

Highly Dispersible Molecular Sieve Carbon Nanoparticles

Jin Liu,^{†,‡} Huanting Wang,^{*,†} and Lixiong Zhang[§]

Department of Chemistry, The University of Hong Kong, Hong Kong, China, Department of Materials Science and Engineering, Anhui Institute of Architecture and Industry, Anhui 230022, China, and Department of Chemical Engineering, Nanjing University of Technology, Nanjing 210009, China

Received April 25, 2004

Revised Manuscript Received July 11, 2004

Molecular sieve carbons (MSCs or carbon molecular sieves) are a class of microporous, amorphous high-carbon materials, and they share with zeolites the ability to distinguish molecules on the basis of size and shape. MSCs have been studied as gas-selective adsorbents¹ and membranes for various gas separations involving air separation and natural gas purification,^{2–4} and for membrane reactors.⁵ Very recently, MSC micro-sized particles have been incorporated into a polymer matrix to improve separation selectivity of a polymeric membrane, and the so-called mixed-matrix membrane can be very promising for commercial gas separations.⁶ Many other applications can be found for microporous carbon such as in lithium batteries and fuel cells.^{7,8} To improve adsorption–desorption efficiency of existing MSCs, and open new applications such as for developing practical MSC–polymer nanocomposite membranes,⁹ MSC nanoparticles are highly desirable.

Although several techniques^{10–15} such as chemical vapor deposition, arc discharge, glow discharge, ultrasonic treatment, and explosion have been developed to fabricate nanometer-sized carbon spheres in gas or

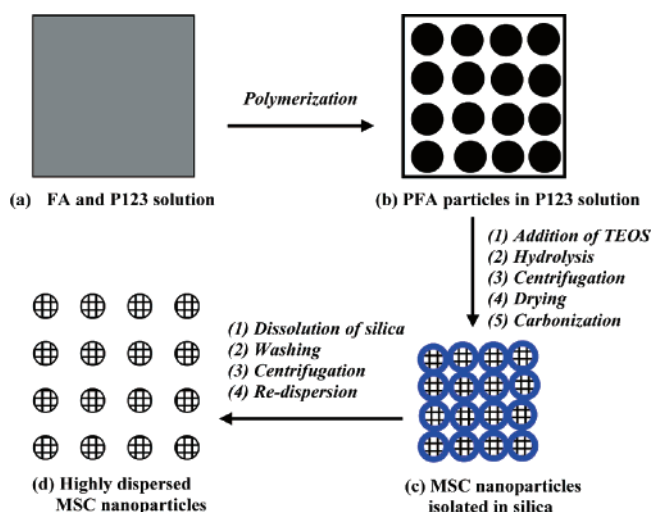


Figure 1. Schematic synthesis procedure for highly dispersible MSC nanoparticles.

liquid phase, they may not be suitable for preparation of MSC nanoparticles because MSCs with well-defined micropores are usually prepared by controlled pyrolysis of solid organic precursors such as pitch-like materials or rigid and cross-linked polymers.¹⁶ In addition, precursor nanoparticles tend to aggregate during drying and subsequent carbonization at high temperature; the dispersibility of microporous carbon nanospheres has not been fully examined up to now.¹⁰ The studies on nanosized molecular size carbons have been very limited so far.

In this communication, we report a novel approach to the synthesis of MSC nanoparticles that can be readily dispersed in various solvents. Poly(furfuryl alcohol) (PFA) is chosen as a precursor of MSC nanoparticles because it has been widely used to make MSCs and other nanostructured carbons.^{2–4,17} An amphiphilic triblock copolymer, P123 [(EO)₂₀(PO)₇₀(EO)₂₀], is used to control formation of PFA particles in the course of polymerization of furfuryl alcohol (FA).³

The synthesis procedure of highly dispersible MSC nanoparticles is illustrated in Figure 1. Typically, 3 g of furfuryl alcohol (FA, 98%, Lancaster), 3 g of P123-[(EO)₂₀(PO)₇₀(EO)₂₀] (M_n ca. 5800, Aldrich), 1.4 g of hydrochloric acid (36.0–38.0%, Uni-Chem), deionized water, and ethanol (absolute GR, Merck) are mixed in a 45-mL capped polypropylene bottle with a magnetic stirrer under rigorous agitation at room temperature to form a homogeneous solution (Figure 1a). The cationic polymerization of FA is conducted at 30–40 °C for 1–2 days under continuous agitation, followed by heating at 60–70 °C overnight to complete polymerization under catalysis of HCl acid.¹⁷ As the polycondensation reaction of FA proceeds, PFA chains pack together and produce particles suspending in the continuous phase of P123 solution due to decrease in hydrophilicity of PFA chains while the transparent homogeneous solution turns dark brown. The resultant PFA suspension obtained is cooled

* To whom correspondence should be addressed. Present address: Australian Key Center for Microscopy and Microanalysis, Electron Microscope Unit, The University of Sydney, Sydney, NSW2006, Australia. Tel: + 61 2 9351 7552. Fax: +61 2 9351 7682. E-mail: huanting.wang@emu.usyd.edu.au.

[†] The University of Hong Kong.

[‡] Anhui Institute of Architecture and Industry.

[§] Nanjing University of Technology.

(1) Shirley, A. I.; Lemcoff, N. O. *Adsorption* **2002**, *8*, 147.

(2) Foley, H. C. *Microporous Mater.* **1995**, *4*, 407.

(3) Wang, H. T.; Zhang, L. X.; Gavalas, G. R. *J. Membr. Sci.* **2000**, *177*, 25.

(4) Shiflett, M. B.; Foley, H. C. *Science* **1999**, *285*, 1902.

(5) Itoh, N.; Haraya, K. *Catal. Today* **2000**, *56*, 103.

(6) Vu, D. Q.; Koros, W. J.; Miller, S. J. *J. Membr. Sci.* **2003**, *211*, 311.

(7) Wang, Q.; Li, H.; Chen, L. Q.; Huang, X. J. *Solid State Ionics* **2002**, *152–153*, 43.

(8) Yazaydin, A. O.; Eroglu, I.; Han, E.; Turker, L. *Chem. Eng. Commun.* **2003**, *190*, 976.

(9) Wang, H. T.; Holmberg, B. A.; Yan, Y. S. *J. Mater. Chem.* **2002**, *12*, 3640. Wang, H. T.; Holmberg, B. A.; Yan, Y. S. *J. Am. Chem. Soc.* **2003**, *125*, 9928.

(10) Lee, S. I.; Yoon, S. H.; Park, C. W.; Korai, Y.; Mochida, I. *Carbon* **2002**, *411*, 1645.

(11) Sano, N.; Wang, H.; Alexandrou, I.; Chhowalla, M.; Teo, K. B. K.; Amarantunga, G. A. J.; Iimura, K. *J. Appl. Phys.* **2002**, *92*, 2783.

(12) Romeoa, M.; Arnault, J. C.; Ehret, G.; Banhart, F.; Le Normanda, F. *Ultramicroscopy* **2002**, *92*, 209.

(13) Serp, P.; Feurer, R.; Kalck, P.; Kihn, Y.; Faria, J. F.; Figueiredo, J. L. *Carbon* **2001**, *39*, 615.

(14) Wang, Z. X.; Yu, L. P.; Zhang, W.; Zhu, Z. Y.; He, G. W.; Chen, Y.; Hu, G. *Phys. Lett. A* **2003**, *307*, 249.

(15) Wu, W. Z.; Zhu, Z. P.; Liu, Z. Y. *Carbon* **2002**, *40*, 2021.

(16) Inagaki, M.; Radovic, L. R. *Carbon* **2002**, *40*, 2279.

(17) Muller, H.; Rehak, P.; Jager, C.; Hartmann, J.; Meyer, N.; Spange, S. *Adv. Mater.* **2000**, *12*, 1671.

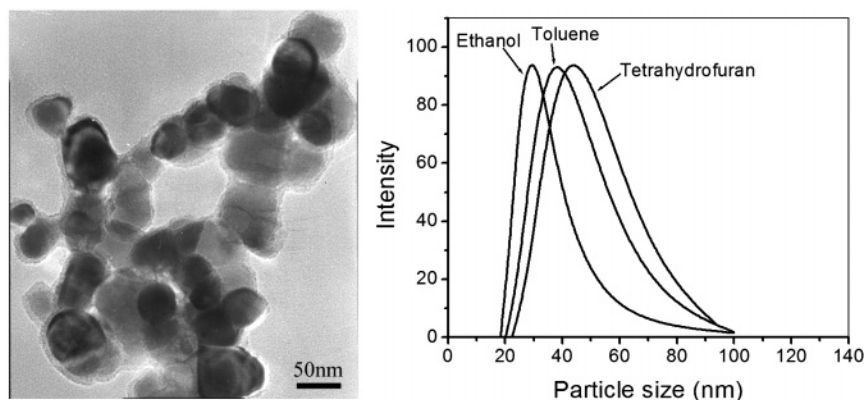


Figure 2. TEM image (left) and particle size distribution (right) of MSC nanoparticles.

to room temperature. Because P123 nonionic surfactant molecules naturally adsorb on PFA particle surfaces, the colloidal suspension is stabilized (Figure 1b). It is noted that the ratio of FA to P123 has a significant influence on the particle size of PFA produced. When the weight ratio of FA to P123 is 70:30 or 30:70, the system gives microsized PFA particles. However, when the ratio of P123 to FA reached ca. 50:50, nanosized PFA particles were produced (see Supporting Information Figure S-1). As a result, the weight ratio of FA to P123 of 50:50 is used through this study.

Initially, the PFA nanoparticles are dried from the suspension, and then they are carbonized, but the resulting MSC nanoparticles irreversibly aggregate. Only micrometer-sized carbon aggregates can be obtained after grinding (see Figures S-1 and S-2). This can be explained by the fact that the as-synthesized PFA surfaces are still chemically active. When the solvent evaporates, the PFA particles come into contact, and the surface active groups react and further cross-link with one another. The reaction rate increases with the temperature, and the polymerization and cross-linking of PFA takes place at up to 200 °C.³ To avoid the PFA particle aggregation through drying and carbonization, a temporary barrier technique¹⁸ is applied to the present system, and silica serves as a temporary barrier since it can be easily removed by using HF or NaOH solution. A solution of 3–6 g of tetraethyl orthosilicate (TEOS, Aldrich) in 10–20 g of ethanol is added into the PFA suspension and heated under stirring at 50–60 °C for 7–10 h allowing for hydrolysis of TEOS under acidic condition. It is anticipated that individual dense PFA nanoparticles are coated by silica because the silica sol formed is well compatible with P123 and PFA surface.¹⁷ The PFA nanoparticles covered with silica gel are retrieved by centrifugation. After the nanoparticles are completely dried at 100 °C overnight, a dark brown solid composite is obtained. The dried solid composite is carbonized by heating at a rate of 1 °C/min, keeping at 200 °C for 2 h, and finally at 550 °C for 2 h under high-purity flowing N₂ gas^{2–4} to obtain the MSC–silica nanocomposite (Figure 1c, also see Figure S-3 for N₂ adsorption result). When the silica in the nanocomposite is completely dissolved in 10% NaOH (98%, Aldrich) solution, isolated MSC nanoparticles without surface reactivity become dispersible, and they are retrieved by

repeating a cycle of centrifugation, decanting, and ultrasonic redispersion in deionized water until the pH value reaches 7.0. The washed MSC nanoparticles (Figure 1d) are finally dispersed in ethanol for sample preparation for characterizations with transmission electron microscopy (TEM), scanning electron microscopy (SEM), and field emission scanning electron microscopy (FE-SEM).

The size and dispersibility of MSC nanoparticles was determined by extensive TEM (Philips Tecnai 20) observations. As can be seen from typical TEM images shown in Figure 2 (and Figure S-4), the MSC nanoparticles have a mean size of 45 nm ranging from 25 to 90 nm (Figure 2, left) and exhibit good dispersibility (Figure S-4). Interestingly, MSC nanoparticles self-assembled into an extremely uniform film with smooth surface throughout the whole carbon film surface after ethanol evaporation (Figure S-5). This again implies that MSC nanoparticles were well dispersed in ethanol. The whole MSC film was studied by an energy-dispersive X-ray analyzer (EDX) attached to the FE-SEM (LEO1530). Neither sodium nor silicon were detected, suggesting that both SiO₂ and NaOH were completely washed away. FT-IR measurements also show that there is no silica in the MSC nanoparticles (Figure S-6).

In view of practical use, it is obviously helpful to study the dispersibility of MSC nanoparticles in organic solvents such as ethanol, toluene, and tetrahydrofuran. Photon correlation spectroscopy (PCS, Zetasizer 3000 HSA, Malvern Instruments, UK) technique was used to conduct in situ measurements at room temperature (25 °C) for the MSC nanoparticles dispersed in ethanol, toluene, and tetrahydrofuran. The results are shown in Figure 2 (right). The MSC nanoparticles are almost in the same size range of 20–100 nm, but their size distribution and peak size somewhat vary with the dispersion medium (solvent). It is well-known that colloidal particles are solvated leading to dispersion in the solvent. In addition to the presence of surface polarity, surface chemical heterogeneity, and surface flatness (pore),¹⁹ our carbon nanoparticles exhibit irregular shapes (e.g., nonsphere),²⁰ this obviously gives rise to different “surface solvation effect” when the nanoparticles are dispersed in different solvents. There-

(18) Wang, H. T.; Wang, Z. B.; Yan, Y. S. *Chem. Commun.* **2000**, 2333.

(19) Ottaviani, M. F.; Retini, G.; Cangiotti, M. *Spectrochim. Acta A* **2002**, 58, 1129.

(20) Bowen, P. J. *J. Dispersion Sci. Technol.* **2002**, 23, 631.

fore, some deviations can be given from both calculation and slight difference in the dispersibility (reversible aggregation) when the scattering data obtained from different solvents are converted into the size and distribution. This particularly makes it difficult to precisely compare the size and distribution obtained from different solvents. Even so, it is still quite useful to measure the size and distribution of MSC nanoparticles in various solvents. One can roughly see the dispersibility of the nanoparticles in different solvents. It is worth mentioning that the MSC nanoparticles have rigid micropore frameworks through high-temperature carbonization, thus they are expected to be stable in organic solvents. This is evidenced by the fact that the pore volume and the surface area remain unchanged after the sample is dried from solvents. From PCS measurements, the mean particle sizes were calculated to be 35, 42, and 55 nm for ethanol, toluene, and tetrahydrofuran, respectively. Their particle size ranges are well consistent with TEM observations. This clearly indicates that there is not a significant amount of agglomerates observed, and the MSC nanoparticles show a good dispersibility in various organic solvents.

The washed MSC nanoparticles were dried for N_2 adsorption–desorption measurement (Micromeritics ASAP 2020). The isotherm and the micropore size distribution (via Horvath–Kawazoe equation based on slit pore geometry) of the sample are shown in Figure 3. An adsorption step is clearly shown at the lowest pressure range (10^{-6} – 10^{-5}) of the isotherm curve. This indicates that the sample has a narrow pore size distribution. The peak pore size is 5.0 Å from the insert of Figure 3, corresponding to 4.8 Å for the PFA-derived molecular sieve carbons.² The micropore volume is calculated to be 0.13 cm³/g by using *t*-plot method. It can be concluded that well-defined micropores were formed in the nanoparticles. The BET surface area and the external surface area are determined to be 558 and 236 m²/g, respectively. This further supports that the sample has very small particle sizes. The hysteresis loop at high relative pressures is a consequence of N_2 filling

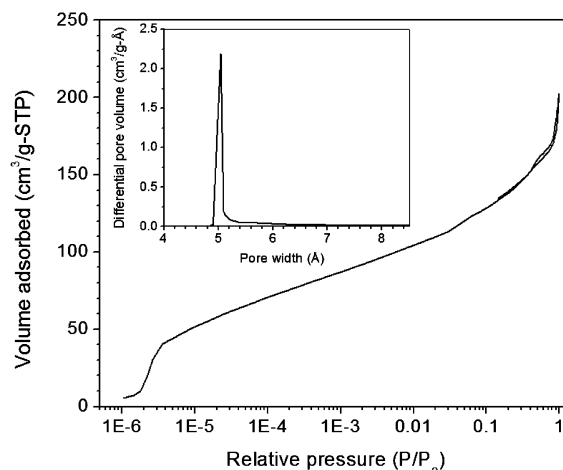


Figure 3. Nitrogen adsorption–desorption isotherm at 77 K and pore size distribution (inset) of MSC nanoparticles.

the large pores that may be associated with loose packing of highly dispersed MSC nanoparticles.

In conclusion, we have successfully synthesized molecular sieve carbon (MSC) nanoparticles by polymerizing furfuryl alcohol in P123 solution, and using silica as a temporary barrier during drying and carbonization. The MSC nanoparticles as-synthesized exhibited a size distribution ranging from 25 to 90 nm, well-defined microporosity, and high-dispersibility in organic solvents. It is believed that the technique developed here is unique and very effective for large-scale synthesis of nanosized microporous carbon materials.

Acknowledgment. This work was supported in part by a seed grant from The University of Hong Kong, and by The Natural Science Foundation of Anhui Province, China (Grant 03045303).

Supporting Information Available: Characterization methods and Figures S-1–S-6 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

CM0493400