Tricomponent Coassembly Approach To Synthesize Ordered Mesoporous Carbon/Silica Nanocomposites and Their Derivative Mesoporous Silicas with Dual Porosities

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ABSTRACT: Highly ordered mesoporous carbon/silica nanocomposites and dual-mesoporous silicas with a 3D cubic structure were successfully synthesized through a facile tricomponent coassembly approach by using the lab-made diblock copolymer poly(ethylene oxide)-b-polystyrene as a template. The mesoporous silicas exhibit a high surface area and uniform bimodal mesopores. The bimodal mesopores can be tuned by simply changing the ratio of carbon/silica precursors and the pyrolysis temperature in N2. Gold nanoparticles were successfully loaded in the primary large mesopores for use as a heterogeneous nanacatalyst, which exhibits excellent performance in the epoxidation of styrene, demonstrating their potential for catalyst support.

INTRODUCTION

Ordered mesoporous materials have received increasing attention over recent decades because of their outstanding physicochemical properties (e.g., high surface area, large porosity, and abundant framework compositions), and as a result, they have potential for applications in diverse fields, including energy storage and conversion,1-5 adsorbents,6-8 catalyst supports,9-11 and hydrogen storage.12 By using commercially available amphiphilic poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) (PEO-b-PPO-b-PEO) triblock copolymers as templates, many ordered mesoporous silicas, including SBA-15,13 SBA-16,14 FDU-5,15 FDU-12,16 and KIT-6,17 have been successfully synthesized. Although these materials possess high surface areas, the pore sizes are generally less than 10 nm, which greatly limits their use in applications involving large guest objects. Recently, many efforts have been focused on the synthesis of ordered mesoporous materials with large accessible pores (>15 nm),18 As is well-known, the pore size is mainly determined by the volume of the hydrophobic segments of the template molecules. Therefore, block copolymers with long hydrophobic chains, such as poly(isoprene)-b-poly(ethylene oxide) (PEO-b-PI),19-21 poly(ethylene oxide)-b-poly (methyl methacrylate) (PEO-b-PMMA),22-24 poly-(ethylene-co-butylene)-b-poly-(ethylene oxide) (KLE),25 and poly(ethylene oxide)-b-poly-styrene (PEO-b-PS),26-31 have been designed to produce large-pore mesoporous materials. For example, Yu and co-workers reported the synthesis of ordered mesoporous silicas with large unit-cell parameters using PEO100-b-PS215 as a template.26-28 Unfortunately, the large pores were closed; thus, they could not be accessed and used effectively. Our research group has synthesized large-pore ordered mesoporous silicas via an effective hydrothermal recrystallization method.29 This method can result in large pores that are open, but the connectivity of the pores is poor, and the window size is still small (<5.0 nm), which is unfavorable for their use in practical applications involving large-molecule transportation. An effective approach to improve the pore connection is to create secondary mesopores, forming a bimodal pore structure. Bimodal mesoporous materials are generally synthesized using two templates of different molecular weights in conventional methods. However, in most cases, dual-mesoporous materials with well-defined pore arrangements and tunable pore sizes could not be synthesized because of the difficulty in controlling the assembly process in the dual-templating system. The two template molecules tend to form either mixed micelles or separated macroscopic phases.35,32 More recently, Liu et al. have reported an approach to synthesize ordered mesoporous materials with a bimodal pore structure using resols as a polymer precursor, tetraethoxysilane (TEOS) as a silica precursor, and triblock copolymer Pluronic F127 as a template through a one-step multicomponent coassembly approach.33

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Herein, we report the facile synthesis of ordered mesoporous carbon/silica nanocomposites with a 3D cubic structure and dual-mesoporous silicas through a tricomponent coassembly approach using the lab-made poly(ethylene oxide)-b-polystyrene (PEO-b-PS) diblock copolymer as the template and resols and tetraethyl orthosilicate (TEOS) as carbon and silica precursors, respectively (Scheme 1). The as-synthesized ordered mesoporous carbon/silica nanocomposites possess a face-centered cubic (fcc) close-packed mesostructure, large pore size (~23 nm), and thick pore wall (~16 nm). To the best of our knowledge, mesoporous carbon/silica nanocomposites with 3D mesostructure have not been reported. By selectively removing the carbon component in the carbon/silica nanocomposites, a secondary mesoporosity (2.3–6.9 nm) can be readily created in the silica pore walls, resulting in mesoporous silicas exhibiting a high surface area (~680 m^2 g^-1) and bimodal pore sizes. These properties can enhance interaction with adsorbants and reduce transport limitation, which are highly desirable for applications in catalysis, sensing, and drug delivery.\(^{34-37}\) Gold nanoparticles were successfully loaded in the primary large mesopores for use as a heterogeneous nanocatalyst, which exhibits excellent performance in the epoxidation of styrene with a high conversion (97.8%) and selectivity (89.4%) toward styrene oxide because of the good accessibility of the mesopores with incorporated well-dispersed Au nanoparticles.

**EXPERIMENTAL SECTION**

**Synthesis of Dual-Mesoporous Silicas.** In a typical synthesis of the mesoporous carbon/silica composites, a THF solution of the lab-made amphiphilic diblock copolymer PEO-b-PS (2 wt %, 5.0 g) was mixed with a 0.2 M HCl solution (0.5 g), and the mixture was stirred for 30 min at room temperature. Then, resol (20 wt %, 2.0 g) and tetraethyl orthosilicate (TEOS) (1.0 g) in a THF solution were added sequentially. After stirring for 2 h, the mixture was transferred into Petri dishes to evaporate THF at room temperature for 8 h followed by further heating in an oven at 100 °C for 24 h. The as-made product was scraped and crushed into a powder. Pyrolysis was carried out in a vacuum oven at 40 °C to burn out the carbon composition, and heated at 82 °C for 30 min, 8 mL of ethanol was added to precipitate the Au(en)_2Cl_3 reaction solution (about 20 μL) into a modified N2 for 30 min with magnetic stirring at room temperature. After adding 10.0 g (76 mmol) of n-butyl hydroperoxide (70 wt % in water), the reaction vessel was immersed in an oil bath and heated at 82 °C. During the reaction process, a minor amount of reaction solution (about 20 μL) was carefully withdrawn at different time intervals for gas chromatography–mass spectrometer (GC–MS) measurements.

**Characterization and Measurements.** \(^{1}H\) NMR spectra were recorded at 25 °C on a DMX 500 MHz spectrometer (Bruker, Germany) with tetramethylsilane as the internal standard and CDCl_3 as the solvent. Gel-permeation chromatography (GPC) was performed on an Agilent 1100 GPC system with a refractive index detector. The GPC system was calibrated with monodispersed polystyrene standards. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA-SDTA851 analyzer (Switzerland) from 30 to 900 °C under air with a heating rate of 5 °C min^-1. Small-angle X-ray scattering (SAXS) measurements were taken on a NanoStar U small-angle X-ray scattering system (Bruker, Germany) using Cu Ka radiation (40 kV, 35 mA). The d-spacing values were calculated by the formula d = 2π/λ = d_{1/2} = 2 − D, where d represents the cell parameter and D is the pore diameter calculated from the N_2 sorption measurements. Nitrogen sorption isotherms were measured at 77 K with a Micromeritics Tristar 3020 analyzer. Before measurements, the samples were degassed in a vacuum at 180 °C for at least 6 h. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area. Using the Barrett–Joyner–Halenda (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 0.995. The calibration curve was obtained using carbon black (part no. 004-16833-00) as the reference material and nitrogen as the adsorption gas. Transmission electron microscopy (TEM) experiments were conducted on a JEOL 1201 microscope (Japan) operated at 200 kV. Field-emission scanning electron microscopy (FESEM) images were collected on a Hitachi Model S-4800 field-emission scanning electron microscope. The dried samples were used directly for observation without any treatment.

**RESULTS AND DISCUSSION**

The amphiphilic PEO-b-PS diblock copolymer was synthesized by using the atom-transfer radical polymerization (ATRP) method, which involved two steps: (i) the preparation of macroinitiator (PEO-Br) by reacting PEO(S000) with 2-bromoisobutylbromide and (ii) the polymerization with a styrene monomer (Figure S3A). The M_n values of the resultant PEO-Br and PEO-b-PS were calculated from \(^1H\) NMR to be about 5300 and 33 300 g mol^-1, respectively (Figure S3B,C). Therefore, the composition of the diblock copolymer can be approximately formulated as PEO_117-b-PS_270. GPC of the diblock copolymer PEO_117-b-PS_270 shows a polydispersity index (PDI) of 1.18, indicating a narrow molecular-weight distribution.

Mesoporous carbon/silica nanocomposites were prepared through an EISA method using diblock copolymer PEO_117-b-PS_270 as the template, THF as the solvent, resols and TEOS as the carbon and silica precursors, respectively. By adjusting the initial mass ratios of TEOS to resol, several carbon/silica nanocomposites with different carbon and silica mass ratios were obtained. SAXS patterns (Figure 1) of the mesoporous carbon/silica nanocomposites obtained after pyrolysis at 600 °C show several scattering peaks, which can be indexed to the 111, 311, and 440 reflections of the ordered fcc mesostructure with the space
group $Fm\bar{3}m$. The scattering peaks shift to low $q$ values with increasing silica content. The $d$-spacing values of the first-order peaks ($q_d$) of samples MCS-2, MCS-26, MCS-42, MCS-55, and MCS-77 were calculated as 25.9, 28.9, 30.8, 31.7, and 34.3 nm, respectively, and the corresponding unit-cell parameters are 44.9, 50.1, 53.3, 54.9, and 59.4 nm. These results clearly indicate that the presence of silica content can effectively lead to a low framework shrinkage. Representative TEM images (Figure 2a–d) of the MCS-55 sample clearly reveal The FESEM image of the MCS-55 sample (Figure 2j) further demonstrates the ordered mesostructures with a pore size of $\sim 23$ nm in a large domain.

$N_2$ sorption isotherms of samples MCS-2, MCS-26, MCS-42, MCS-55, and MCS-77 show representative type IV curves with a sharp capillary condensation step in the relative pressure range of $P/P_0 = 0.85-0.90$ (Figure 3A), suggesting the existence of uniform mesopores with a large pore size. Very large $H_2$-type hysteresis loops with delayed capillary evaporation can be observed at a relative pressure of $P/P_0 \sim 0.5$, implying caged mesopores with a window size smaller than 5.0 nm. The sample with a low silica content of 26 wt % (MCS-26) has a large pore size of $\sim 23.6$ nm, a high BET surface area of $\sim 426$ m$^2$ g$^{-1}$, and a pore wall thickness of 11.8 nm, respectively. However, the BET surface area of the sample with a high silica content of 77 wt % (MCS-77) decreases to 192 m$^2$ g$^{-1}$, and the pore wall thickness increases to 19.2 nm. The higher silica content in the carbon/silica nanocomposites leads to a lower BET surface area, a smaller pore size, and a thicker pore wall (Table 1). Silicate oligomers and resols can interact with the long EO chain of the template, forming a thick pore wall during the pyrolysis. During the pyrolysis in $N_2$, the PS segments of the PEO-$b$-PS templates could be carbonized in pores and converted into amorphous carbon. Notably, the adsorption–desorption isotherms of the MCS-55 and MCS-77 samples are not close at a low relative pressure, which may be attributed to the organic polymer materials. Therefore, as the silica content increases, the pore size becomes smaller and the pore wall becomes thicker. The higher silica content in the carbon/silica nanocomposites leads to a lower BET surface area. This is reasonable because silica has a higher density than carbon and because the pore wall becomes thicker with the increase of the silica content.

Further removal of the carbon component results in the formation of the ordered mesoporous silicas with bimodal pore sizes, suggesting that the carbon species in the composites exist in the form of nanoparticles. The SAXS pattern (Figure 4b) of the MS-55 sample after burning out the carbon component in air at 550 °C exhibits three resolved scattering peaks, suggesting that the cubic mesostructure is well-retained. TEM images further confirm that the mesoporous silica MS-55 possesses ordered mesostructures over large domains viewed from the [110], [211], and [411] directions (Figure 2e–h). Numerous wormlike small pores can be clearly observed in the silica pore walls (Figure 2f). The uniform and regular mesopores can be further seen from the FESEM image (Figure 2k). The pore
The BET surface area and the total pore volume of mesoporous carbon MS-55 is 492 and 0.42 cm$^3$ g$^{-1}$, respectively. The BET surface area of the carbon/silica composite MCS-55 is 367 m$^2$ g$^{-1}$, and the total pore volume is 0.27 cm$^3$ g$^{-1}$, which is larger than that of the carbon/silica composite with different textural properties. This suggests that secondary pore sizes and surface areas of the silicas can be tuned by changing the mass ratio of resols and TEOS.

In addition, the secondary pores size can be tuned by changing the temperature of pyrolysis in N$_2$. The as-prepared MS-55 sample is first annealed in N$_2$ at different temperatures (0, 300, 400, 500, 600, and 800 °C) and then the carbon is burned out at 550 °C in air, giving rise to several silica samples with different textural properties (Table S1). The obtained mesoporous silicas are denoted MS-$y$, where $y$ is the annealed temperature in N$_2$. The N$_2$ sorption isotherms of the MS-$y$ samples ($y = 0, 300, 400, 500$, and 600) show representational type-IV curves with two capillary condensation steps and a H$_2$-type hysteresis loop, implying large and uniform spherical pores (Figure 4C). However, the N$_2$ sorption isotherms of the MS-42-800 sample show type-IV curves and a deformed H$_2$-type hysteresis loop, implying irregular pores that are probably caused by asymmetric shrinkage of resols and silicates at a high pyrolysis temperature (Figure 4C). The secondary pore size can be changed from 2.3 to 5.3 nm, and the surface area increases with elevating calcination temperature in N$_2$. This phenomenon may be related to further cross-linking and dehydrogenation of the resol species during the pyrolysis in N$_2$, thus forming numerous nanosized carbon domains in the silica walls. When the carbon components are removed, numerous secondary pores in the silica walls can be generated.

On the basis of these results, we propose a tricomponent coassembly process for the formation of 3D ordered mesoporous carbon/silica nanocomposites and bimodal mesoporous silica with tailorable large pore sizes (Scheme 1). First, the diblock copolymer PEO-b-PS template, resols, and TEOS can be well-dissolved in an acidic THF/H$_2$O solution. Simultaneously, TEOS is hydrolyzed by acid catalysis to yield silicate oligomers. Along with the evaporation of THF solvent at room temperature, the diblock copolymer PEO-b-PS template, resols, and TEOS can associate with abundant -OH groups can associate with the PEO domains, forming large spherical composite core—shell micelles. With the continuous evaporation of THF, the large spherical composite micelles can coassemble and pack into nanostructured composites in a fcc-packing manner because it is stable from the viewpoint of thermodynamics (Scheme 1, step 1). Upon thermosetting treatment at 100 °C, the resin precursors can be further polymerized, forming a 3D network structure with a benzene ring as three- or four-linking sites. The abundant hydroxyl groups can interact with the PEO domains and silicate oligomers. As previously reported, only...
Scheme 1. Formation Process of 3D Ordered Mesoporous Carbon/Silica Nanocomposites and the Corresponding Bimodal Mesoporous Silica

"Steps of the process are as follows: (1) formation of spherical composite core–shell micelles with a core of hydrophobic PS blocks and a shell of PEO segments decorated by resols and silicate oligomers through hydrogen-bonding interactions, (2) formation of the PEO-b-PS/resol/silica nanocomposites by thermosetting processing at 100 °C, (3) formation of carbon/silica nanocomposites by heat treatment at 600 °C in N₂ to partially decompose the PEO-b-PS templates and carbonize the resols, and (4) formation of the dual-mesoporous silica by further calcination at 550 °C in air to remove the amorphous carbon derived from the PS and resols.

weak hydrogen-bonding interaction occurs between silicate and carbon species, but no Si–C bonds are formed in nanocomposites. Therefore, the resol precursors form nanosized resin polymers in the nanocomposites during the thermosetting process. Meanwhile, the silicate oligomers not only assemble with the diblock copolymers but also condense and cross-link together to form the 3D framework. The cooperative process gives rise to a PEO-b-PS/resol/silica nanocomposite with ordered mesostructure, and the ordered mesopore is solidified through thermosetting (Scheme 1, step 2). After subsequent pyrolysis in N₂, the carbon/silica nanocomposites with a fcc mesostructure can be obtained (Scheme 1, step 3). Upon pyrolysis in N₂, the PEO-b-PS templates can be partially decomposed inside the pore cages, leaving uniform mesopores and amorphous carbon lining the inner walls of the carbon/silica nanocomposites. Meanwhile, the resols undergo further cross-linking and carbonization, resulting in numerous nanosized carbon domains interpenetrated with silica networks (Scheme 1, step 3). During further treatment at 550 °C in air, the amorphous carbon derived from the PS and resols can be removed. The obtained silica walls become thinner, the main mesopore size becomes larger, and another set of pores in the silica walls can be generated, thus leading to a kind of dual-mesoporous silica material (Scheme 1, step 4).

To evaluate the performance of the obtained dual-mesoporous silica materials for application in catalysis, Au nanoparticles were successfully loaded in the MS-55 sample using the in situ reduction method. The Au/MS-55 sample obtained after the Au nanoparticles are loaded retains the ordered mesostructure, as indicated by TEM images (Figure S6A). Au nanoparticles with a mean diameter of 5.0 nm are mainly located in the large mesopores and are highly dispersed in the silica matrixes (Figure S6A). The Au nanoparticles are confined in the large primary mesopores, and they can be accessible for guest molecules through the secondary mesopores in the walls. For comparison, using the same method, Au nanoparticles were loaded in FDU-18 and SBA-15. The Au nanoparticles in FDU-18 and SBA-15 have a larger diameter and lower dispersity (Figure S6B,C). Au/MS-55, Au/FDU-18, and Au/SBA-15 were utilized as catalysts for the oxidation of styrene using tert-butylhydroperoxide (TBHP) as an oxidant. In the Au/MS-55 catalyst system, the conversion of styrene increases rapidly with the extension of the reaction time and reaches 97.8% after 11 h. For Au/FDU-18 and Au/SBA-15, the conversion is ~61.7 and 48.1%, respectively (Figure S5A). The catalytic performance of Au/MS-55 is much better than that of the Au/FDU-18 and Au/SBA-15 samples. The catalytic selectivity of epoxidation for the Au/MS-55 sample reaches about 94.3% after a reaction time of 5 h and then decreases slightly as the time is prolonged owing to the isomerization of styrene oxide or overoxidation; however, the selectivity of epoxidation is still as high as 82.4% after a reaction time of 32 h (Figure S5B). Au/SBA-15 shows comparable catalytic selectivity in the early stage of the reaction, but the selectivity decreases rapidly after 11 h, which might be attributed to the smaller and cylindric mesopore of SBA-15. The 2D hexagonal mesopore structure is not favorable for molecular diffusion, which can lead to isomerization of styrene oxide or overoxidation.

In a comprehensive evaluation of both conversion and selectivity, the Au/MS-55 sample displays a high conversion (97.8%) and selectivity (89.4%) after reaction for 11 h. These results clearly indicate that the Au/MS-55 sample has higher catalytic activity and selectivity than Au/FDU-18 and Au/SBA-15 under the same conditions as a result of its unique dual-mesoporous structure and because of the better accessibility of the mesopores with incorporated well-dispersed Au nanoparticles. Note that the performance of the Au/MS-55 sample is better than that of most of the heterogeneous catalysts reported previously. Therefore, it can be concluded that the dual-mesoporous structure is favorable for catalysis because of its improved mass transport.

CONCLUSIONS

Highly ordered mesoporous carbon/silica nanocomposites and dual-mesoporous silica with a 3D cubic structure have been successfully synthesized through a facile tricomponent coassembly approach using the lab-made diblock copolymer PEO-b-PS as a template and resol and TEOS as carbon and silica precursors, respectively. The mesoporous silicas exhibit a high surface area (~680 m² g⁻¹) and uniform bimodal mesopores. The bimodal mesopores can be tuned (2.3–6.9 and 21.4–27.9 nm) by simply changing the ratio of the carbon/silica precursors and the pyrolysis temperature in N₂. To the...
best of our knowledge, this is the first time that mesoporous silica with a controlled pore size in the walls has been reported. By deposition of nanosized Au nanoparticles in the ordered mesoporous silica MS-55 via an in situ reduction method, the obtained Au/MS-55 catalyst exhibited an excellent performance in the epoxidation of styrene with a high conversion (97.8%) and selectivity (89.4%) because of the good accessibility of the mesopores with incorporated well-dispersed Au nanoparticles. In addition, it is expected that the tricomponent coassembly approach could be extended to synthesize various metal oxides (e.g., WO_3, SnO_2, Nb_2O_5) with high surface areas and dual porosity, which could be useful in applications of catalysis, adsorption, separation, sensing, and lithium batteries.

ASSOCIATED CONTENT

1 Supporting Information

Additional methods; TG curves of the mesostructured carbon/silica composites with different silica content after being calcined at 600 °C in N_2; N_2 adsorption−desorption isotherms and the corresponding pore-size distribution curves of FDU-18 and SBA-15; synthetic route for the PEO-b-PS diblock copolymer; 'H NMR spectra of PEO-Br and PEO-b-PS; SAXS patterns of the mesoporous silicas; N_2 adsorption−desorption isotherms and the corresponding pore-size distribution curves of the mesoporous carbon/silica composite MCS-77 and ordered mesoporous silica MS-77; TEM images of Au/MS-55, Au/FDU-18, and Au/SBA-15; and textural properties of the bimodal mesoporous materials. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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