Versatile preparation of monodisperse poly(furfuryl alcohol) and carbon hollow spheres in a simple microfluidic device†

Yichang Pan, Minhua Ju, Chongqing Wang, Lixiong Zhang* and Nanping Xu

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Monodisperse PFA and carbon hollow microspheres have been prepared without templates in a single synthesis process by a microfluidic methodology.

Hollow microspheres composed of polymeric or inorganic materials are of great interest because of their potential application as catalyst supports, carriers for cosmetics, drugs, protein and DNA delivery, electrodes, sensors, and so on.[1] They are prepared by various methods such as emulsion/micelles/vesicle polymerization,[2,3] spray drying,[4] template methods,[5] and self-template method.[6] Recently, a new technique was developed to synthesize uniform-sized hollow microspheres using a microfluidic emulsion technique *via* interfacial polymerization at the surface of the microdroplet,[7–10] which has provided a facile and scalable approach to fabricate monodisperse hollow microspheres, such as nylon,[7] biopolymer,[8] organosilicon[9] and TiO_2.[10] However, only a single product was prepared each time in these above-mentioned reports. In addition, control of the wall thickness of the hollow microspheres was seldom investigated.

Here, we present the preparation of monodisperse poly(furfuryl alcohol) (PFA) hollow microspheres (PFAHM) in a microfluidic device assembled by inserting a syringe needle (100 μm i.d.) perpendicularly into a poly(vinyl chloride) (PVC) tube (1.2 mm i.d., 1.6 mm o.d.), as shown in Fig. 1a. The PFAHMs in turn can be transformed to microporous carbon hollow microspheres by carbonization. Thus, both PFA and carbon hollow microspheres can be obtained in a single synthesis process. PFA, which can be easily obtained from polymerization of FA by acidic catalysis, is widely used in metal-casting molds, corrosion-resistant materials, negative photoresists, reverse osmosis desalination membranes, and as a precursor for the fabrication of different nanostructured carbons.[11] Carbon hollow microspheres (CHM) are known for their intrinsic properties, such as high strength, high thermal resistance, low density and bio-compatibility. They are expected to show high performances when used as catalyst supports,[12] electrodes of fuel cells and lithium-ion batteries,[13] electrochemical hydrogen storage materials,[14] and adsorbents.[15] CHMs are commonly prepared by template methods using silica particles and polymer latex colloids as templates,[16] which requires uniform sacrificial templates and multistep operations to obtain monodisperse CHMs. In addition, they can also be prepared by hydrothermal or solvothermal synthesis[17] of organic materials and pyrolysis of organic gases.[18] However, the particle size distribution of the resultant CHMs is broad, and high temperature, high pressure and long reaction times have to be applied. To the best of our knowledge, no report about easy synthesis of monodisperse PFAHMs and CHMs without templates in a microfluidic device have been given.

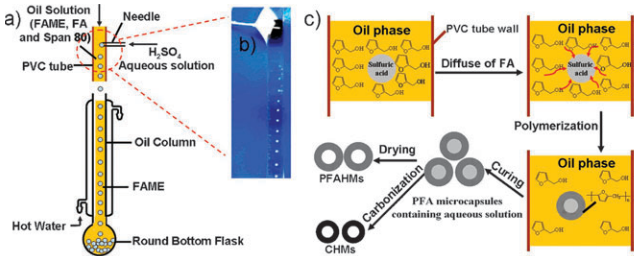

Fig. 1 (a) Schematic illustration of the microfluidic device to fabricate monodisperse PFAHMs. (b) Optical images showing droplets created in the microfluidic device. (c) Schematic diagram for formation of PFAHMs and CHMs in the microfluidic device.

Experiments were carried out at room temperature by feeding an oil solution containing FA, fatty acid methyl ester (FAME) and a surfactant (Span 80) and an 8 M sulfuric acid aqueous solution separately into the PVC tube and the syringe needle (see ESI†). Aqueous solution microdroplets were thus formed at the end of the needle by shearing force from the oil phase. Once a water droplet was formed, FA in the oil phase would diffuse into the droplet, and consequently start to polymerize upon catalysis by sulfuric acid (Fig. 1b). Thus, a layer of PFA would be formed at the surface of the aqueous droplet, resulting in formation of PFA microcapsules containing aqueous solution (Fig. 1b and c). After further curing and drying, we could obtain PFAHMs. The advantages of this technique include easy control of the particle size and wall thickness of resultant microspheres by changing the flow rates of the oil and water solutions and the hydraulic diameter of the needle, with simple adjustment of hollow or solid structures by changing the concentration of FA in the oil solution and the residence time of microdroplets in the PVC tube, and ready functionalization of the microspheres by adding suitable materials in the aqueous solution.

Fig. 2a and b show typical optical and SEM micrographs of PFAHMs prepared at flow rates of the aqueous solution and oil solution of 0.2 and 20 mL h^{-1}, respectively. One can see that the PFAHMs are of good spherical morphology and uniform particle size. The particle size distribution of products illustrated in Fig. 2c shows that the sizes of PFAHMs range

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State Key Laboratory of Materials-Oriented Chemical Engineering and College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing 210009, P. R. China. E-mail: lixiongzhang@yahoo.com; Fax: 86 25 8317 2263; Tel: 86 25 8317 2265

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from 243 to 281 μm, the average diameter is 262 μm with a coefficient of variation (CV) value of 2.7%. The CV value is smaller than 5%, which is the commonly accepted value for definition of monodispersity of particles.[7] Furthermore, we did not find any broken or deformed products during the experiment. The hollow structure of these microspheres with a wall thickness of *ca.* 90 μm can be obviously observed from the SEM image of a purposely broken PFAHM (Fig. 2d).

The particle size of PFAHM can be easily adjusted by changing the flow rates of the aqueous solution and oil solution (Fig. 3a). At a fixed flow rate of aqueous solution, the diameter of the resultant PFAHM decreases almost linearly with increase in the flow rate of oil solution due to the increase in shear stress imposed on the droplet. On the other hand, at a fixed flow rate of oil solution, a lower flow rate of aqueous solution leads to a decrease in the diameter of the resultant PFAHM. These results are consistent with those of reported work in a cross-flow microfluidic device,[19] which results from the increase in the shear stress imposed on the droplet caused by increase in the flow rate of the continuous phase or a decrease in the flow rate of the discontinuous phase. Therefore, we can easily prepare PFAHMs with average diameters in the range of 234–380 μm and a CV of less than 5% by changing the flow rates of feeds using a needle with a hydraulic diameter of 100 μm. However, there is a limitation in reducing the sphere size by changing the flow rates of two phases. To further decrease the diameter of PFAHM, we replaced the needle with a glass capillary with 50 μm i.d. The average size of the thus prepared PFAHMs is 110 μm (Fig. 3b).

In order to adjust the thickness of PFA layer in the PFAHM, we conducted a series of experiments by changing the concentration of FA (c_{FA}) in the oil solution and the residence time (t_{R}) of the microdroplets in the PVC tube using fixed flow rates of two phases, as listed in Table 1. One can see that particle diameters of all products are quite close, indicating that the diameter (d_{sphere}) of PFAHM is mainly determined by the diameter of the aqueous microdroplets. In addition, the average wall thickness (d_{wall}) of PFAHMs increases with increasing concentration of FA in the oil solution (Table 1, Fig. S1†). PFAHMs with wall thicknesses ranging from 40 to 90 μm are prepared when the FA concentration is adjusted from 3.3 to 9.1 wt%. On the other hand, the average wall thickness of PFAHMs increases with prolongation of the residence time of microdroplets in the PVC tube (Table 1, Fig. S1c†), indicating that more FA diffuses from the oil solution to the aqueous droplets at longer residence times. Therefore, we speculated that solid PFA microspheres would be prepared when the residence time of microdroplets was long enough. As expected, solid PFA microspheres were prepared at residence times of 20–40 s with a FA concentration of 9.1 wt% (Fig. S1d†). However, the PFA spheres were deformed when the residence times were 2–4 s (Fig. S1e,f, ESI†), quite possibly resulting from weak mechanical strength of the spheres because of too thin a PFA shell thickness. In addition, the curing temperature also has strong influence on the shape of resultant microspheres. When the curing temperature is above 75 °C, non-spherical PFAHMs are obtained (Fig. S2†). This may possibly result from rapid diffusion of water encapsulated in PFAHMs at high temperatures.

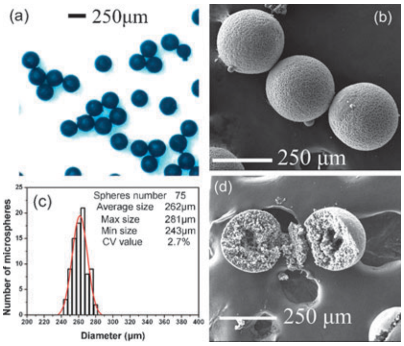

Fig. 2 (a) Optical micrograph, (b) SEM pictures, (c) particle size distribution of PFAHMs and (d) a purposely broken PFAHM prepared using flow rates for aqueous and oil solutions of 0.2 and 20 mL h^{-1}, respectively.

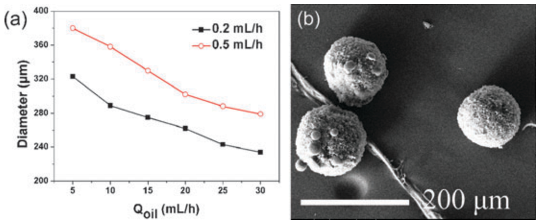

Fig. 3 (a) A plot of the average diameter of PFAHMs as a function of the flow rate of oil solution at flow rate of aqueous solutions of 0.2 and 0.5 mL h^{-1}. (b) SEM picture of PFAHMs prepared with a 50 μm i.d. glass capillary at flow rates for the water and oil phase of 0.2 and 30 mL h^{-1}, respectively.

PFAHMs can be easily transformed to CHMs by carbonization. The resulting CHMs carbonized at 550 °C in N_2 atmosphere still retain spherical morphology, monodisperse size and the hollow structure of the corresponding PFAHMs (Fig. 4, Fig. S3†). Compared with their precursors, average diameters and average wall thicknesses of resultant CHMs for samples 1–4 decrease by about 1/4 and 1/2–2/3, respectively (Table 1). They all exhibit CV values less than 5%, indicating monodisperse particle sizes. For sample 5, the PFA spheres are solid spheres while the corresponding carbon spheres are hollow (Fig. S1d, S3d†). For sample 6, both the PFA and the corresponding carbon microspheres are solid spheres (Fig. S3e†). These results possibly result from different packing densities of PFA in the PFA spheres at different residence time. N_2 adsorption/desorption isotherms of these CHMs are of type I (Fig. S4†), typical of microporous materials. The average pore size of these CHMs is 0.43 nm, close to the reported pore size of 0.48 nm for PFA-derived molecular sieve carbons.[20] The BET surface areas and micropore volumes of the CHMs for samples 1–4 are quite close, resulting from similar compact carbon structures (Fig. S5a,b†). However, CHMs for samples 5 and 6 exhibit smaller BET surface areas and micropore volumes than samples 1–4, which may be due to their interior loose structure (Fig. S5c†). The CHMs exhibited 10% higher CO_2 saturation capacities than commercial carbon molecular sieves (Takeda 3A).[21] Furthermore, the CO_2 saturation capacities on CHMs were higher than CH_4 saturation capacities (Fig. S6†), suggesting potential application

Table 1 Experimental conditions for synthesis and results of PFAHMs and CHMs in the microfluidic device[a]

	Poly(furfuryl alcohol) hollow microspheres				Carbon hollow microspheres			
Sample	c_{FA} (wt%)	t_R/s	d_{sphere}/μm	d_{wall}/μm	d_{sphere}/μm	d_{wall}/μm	S_A/m^2 g^{-1}	V_p/cm^3 g^{-1}
1	9.1	8	262	90	194	32	600	0.25
2	5	8	266	70	190	27	586	0.24
3	3.3	8	275	40	205	21	593	0.25
4	9.1	6	275	63	208	30	566	0.22
5[b]	9.1	20	272	136	206	70	430	0.17
6[c]	9.1	40	268	134	200	100	389	0.15

[a] Experiments were all conducted at flow rates for aqueous and oil solutions of 0.2 and 20 mL h^{-1}, respectively. [b] The PFA spheres are solid spheres whereas the carbon spheres are hollow. [c] Both the PFA and the corresponding carbon microspheres are solid spheres.

in CO_2/CH_4 separation. Furthermore, all these CHMs show strong mechanical strength, exhibited by difficulty in cutting the spheres with a sharp blade.

The CHMs can be easily functionalized with magnetic property by simply adding $CoSO_4$ into the aqueous solution during preparation of the PFAHMs and reduction with hydrogen during carbonization. Addition of $CoSO_4$ does not have influence on the particle size and morphology of resultant magnetic CHMs (Fig. S7a, S8†). These magnetic CHMs can be easily attracted by a magnet quickly (Fig. S7b†). Their magnetic property can be adjusted by regulating the amount of $CoSO_4$, which can be sensed by the speed of attraction. These results demonstrate that it is straightforward to fabricate some functional carbon materials.

In summary, we have demonstrated that monodisperse PFA hollow microspheres can be prepared without templates in a simple microfluidic device. By changing the flow rates of oil and aqueous solutions, residence time of aqueous micro-droplets in the fluidic device, FA concentration in oil solution and curing temperature, the particle size and wall thickness of PFA hollow microspheres can be easily adjusted. These PFA microcapsules can be easily transformed to microporous carbon hollow microspheres exhibiting monodisperse particle size and strong mechanical strength by carbonization. Thus, both PFA and carbon hollow microspheres can be obtained in a single synthesis process. In addition, a magnetic precursor can be simply incorporated in PFA microspheres, leading to formation of magnetic carbon hollow microspheres.

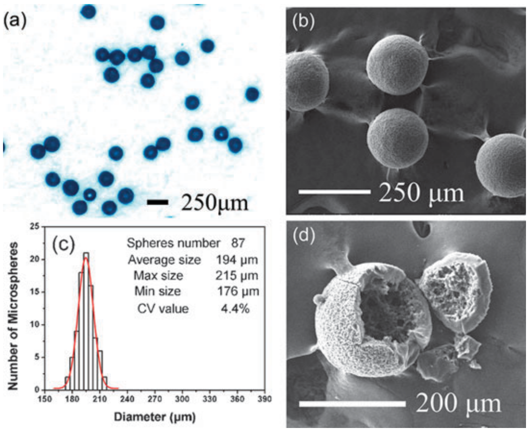

Fig. 4 (a) Optical micrograph, (b) SEM images, (c) particle size distribution of CHMs and (d) a purposely broken CHM carbonized from corresponding PFAHM (sample 1).

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