Synthesis of Carbon Nanofoams and Nanospheres by Varying Ratio of Phenol–Formaldehyde Resin to Mesoporous Silica Foams

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Carbon nanofoams and nanospheres of 25–30 nm were conveniently synthesized by using silica nanofoams as a template and commercial-grade phenol–formaldehyde resin as carbon source at different weight ratio of PF resin to silica template.

Mesoporous carbons with high surface area, large porosity, and fine electric conductivity have been regarded as an advanced material for many potential applications in nanotechnology.[1] On the concern of the diffusion restriction, the monomer carbon sources (e.g. sucrose, furfuryl alcohol, phenol–aldehyde mixture, acrylonitrile, etc.) have been typically performed to prepare the mesoporous carbons modeled with the porous silica-based templates.[1–5] However, these monomers basically require polymerization-catalysts to generate a rigid polymer structure. Thus, a complicated incorporation of the reactive sites (i.e. aluminum oxide) onto the mesoporous silica templates or addition of strong acids (i.e. H_2SO_4) in the reaction mixture is still essentially required. Up to now, an efficient synthetic method to prepare the mesoporous carbons in different forms is desired.

Based on the supramolecular chemistry, guest molecules with multiple attachments (i.e. chelates) to a host can result in a great interaction energy and hence a stable guest–host complex.[6] Accordingly, the polymers and proteins with the interaction-matching functional groups (i.e. –OH, –NH, –CO, and cationic groups) toward the SiOH or SiO^- group can be strongly adsorbed on the silica surface.[7] As having many $-CH_2OH$ groups in the phenol–formaldehyde (PF) oligomers, the commercially-available PF resins widely used as carbon source for mass-production of carbon fibers in industry are reasonably supposed to be tightly adsorbed on the silica surface or even into the mesoporous silica nanochannels larger than the chain-width of the PF oligomers.[8,9] Therefore, the commercial-grade PF resins could be used as a very cheap carbon source to obtain the mesoporous carbons when using the mesoporous silica of proper pore size as nanotemplates. Moreover, the thermal-setting PF polymers can mutually crosslink into a rigid polymer structure to cast the mesostructure of the solid silica template via a simple heat-treatment.[10] This advantage can avoid an extra addition or post-introducing of the polymerization-initiators for the monomer carbon sources.

From this concept, in this study, we used a simple impregnation procedure to allow the PF oligomers to be adsorbed into the silica nanofoams with a window size around 15 nm.[11] Because of the strong interaction between silica surface and PF resin and the large pore size, the PF oligomers could be coated on or fully filled in the silica foams, depending on the weight ratio of the PF resin to mesoporous silica template. And then, the carbon nanofoams, carbon nanospheres and a mixture of carbon nanofoams and nanospheres have been feasibly prepared after a high-temperature pyrolysis under nitrogen atmosphere.

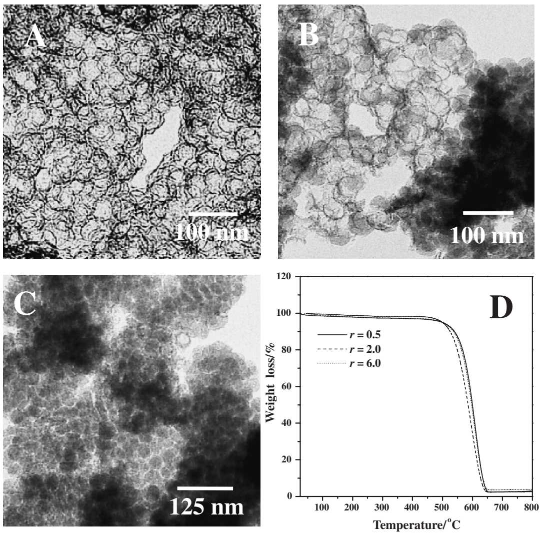

Figure 1. The TEM images (A–C) and the TGA (D) profiles of the mesoporous carbons prepared with different r value. (A) Carbon nanofoams at $r = 0.5$; (B) A mixture of carbon nanofoams and nanospheres at $r = 2.0$; (C) Carbon nanospheres at $r = 6.0$. D. TGA plots taken in air flow of $50\,cm^3\,min^{-1}$ at heating rate of $10\,^\circ C\,min^{-1}$.

The silica nanofoams template was synthesized as reported previously.[11] Typically, 2.0 g tri-block copolymer $EO_{20}PO_{70}EO_{20}$ (Pluronic P123) and 2.0–4.0-g toluene were dissolved in 75–100 mL of a 1.6 M HCl aq solution at 40 °C. After a 12 h-stirring, a cloudy solution was formed. Then, that solution was combined with 4.4–5.0 g tetraethyl orthosilicate and the resulting mixture was allowed to react at 40 °C for 6 h. Finally, that gel solution sealed in an autoclave was kept statically at 100 °C for 24 h. The filtered precipitate was dried in air. The as-synthesized silicas were calcined at 560 °C for 6 h in air to remove the surfactant. The calcined silica nanofoams have surface area of $280\,m^2\,g^{-1}$, pore volume of $1.60\,cm^3\,g^{-1}$, and pore size of around 35.0 nm.

The synthetic procedures of carbon nanofoams and nanospheres were as followed: (0.5–6.0) g PF resin in a resole type (phenol/formaldehyde = 0.9–0.8; PF650, ca. 96000 in molecular weight, Chang-Chun Plastics, Taiwan) was dissolved in 50.0 g ethanol (95 wt %) to form a low-viscosity solution, and then 1.0 g mesoporous silica nanofoams was added into that PF resin ethanol solution. The resulting mixture was opened to allow a slow evaporation of solvent under stirring for about 12 h. The resulting gel was kept at 100 °C for 1–2 days to let a completely cross-linking reaction between the PF oligomers. After that, the dried PF-resin containing mesoporous silica nanofoams was heated at a rate of $20\,^\circ C\,min^{-1}$ and carbonized at 900 °C for 2.0 h under nitrogen atmosphere. Finally, the silica template was removed by HF (6.0 wt %) etching. Filtrating, washing, and drying gave the carbon products.

Figures 1A–1C show the representative transmission electron microscope (TEM) images of the carbons obtained with different weight ratios (denoted as r) of PF resin/mesoporous silica foams. At $r = 0.5$, one can clearly found the nanofoams with the diameter of about 30 nm (Figure 1A). When the r value was increased to 2.0, a mixture of carbon nanospheres and nanofoams was formed (Figure 1B). As the PF resin content was raised to $r = 6.0$, the carbons are almost in sphere-shape with the diameter of around 25 nm (Figure 1C). To analyze the thermal stability of the PF-resin made carbon nanofoams and spheres, the thermogravimetric analysis in an air flow ($50\,\mathrm{cm^3\,min^{-1}}$) was commonly performed. The TGA weight-change profiles of the carbon nanospheres and nanofoams exhibit a sharp weight-loss in a temperature range of 550 to 650 °C (Figure 1D). The remaining weight percent at temperature above 650 °C is less than 4.0 wt %, confirming that the silica residue is low after HF-etching. Elemental analysis of the PF-resin-made mesoporous carbons gave C/H molar ratio of about 50.0. Analyzing the TGA profiles of the PF-resin containing silica nanofoams before and after pyrolysis, the conversion percentage of the PF-resin to carbon is about 85%. Consequently, a high carbonization and carbon conversion could be achieved by using the PF-resin as the carbon source.

To obtain the physical properties of the PF-made mesoporous carbons, the N_2 adsorption–desorption isotherms of the carbon samples with various r values were examined (Figure 2A). It is clear that the carbon nanofoams (i.e. at $r = 0.5$) possess two capillary condensations occurring at P/P_0 of about 0.8 and at P/P_0 around 0.95.[2] In parallel to the TEM observations, the nanofoams essentially have bimodal mesoporosity. The smaller pore is generated by the removal of the silica framework, and the larger pore results from the hollow interior of the nanofoams. Furthermore, as the r value increases, all carbon samples still exhibit the apparent capillary adsorption at P/P_0 of 0.80, but the adsorption amount of the capillary condensation at P/P_0 around 0.95 gradually decreases. At r close to 6.0, only a capillary condensation at P/P_0 of 0.80 was remained. These results reveal that the PF resin was preferred to be adsorbed on the silica wall of the mesoporous silica foams at low r value, and then the void space was progressively filled as increasing the added amount of PF-resin. Thus, one can reasonably expect that the fraction of the nanospheres increase with the r value. Because of the dense interior of the carbon spheres, the increase of the amount of nanospheres rationally leads to a decrease in surface area (i.e. unit: $\mathrm{m^2\,g^{-1}}$) and pore volume of the carbon samples (Figure 2B). While, the surface area of these carbon samples was controlled at high value of $520\text{–}700\,\mathrm{m^2\,g^{-1}}$. With examinations on the t-plot of these samples, all mesoporous carbon samples almost have the same microporous volume ($\approx 0.12\text{–}0.14\,\mathrm{cm^3\,g^{-1}}$) and surface area ($\approx 250\text{–}280\,\mathrm{m^2\,g^{-1}}$). Consequently, we provided a new synthetic method to conveniently prepare the mesoporous carbons of different forms, high pore volume and bi- and tri-modal porosity.

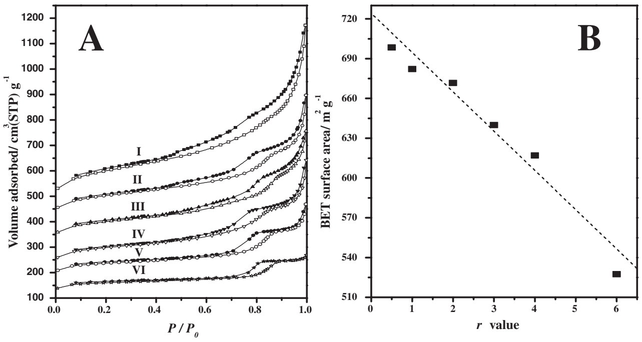

Figure 2. (A) The N_2 adsorption–desorption isotherms of the mesoporous silica synthesized with different r value. (B) A plot of surface area of mesoporous carbons vs r value. I. $r = 0.5$; II. $r = 1.0$; III. $r = 2.0$; IV. $r = 3.0$; V. $r = 4.0$; IV. $r = 6.0$. The II–IV isotherms were vertically shifted with the values of 100, 200, 300, 400, and $500\,\mathrm{cm^3\,g^{-1}}$, respectively.

Here, we attempt to explain the reasons for the formation of nanofoams and nanospheres. Being different from the microporous templates (e.g. zeolite with pore size less than 1.0 nm),[12] the mesoporous silica nanofoams possess the large pore size that allows feasible entrance of the larger molecules such as the PF oligomers as well as the monomers. Moreover, the ethanol solution of the PF-resin and silica foams is slight alkaline (pH ≈ 8.0), in which the silica surface is negatively charged (i.e., the existence of $\mathrm{Si\text{–}O^-}$ groups). Because a strong hydrogen-bonding interaction matching occurs between the $\mathrm{Si\text{–}O^-}$ (hydrogen-bonding acceptor) and the $\mathrm{–CH_2OH}$ groups (hydrogen-bonding donor) of the PF oligomers, the PF oligomers with multiple chelates, thus, thermodynamically favored to be adsorbed onto the silica wall at low r value, instead of self-aggregation. When the PF-resin content increases, the pore-filling procedure was gradually occurred until the hollow space of the silica foams was fully filled. For the monomer carbon sources, a complicated synthetic procedure was essentially needed to achieve a strong polymer structure.[1–5] In contrast, the PF oligomers only required a simple heat treatment to form the rigid polymer structure that could replicate entirely the nanostructure of the solid template, and the nanofoams-like structure was preserved even after a high-temperature pyrolysis. This simple synthetic method would open a new route to mass production of the mesoporous carbons with the desired pore volume and structure.

In conclusion, the commercial-grade PF resins have been directly utilized as carbon source to synthesize the carbon nanofoams and nanospheres with the silica foams. Both the surface area and pore volume of the carbon nanofoams and nanospheres are large enough to serve as high-capacity adsorbents and catalyst support of high electric conductivity.[13] This simple and efficient PF resin-replication method would be widely extended to prepare the mesoporous carbons and carbon tubes by using other mesoporous silica templates with the pore size allowing the access of the PF oligomers. Since various forms and mesostructures of the silica templates have been provided, the mesostructure and morphologies of the prepared mesoporous carbons could be tuned to match the applications in nanotechnologies.[14]

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