

Electronic supplementary information (ESI)

Versatile Preparation of Monodisperse Poly (furfuryl alcohol) and Carbon Hollow Spheres in a Simple Microfluidic Device[†]

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Experimental Section

The fluidic device

The microfluidic device was assembled by inserting a syringe needle (100 μm i.d.) perpendicularly into a polyvinyl chloride (PVC) tube (1.2 mm i.d., 1.6 mm o.d.), and the joint between the needle and the PVC tube was fixed with epoxy adhesive. The PVC tube was oriented vertically in all experiments to avoid the accumulation of microdroplets on the microchannel wall.

Preparation of PFA hollow microspheres

Preparation of PFA microspheres were carried out at room temperature by feeding an oil solution and a 8 M sulfuric acid aqueous solution separately into the PVC tube and the syringe needle using two syringe pumps (LSP02-1B, LongerPump, China) at independently adjusted flow rates. The oil solution was prepared by adding 3.3–9.1 wt% FA (Sinopharm, China) and 3 wt% Span 80 (Sinopharm, China) to fatty acid methyl ester (FAME), which was prepared by transesterification of cotton-seed oil with methanol in a microstructured reactor¹ and used as a green solvent. In our experiments, we found that the concentration of sulfuric acid is very sensitive. When the concentration was 7 M, the resulting PFAHMs could not be solidified through the FAME column. On the other hand, when the concentration was higher than 8.5 M, the polymerization

reaction of FA was too fast in microfluidic device, and no microspheres could be formed. Therefore, the concentration of sulfuric acid was selected as 8 M. In a typical demonstration, the aqueous and oil solutions were fed into the microfluidic device at flow rates of 0.2 and 20 mL/h, respectively. The resultant PFA microcapsules were dropped into a 60 °C FAME column (60 cm long), which was heated by circulating hot water, for further curing and solidification. These microspheres were subsequently filtrated, washed by hexane five times, and dried at 150 °C for 2 h with a heating rate of 1 °C/min.

Preparation of carbon hollow microspheres

Carbon hollow microspheres were prepared by carbonization of PFA microcapsules in N₂ atmosphere at 550 °C for 6 h, with a heating rate of 1 °C/min and a N₂ flow rate of 12 mL/min.

Preparation of magnetic carbon hollow microspheres

First, an aqueous solution was prepared by dissolving 1 mol of CoSO₄ in 1 L of 8 M sulfuric acid aqueous solution. The amount of CoSO₄ can be changed depending on the needed magnetic property of CHMs. Then, PFA microcapsules containing CoSO₄ were prepared following the same method mentioned above. At last, these microcapsules were carbonized in a 5% H₂/N₂ atmosphere at 550 °C for 6 h with a heating rate of 1 °C/min.

Characterization

The generation processes of aqueous solution microdroplets in our microfluidic device were recorded by macro lenses (Pentax, Japan) connected to a high-speed CCD video camera (Microview, Beijing). Optical microscopy (Pentax) and SEM (Quanta 200) were used to investigate the particle size and morphology of microspheres. To investigate the wall thicknesses of microspheres, samples were cut with a sharp knife before observation. N₂ adsorption/desorption measurements and were

performed at 77 K on Micromeritics ASAP 2020 instrument to determine the Brunauer–Emmett–Teller (BET) surface area and pore size distribution (Horvath–Kawazoe). CO₂ and CH₄ adsorption measurements were performed at 298 K on Micromeritics ASAP 2020 instrument. The samples were all outgassed at 200 °C for 5 h before the measurement. Results showed that CO₂ saturation capacities of sample 1 and sample 6 were 44.5 and 42 cm³/g, respectively. While the CO₂ saturation capacities of commercial carbon molecular sieve (Takeda 3A) is ca. 36 cm³/g.²¹ Therefore, CHMs we synthesized exhibited 10% higher CO₂ saturation capacities than the commercial carbon molecular sieve (Takeda 3A). In addition, the CH₄ saturation capacity of sample 1 was 18.4 cm³/g, much lower than its CO₂ saturation capacity, suggesting potential application in CO₂/CH₄ separation. EDX characterizations were conducted in FESEM (Hitachi S-4800) to illustrate the distribution of metal nanoparticles in the wall of CHMs. The average size, particle size distribution and coefficient variation (CV) of samples were also determined by manual measurement of over 50 microspheres in optical and SEM pictures by Adobe Photoshop 7.0 software.² The CV value is defined as $CV = (\sigma_d / \bar{d}) \times 100\%$, where σ_d is the standard deviation of the diameter, and \bar{d} is its mean value. The lower the CV value, the more uniform particle size of microspheres becomes.²

Figures

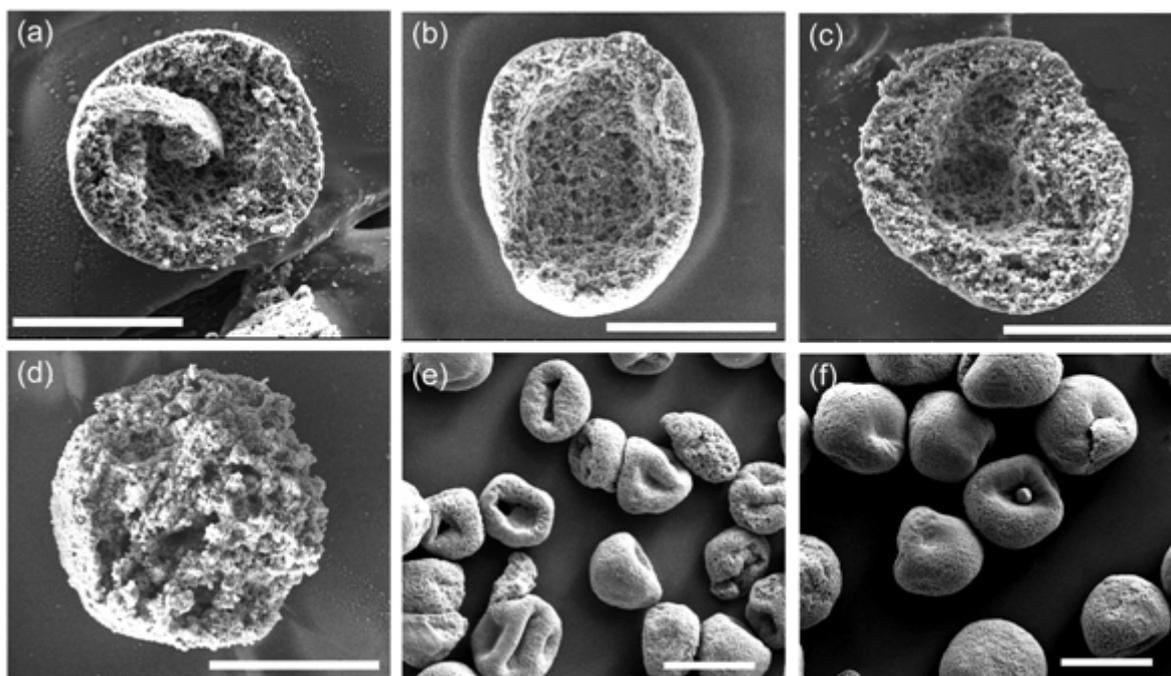


Figure S1. SEM pictures of PFA microspheres: a) sample 2, b) sample 3, c) sample 4, d) sample 5, and e,f) SEM pictures of PFAHMs prepared with a FA concentration of 9.1 wt% and residence times of 2 and 4 s, respectively, using flow rates for aqueous and oil solutions of 0.2 and 20 mL/h. Scale bar is 200 μm .

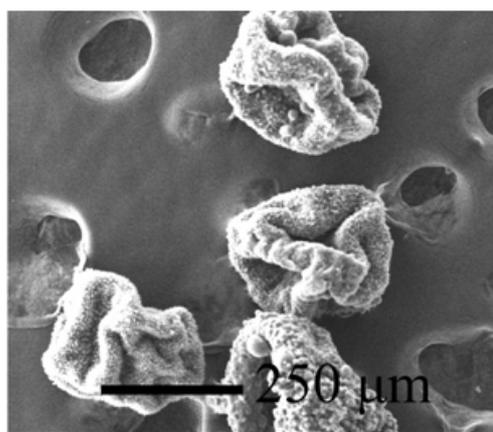


Figure S2. SEM picture of PFAHMs cured in 75 $^{\circ}\text{C}$ FAME column.

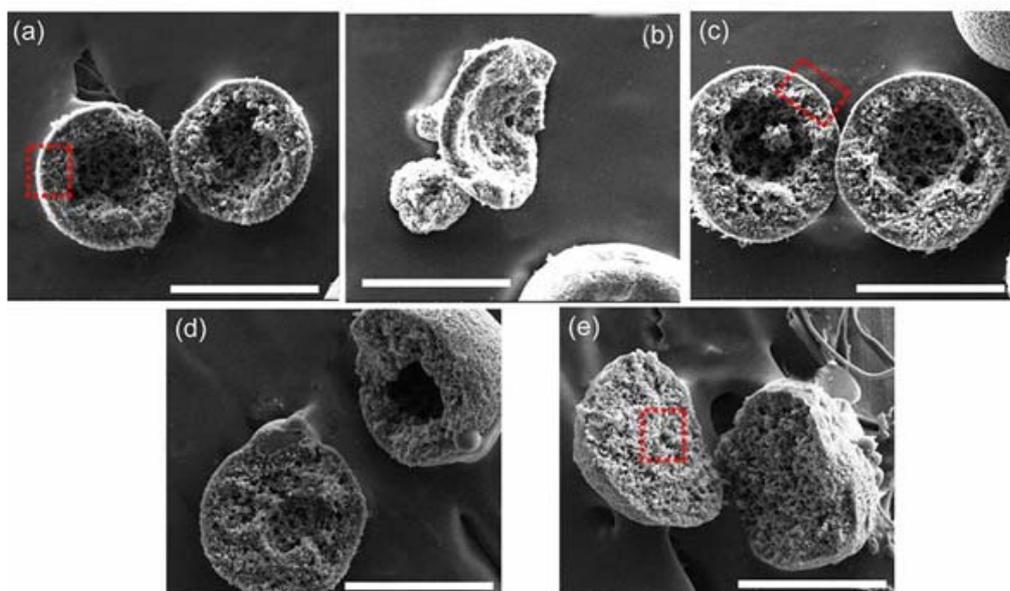


Figure S3. SEM pictures of carbon microspheres: a) sample 2, b) sample 3, c) sample 4, d) sample 5, e) sample 6. Scale bar is 200 μm .

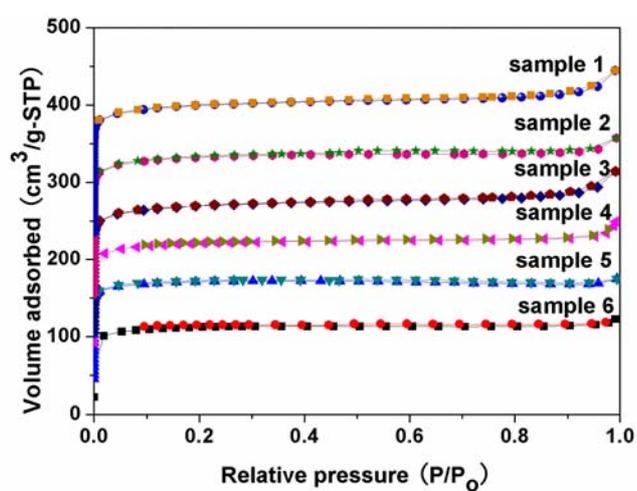


Figure S4. N_2 adsorption/desorption isotherms of carbon microspheres. (The isotherms of samples are offset vertically by 30, 60, 90, 120 and 150 $\text{cm}^3/\text{g}\cdot\text{STP}$.)

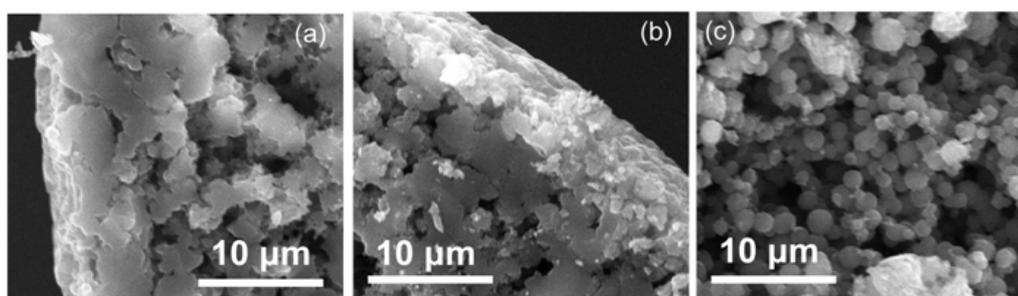


Figure S5. Magnified images of carbon microspheres (red rectangle shown in Figure S3): a) sample 2, b) sample 4, and c) sample 6.

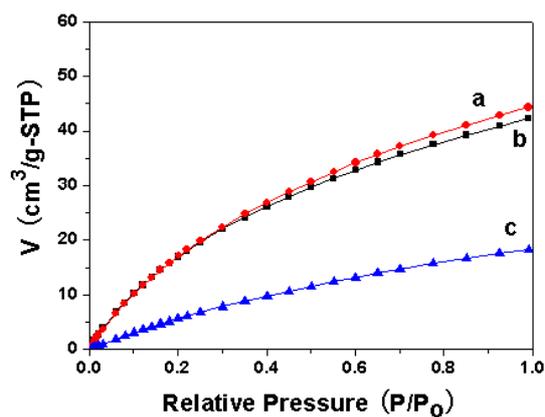


Figure S6. Adsorption isotherms at 298 K of CO₂ on sample 1 (a), CO₂ on sample 6 (b), and CH₄ on sample 1 (c).

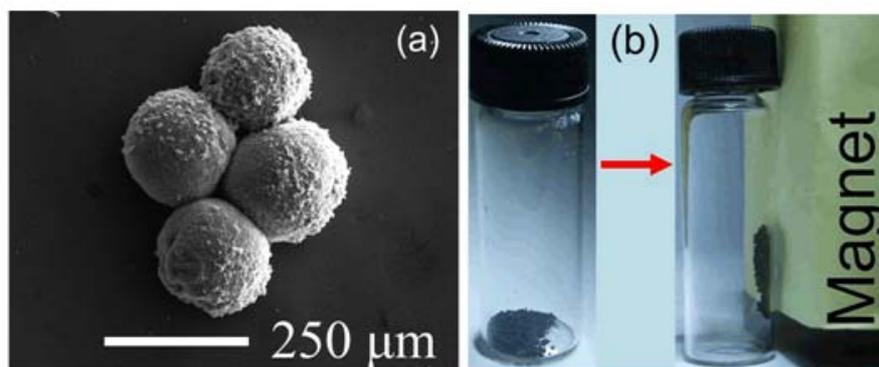


Figure S7. a) SEM picture of magnetic CHMs prepared with flow rates of aqueous solution (containing CoSO₄) and oil solutions of 0.2 and 20 mL/h, respectively and b) photo image demonstrating attraction of magnetic CHMs by a magnet.

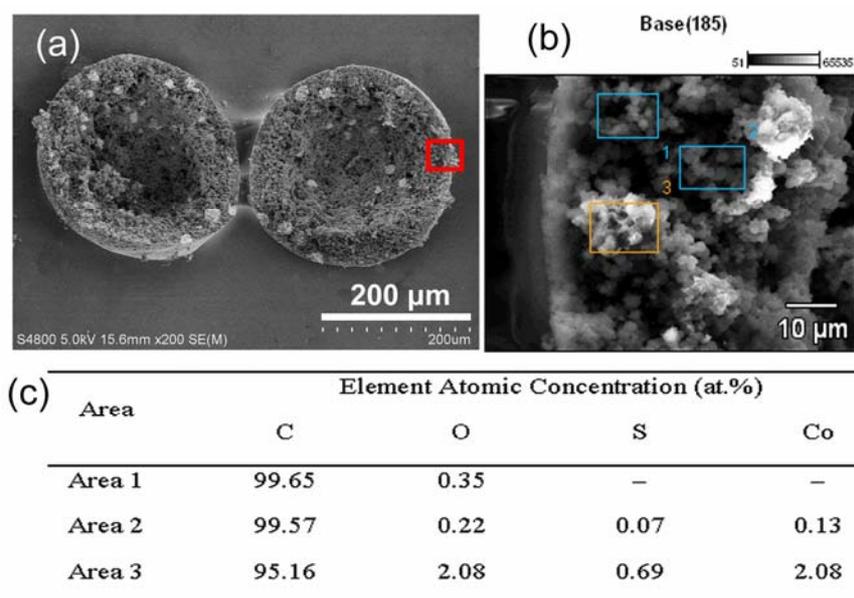


Figure S8. (a) FESEM picture of a purposely broken magnetic CHM prepared with flow rates of aqueous solution (containing CoSO_4) and oil solutions of 0.2 and 20 mL/h, respectively. (b) FEMSEM picture and (c) corresponding EDX results of the wall of this microsphere (red rectangle in part a).

Literature Cited

- 1 J. Sun, J. X. Ju, L. Ji, L. X. Zhang and N. P. Xu, *Ind. Eng. Chem. Res.*, 2008, **47**, 1398.
- 2 (a) Y. C. Pan, J. F. Yao, L. X. Zhang, N. P. Xu, *Ind. Eng. Chem. Res.*, 2009, **48**, 8471; (b) Y. C. Pan, M. H. Ju, J. F. Yao, L. X. Zhang and N. P. Xu, *Chem. Commun.*, 2009, 7233.