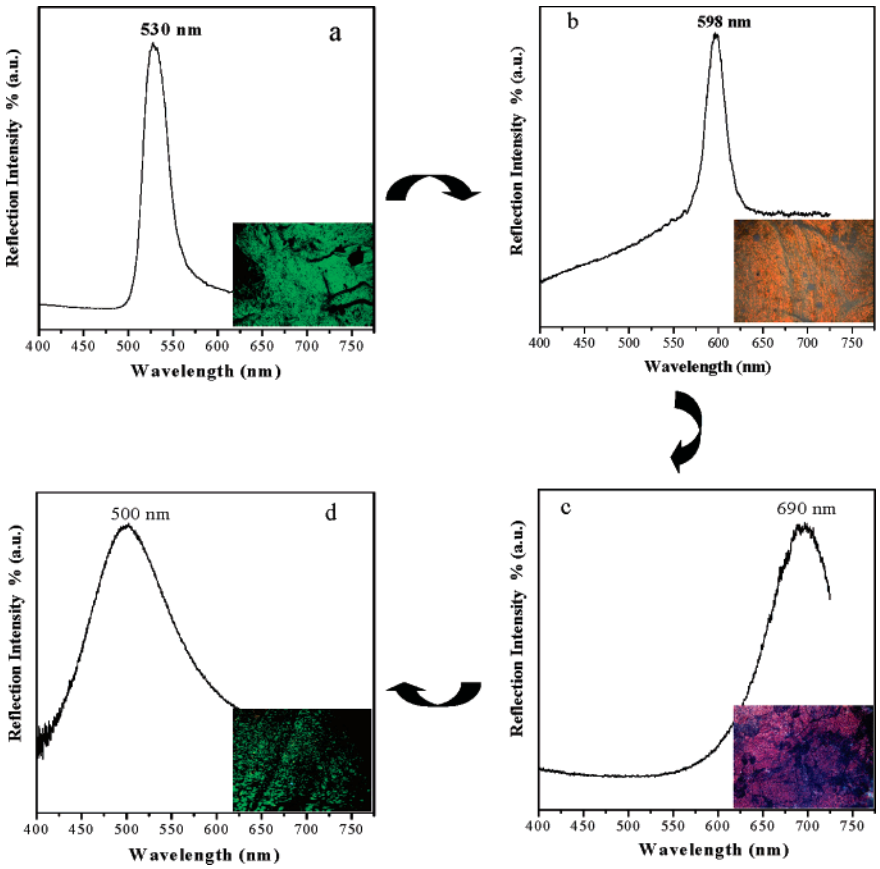

Figure 5. Reflection spectra of (a) as-made colloidal crystals of 240 nm silica microspheres, (b) silica/PF/F127 composites obtained by thermosetting treatment of the impregnated colloidal crystals, (c) silica/carbon composites obtained by further carbonization at 800 °C in N_2, and (d) ordered macro-/mesoporous carbons obtained after HF etching. The insets are the photographs taken by an optical microscope in reflection mode.

carbon composite monoliths (Figure 4b inset), probably because of the pore opening after the silica spheres are removed. Remarkably, the obtained porous carbon monoliths possess a BET surface area of 441 cm^2/g and a total pore volume of 0.84 cm^3/g, both 10 times larger than the corresponding values for the silica/carbon composite monoliths. These results imply that the carbons account for less than 10 wt % in the carbon/silica composites because of limited space for loading the resol/F127 precursor with a large molecule size.

The macropore size can be varied by tuning the diameter size of the silica microspheres. By using silica colloidal crystals with large diameters of 320 and 450 nm (see the Supporting Information, Figure S1), hierarchically ordered porous carbon materials with large macropore (312−438 nm) and ordered mesopores (∼12 nm) can be readily obtained (see the Supporting Information, Figure S2). The obtained macro-/mesoporous carbon materials exhibit similar nitrogen sorption isotherms (see the Supporting Information, Figure S3), but they possess larger BET surface areas (566 and 766 m^2/g, respectively) and total pore volumes (1.25 and 0.96 cm^3/g, respectively). It is mainly contributed by the increased microporosity due to favorable organization of the mesostructure and phenolic frameworks in large voids of the silica colloidal crystals (Table 1). Additionally, the window sizes of the macropores as determinated from SEM images also increase to 47 and 65 nm, respectively (see the Supporting Information, Figure S2).

The reflection spectra (Figure 5) show intense Bragg diffractions at the range of 500−690 nm, further confirming that the ordered macrostructures are retained during the whole process, including impregnation, carbonization, and HF etching. It also reveals that the photonic bands vary by different treatments. The silica colloidal crystals packed by the simple sedimentation method show a narrow diffraction peak (λ_{min}) at 530 nm (Figure 5a). After impregnation of carbonaceous species into the voids, the diffractions dramatically red-shift to 590 and 690 nm, respectively (panels b and c in Figure 5), which is predominantly caused by the increase of the effective refraction index (n_{eff}) because the voids are occupied with phenolic polymers and carbons, respectively.[22] Conversely, after etching of the silica microspheres, the n_{eff} value decreases, resulting in a large blue shift of the Bragg reflection to 500 nm (Figure 5d). It should be noted that the diffraction peaks become broadened after the carbonization and removal of silica, suggesting that the regularity of the macrostructures becomes poor. Meanwhile, the colors of the obtained samples observed under an optical microscope also changed from green to yellow, to violet red, and to green (insets in Figure 5), in good agreement with the wavelength of their corresponding diffraction peaks.

The Raman spectrum of the obtained bimodal porous carbon materials shows a strong G band at 1585 cm^{-1} and D band at 1345 cm^{-1} (Figure 6). Considering the fact that the G band is associated with graphitic sp^2 carbon struc-

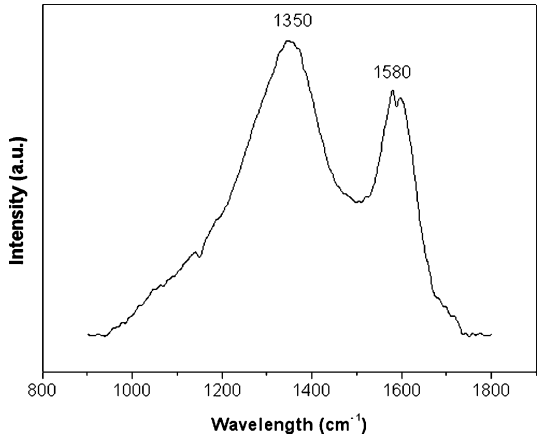

Figure 6. Raman spectrum of the ordered macro-/mesoporous carbons obtained after carbonization at 800 °C in N_2 and the removal of silica microspheres (240 nm), showing D band at 1350 cm^{-1} and G band at 1580 cm^{-1} with an intensity ratio of 1.2.

tures,[22,48] the comparable intensities of the G and D bands (intensity ratio ∼1.2) suggest that the obtained carbon materials are partially composed of graphites.

Conclusions

Hierarchically ordered macro-/mesoporous carbons were synthesized via a facile dual-templating approach using colloidal silica crystals and triblock copolymers PEO−PPO−PEO as templates and soluble resols as the carbon source. The obtained porous carbons have a highly ordered fcc macrostructure with tunable pore sizes of 230−430 nm and 3D interconnected windows with sizes of 30−65 nm. The mesostructures can be assembled by organic−organic assembly of phenolic resols and PEO−PPO−PEO copolymer, showing the regularity in small domains. The rigid silica spheres can prevent the shrinkage of the mesostructure during the thermosetting and carbonization procedure, resulting in large cell parameters (∼18 nm) and pore sizes (∼11 nm). Our results show that the bimodal porous carbon materials have large BET surface area (up to 760 m^2/g) and large pore volumes (∼1.25 cm^3/g), with partially graphitized frameworks. With the increase in the silica sphere diameter, the interconnected window sizes and the BET surface areas also increase. The hierarchically ordered carbon structures show a photonic band gap at 500−690 nm dependent on the treatments. Because of their unique porosities, the hierarchically porous carbons would have great potential for application as catalysts, controlled release materials, selective enrichment materials, adsorbents, optical waveguide, and so on.

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Supporting Information Available: Various SEM and TEM images and N_2 sorption isotherms and pore size distributions. This material is available free of charge via the Internet at http://pubs.acs.org.

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