

Highly Dispersible Microporous Carbon Particles from Furfuryl Alcohol

Jin Liu^a, Jianfeng Yao^a, Huanting Wang^{a,b*}, Kwon-Yu Chan^a

^aDepartment of Chemistry, The University of Hong Kong, China

^bAustralian Key Centre for Microscopy & Microanalysis, Electron Microscope Unit, The University of Sydney, Sydney, NSW 2006, Australia. Tel: +61 2 9351 7552 E-mail: huanting.wang@emu.usyd.edu.au

ABSTRACT

This paper reports the preparation of microporous carbon (MC) nanoparticles (25–90 nm) and spheres (260–320 nm) by carbonization of poly(furfuryl alcohol) (PFA) particles from furfuryl alcohol. Two synthetic routes were developed for forming “nonstick” PFA particles, which include (1) using silica as temporary barrier to isolate surface-reactive PFA nanoparticles and (2) a two-step polymerization of furfuryl alcohol (FA) involving slow polymerization (1st step) and sphere formation (2nd step). The high dispersibility of the MC spheres was realized by removing surface functional groups of the PFA spheres with the evaporation-induced concentrated sulfuric acid (2nd step). Both routes were effective in preventing irreversible aggregation of nanoparticles and spheres. Scanning electron microscopy, transmission electron microscopy, photon correlation spectroscopy and nitrogen adsorption were used to characterize the nanoparticles and spheres. The MC nanoparticles and spheres obtained showed good dispersibility in water and various organic solvents. They had a micropore volume of 0.13–0.14 cm³/g, and a pore size of 0.49–0.56 nm. This synthetic routes presented here are very efficient for large-scale synthesis of MC nanoparticles and spheres.

KEYWORDS

Microporous carbon, Carbonization, Nanoparticle, Sphere, Furfuryl alcohol

1 INTRODUCTION

Microporous carbons (MCs) have been long attractive for many important applications, e.g., as gas-selective adsorbents, membranes and catalyst supports and electrode materials for lithium ion batteries [1-6]. In particular, colloidal MC particles are of great interest because the diffusion of guest species through the MCs can be significantly manipulated by changing their particle sizes and shapes; the MC colloids would be useful as molecular sieves for developing the so-called mixed-matrix membranes that show high potential for industrial gas separations [6]. In addition, the MC particles with functionalized shells could provide with specific catalytic, magnetic, electronic, optical, or optoelectronic properties and thus broaden their uses. It is well known that MCs are usually prepared by carbonizing

solid organic precursors, and only the rigid and crosslinked polymers and the pitch-like materials are widely chosen as the carbon source for desired microporous structures. Very recently, we have synthesized highly dispersible MC nanoparticles (25–90 nm) with irregular shapes by the pyrolysis of poly(furfuryl alcohol) (PFA) nanoparticles. Silica gel was used as the sacrificial barrier to prevent irreversible aggregation of highly reactive PFA nanoparticles throughout drying and carbonization [7]. We have also developed a novel two-step polymerization of furfuryl alcohol (FA) to the synthesis of colloidal MC spherical particles with larger size [8]. Here, we summarize the preparation and characterization of MC nanoparticles and spheres with high dispersibility from FA.

2 EXPERIMENTAL

Two synthetic routes to synthesize microporous carbon particles are described as follows.

The synthesis procedure of highly dispersible MC nanoparticles by using silica temporary barrier (Route 1) is illustrated in Figure. 1. Typically, 3 g of furfuryl alcohol, 3 g of P123 [(EO)20-(PO)70-(EO)20] (Aldrich), 1.4 g hydrochloric acid (36.0–38.0%), deionized water and ethanol were mixed under rigorous agitation at room temperature to form a homogeneous solution (Figure 1a). The cationic polymerization of FA was 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. The resultant PFA suspension obtained was cooled to room temperature (Figure 1b). To avoid the PFA particle aggregation through drying and carbonization, a temporary barrier technique was 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 was 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. The PFA nanoparticles covered with silica gel were retrieved by centrifugation. After the nanoparticles were completely dried at 100 °C overnight, a dark brown solid composite was obtained. The dried solid composite was 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 Ar gas 2-4 to obtain the MC–silica nanocomposites. When the silica in the nanocomposite was completely dissolved in 10% NaOH solution, isolated MC nanoparticles without surface reactivity became dispersible, and they were retrieved by repeating a cycle of

centrifugation, decanting, and ultrasonic redispersion in deionized water until the pH value reaches 7.0. The MC nanoparticles obtained were denoted as C-P-NP.

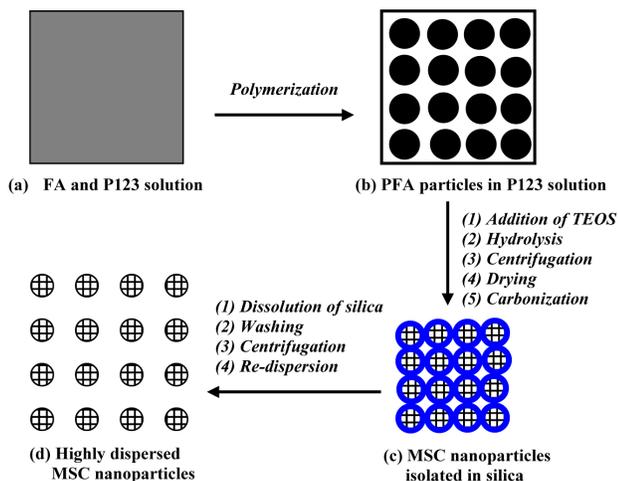


Figure 1 Synthesis procedure of highly dispersible MC nanoparticles by using silica as temporary barrier

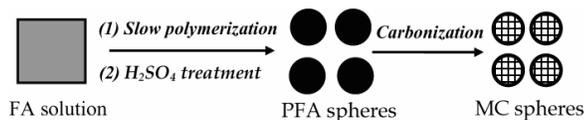


Figure 2 Synthesis of MC spheres by a two-step polymerization of FA combining with H₂SO₄ treatment

The MC spheres were synthesized by a two-step polymerization of FA, followed by retrieval of PFA spheres, drying and carbonization (Route 2, Figure 2). In the 1st step, the slow polymerization of FA was carried out in a FA-surfactant solution with a low concentration of HCl acid, and the FA pre-polymerized to form PFA oligomers. Amphiphilic triblock copolymers, Pluronic F127 (Sigma-Aldrich) and P123 were used as surfactants. Typically, 3 g of FA, 3 g of surfactant, 6 g of water, 1.4 g of HCl (36-38%, Merck) and 20 ml of ethanol were mixed in a 60 mL capped polypropylene bottle, and the obtained solution with a weight ratio of 1 FA: 1 surfactant: 6 ethanol: 2 H₂O: 0.17 HCl was continuously stirred at room temperature overnight. In the second step, H₂SO₄ solution with different concentrations at a volume ratio of 1 H₂SO₄ solution: 2 PFA solution was added into the above PFA solution under stirring. The mixture obtained was transferred into a glass beaker with a magnetic stirrer, and heated at 90 °C for 1 h allowing the solvents (water and ethanol) to evaporate. As a comparison, in the 2nd step, some syntheses were also carried out in the closed polypropylene bottles. The PFA spheres as-synthesized were collected by repeating three cycles of deionized water washing and centrifugation, followed by drying at 90–100 °C

overnight. The MC spheres were finally prepared by carbonization of the PFA obtained with a heating program consisting of a heat rate of 1 °C/min, 200 °C for 2 h, and 650 °C for 5 h under high-purity flowing argon gas. The MC spheres by using P123 and F127 were denoted as C-P-RT and C-F-RT, respectively.

A Cambridge Stereoscan S440 scanning electron microscope (SEM) and a Philips Tecnai 20 transmission electron microscope (TEM) were used to examine the morphology and particle size of the samples. Nitrogen adsorption-desorption experiments on the MCs were performed at 77 K on a Micromeritics ASAP 2020MC instrument to determine the Brunauer-Emmett-Teller (BET) surface area and micropore volume (t-plot method) and pore size distribution (Horvath-Kawazoe method based on slit-pore geometry). The samples were outgassed at 200 °C for 5 h before the measurement. Photon correlation spectroscopy (PCS) with a Zetasizer 3000 HSa equipment (Malvern Instruments Ltd. UK) at room temperature (25 °C) was used to determine the mean particle size and particle size distribution of MCs that were dispersed in ethanol. The wavelength of the internal laser was 633 nm and the selected measurement scattering angle was 90 degrees.

3 RESULTS AND DISCUSSION

3.1 Electron microscopy and dispersibility

The size and dispersibility of MC nanoparticles were determined by extensive TEM observations. As can be seen from typical TEM images shown in Figure 3 (a, c), the MC nanoparticles have a mean size of 45 nm ranging from 25 to 90 nm and exhibit good dispersibility (Figure 3c). MC nanoparticles self assembled into an extremely uniform film with smooth surface throughout the whole carbon film surface after ethanol evaporation (Figure 3d). This again implies that MC nanoparticles were well dispersed in ethanol.

The dispersibility of MC nanoparticles in organic solvents such as ethanol, toluene and tetrahydrofuran by photon correlation spectroscopy is shown in Figure 3b. The MC 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), our carbon nanoparticles exhibit irregular shapes (e.g. nonsphere), this obviously gives rise to different “surface solvation effect” when the nanoparticles are dispersed in different solvents. Therefore, 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 MC nanoparticles in various solvents. One can roughly see the dispersibility of the

nanoparticles in different solvents. It is worth mentioning that the MC 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 MC nanoparticles show good dispersibility in various organic solvents.

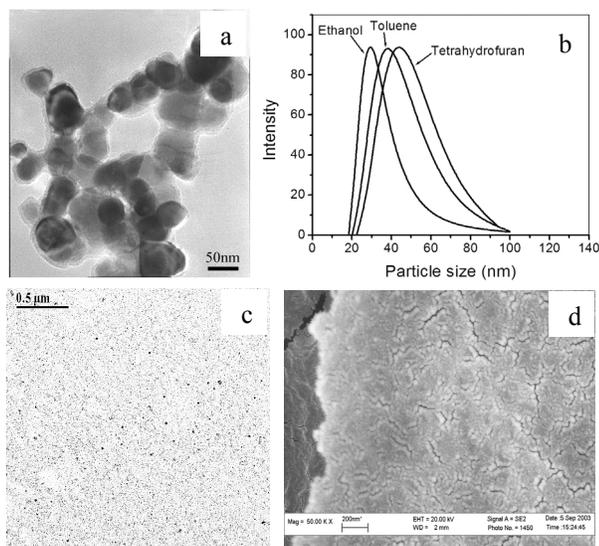


Figure 3 TEM images (a,c), FESEM image (d) and particle size distribution (b) of MC nanoparticles by Route 1.

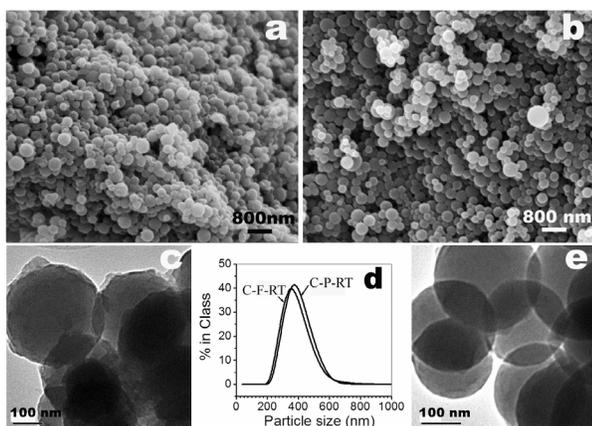


Figure 4. Electron microscopy images and particle size distribution (PSD) of the MC spheres by Route 2. (a, c) C-P-RT, FA polymerization with P123 at room temperature, (b,e) C-F-RT, FA polymerization with F127 at room temperature, C-R-RT (TEM), (d) PSD.

The MC spheres were observed with a scanning electron microscope and a transmission electron microscope. The SEM and TEM images (Figure 4) clearly show that both C-P-RT and C-F-RT spheres are fairly uniform. Their average sphere sizes are 320 nm, and 260 nm for C-P-RT and C-F-RT, respectively. The C-P-RT spheres have rough surface whereas C-F-RT spheres possess very smooth surface (Figure 4c, e). This is probably due to a lower cloud point of P123, which tends to phase separate at 90 °C (2nd step) and is less effective in functioning as the surfactant. The colloidal suspension of MC spheres in ethanol was studied by PCS method. Their particle size distribution is shown in Figure 4d. The sphere sizes are in the range of 270—550 nm, and 230—465 nm, and the average sizes are 370 nm and 340 nm for C-P-RT and C-F-RT, respectively. This confirms that both C-P-RT and C-F-RT exhibit good dispersibility.

3.2 Nitrogen adsorption

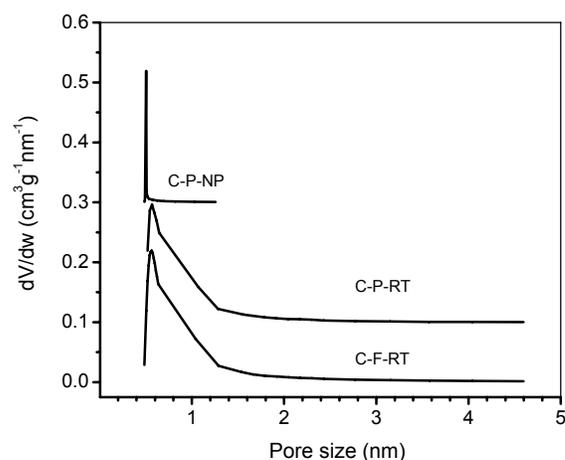
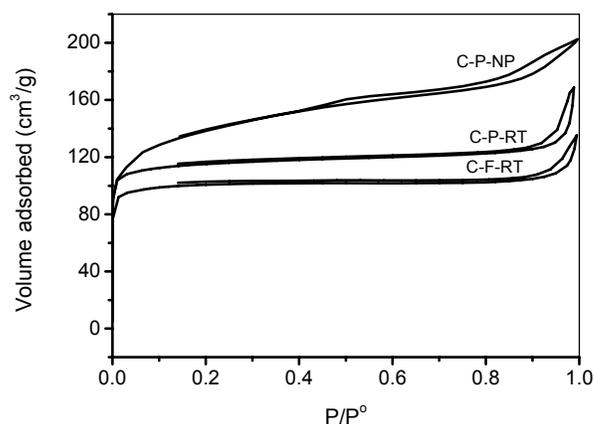


Figure 5. Nitrogen adsorption-desorption isotherms (upper) and pore size distribution (lower) of MC nanoparticles and spheres.

The washed MC nanoparticles were dried for N₂ adsorption-desorption measurement. The isotherm and the micropore size distribution of the sample (C-P-NP) are shown in Figure 5. The C-P-NP has a narrow pore size distribution, and its peak pore size is 5.0 Å corresponding to 4.8 Å for the PFA-derived molecular sieve carbons [1]. The micropore volume is calculated to be 0.13 cm³/g. The BET surface area and the external surface area are determined to be 558 and 236 m²/g, respectively. It can be concluded that well-defined micropores were formed in the nanoparticles, and the MC nanoparticles have very small particle sizes. On the other hand, the hysteresis loop at high relative pressures is a consequence of N₂ filling the large pores that may be associated with loose packing of highly dispersed MC nanoparticles. The nitrogen adsorption isotherms and pore size distribution of the MC spheres are also included in Figure 5. The BET surface area of the MC spheres is determined to 392 and 376 m²/g for C-P-RT and C-F-RT, respectively. Obviously, the MC spheres possess smaller surface area as compared with C-P-NP because they have larger particle size. Both C-F-RT and C-P-RT have almost the same micropore volume (0.14 cm³/g) and well-defined pore size distributions, and their pore sizes center at 0.56 nm.

4 CONCLUSIONS

We have successfully synthesized microporous carbon (MC) nanoparticles and spheres by polymerizing furfuryl alcohol in the P123 or F127 solution using silica as temporary barrier or H₂SO₄ treatment. The MC particles through carbonization exhibited a size range of 25–90 nm for the nanoparticles and 260–320 nm for the spheres, and they both had well-defined microporosity and high-dispersibility in water and organic solvents.

ACKNOWLEDGMENT

This work was supported in part by a seed grant from The University of Hong Kong. HW thanks the Australian Research Council for the QEII fellowship.

REFERENCES

1. H. C. Foley, *Micropor. Mater.* **1995**, *4*, 407-433.
2. M. B. Shiflett, H. C. Foley, *Science* **1999**, *285*, 1902-1905.
3. H. T. Wang, L. X. Zhang, G. R. Gavalas, *J. Membr. Sci.* **2000**, *177*, 25-31.
4. L. X. Zhang, K. E. Gilbert, R. M. Baldwin, J. D. Way, *Chem. Eng. Comm.* **2004**, *191*, 665-681.
5. D. Q. Vu, W. J. Koros, S. J. Miller, *J. Membr. Sci.* **2003**, *211*, 311-334.
6. Q. Wang, H. Li, L. Q. Chen, X. J. Huang, *Solid State Ionics*, **2002**, *152*, 43–50.
7. J. Liu, H. T. Wang, L. X. Zhang, *Chem. Mater.* **2004**, *16*, 4205-4207.

8. J. F. Yao, H. T. Wang, J. Liu, K. Y. Chan, L. X. Zhang, and X. P. Xu, *Carbon* **2005**, in press.