

Microfluidic production of porous carbon spheres with tunable size and pores



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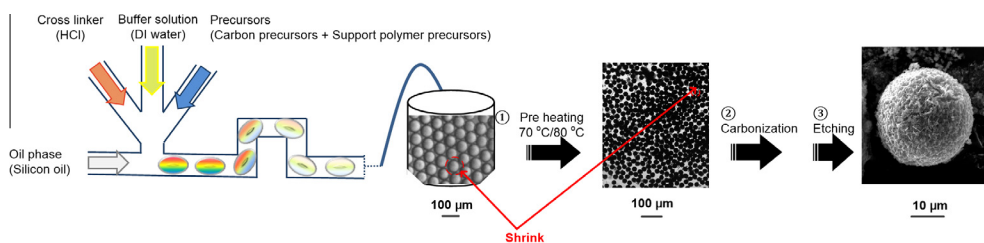
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GRAPHICAL ABSTRACT



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ABSTRACT

Porous carbon particles have been widely used in many areas including energy storage. Production of carbon microspheres in an efficient, controlled, and low-cost manner, however, is challenging. Here, we demonstrate a microfluidic approach to generate porous carbon particles using inexpensive precursors and show that the size of the particle and pores can be tuned by adjusting the deionized (DI) water content in droplets and preheating temperature. The developed strategy offers an effective approach to control the production of porous carbon spheres with a well-defined diameter, narrow size distribution and pore size.

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1. Introduction

Carbon materials, especially porous carbons are of great interest due to their wide range of applications in environment [1], energy [2] and biomedicine [3]. Spherical carbon particles, for examples, have been used for pollutant adsorption [4], water purification [5], and drug delivery [6]. In particular, because of their large surface-volume ratio and high packing capacity, porous carbon microspheres are promising materials for construction of effective electrical energy storage devices such as super capacitors [7].

Indeed, a recently developed electrochemical flow capacitor (EFC) has utilized a flowable carbon microspheres–electrolyte mixture as the active material for capacitive energy storage and shown combined advantages of both super capacitors and flow batteries [8]. For EFC, the composition of the carbon slurry determines the rheological and electrochemical properties of the slurry and thus is critically important for the development of effective EFC. Spherical carbon particles with a narrow size distribution can achieve a smooth flow pattern by minimizing the flow-induced particle segregation and clogging and are highly preferred in EFC.

Conventional approaches used to produce porous spherical carbons such as sol–gel reaction [9], hydrothermal treatment [5], nanocasting [10] and atomizer spray [11], have either harsh reactive conditions or the size of obtained particles are

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poly-dispersed. Although the size of porous carbon particles generated via the nanocasting method could be mono-dispersed given that the template particles have a uniform size, it becomes time consuming and tedious when change of the size of particles is required [10]. Herein, we develop a microfluidic approach to synthesize porous carbon spheres with a narrow particle size distribution and demonstrate that the size of the carbon particles and pores can be controlled effectively. In particular, we utilize inexpensive and environment-friendly sucrose as the carbon precursor to produce sucrose-containing aqueous droplets via double emulsion (water-in-oil) microfluidics. When the aqueous droplets are solidified at an elevated temperature and carbonized, micrometer diameter spherical carbons are obtained with a much smaller diameter than that of droplets. Most importantly, by changing the deionized (DI) water content of sucrose-containing droplets and preheating temperature, we are able to control the diameter and pore size of obtained carbon particles.

2. Methods

2.1. Materials and microfluidic methods

The microfluidic chips were fabricated in Polydimethylsiloxane (PDMS) using the soft lithograph method [12], and treated with n-octyltriethoxy silane before using to make the glass surface of the channel hydrophobic. The aqueous phase consists of a precursor solution, DI water and a solution of hydrogen chloride (HCl) (37 wt% in water, Aldrich). The precursor solution is made by dissolving 5 g sucrose in a 5 ml sodium silicate solution (~14% sodium hydroxide (NaOH) and ~27% silicon dioxide (SiO₂), Aldrich) and 5 ml DI water at 50–80 °C. The reaction takes place when pH < 1, and the molar ratio of sucrose to SiO₂ is kept as 0.65 to ensure the *in-situ* formation of silica networks [13]. Silicon oil with 1 wt% 749 (Dow corning) is used as the continuous oil phase. All the liquids are loaded into four 1 ml syringes and pumped into the microfluidic channel by four syringe pumps (NE 300). The three vertical inlet channels are for the aqueous phases: carbon/silica precursors and HCl solutions are injected from the side channels whereas DI water is introduced from the middle channel and acts as the separating phase. The continuous oil phase is introduced from the lateral channel in which aqueous droplets containing a mixture of carbon/silica precursors, HCl, and DI water are generated. The height of the channels, which is defined as the distance from the glass surface to the top of the PDMS channel, is uniformly 30 μm. The width of the channel, which is defined as the distance between the two opposite PDMS channel walls, for aqueous phase and oil phase is 50 μm and 100 μm, respectively. In our experiment, the flow rate of aqueous phase is adjusted between 0.2 μl min⁻¹ and 1 μl min⁻¹, and the oil phase is adjusted between 1 μl min⁻¹ and 15 μl min⁻¹.

2.2. Generation of carbon particles

Sucrose-containing drops are collected into oil with surfactant 749, and heated at 70 °C or 80 °C in a convection oven for 24 h to polymerize the drops and evaporate water. Then, the obtained solid particles are collected on a ceramic crucible after washing out the oil with petroleum ether for more than 5 times. After that, the solid particles will be heated at 200 °C (with a heating rate of 3 °C/min from room temperature) for 12 h under a nitrogen atmosphere. The temperature is then increased to 850 °C with a heating rate of 5 °C/min, and maintained for 3 h. The resulting carbon/silica composites are immersed in a 3 M NaOH solution for 120 h at 70 °C to remove the silica template. The final carbon particles are retrieved by filtration and washed using DI water and ethanol.

Note that the overall yield of the production of porous carbon particles is about 80%. Although the yield of the generation of cured particles from emulsion drops is high (~100%), decreased number of carbon/silica particles during the carbonization process and uncompleted removal of silica from carbon/silica particles lead to a decreased overall yield of porous carbon particles. Comparing to other approaches where the yield of controlled carbonization of sucrose using sulfuric acid is about 50% [14], however, the yield of porous carbon particles in our approaches can be considered high.

2.3. Data analysis and SEM imaging

The generation of droplets is observed directly using a high-speed video camera (Phantom M110, 1600 frames per second) mounted on a Leica microscope. The size and size distributions of droplets gathered from the microfluidic channel and polymerized solid particles are analyzed by ImageJ[®]. Also, to check the water evaporation extent of the droplets, the structure of the droplets before and after heating is analyzed by Fourier Transform Infrared Spectroscopy (FTIR) (Bruker). The surface morphology, pores of the particles, and element composition of the particles are analyzed by Scanning Electron Microscopy (SEM) (LYRA3 TESCAN). For each sets of experiments, we have collected data from 3 to 5 pictures, and measured 100 particles and 10 pore size for each particle. The resolution of the images is 300 × 326 pixels per inch (ppi).

Before the SEM analysis, cured particles are washed with petroleum ether for 5–6 times to remove the remained silicon oil. The NaOH etched particles are washed with ethanol and DI water for 5 times before transferred onto the conducted tape. To increase the conductivity of the particles for SEM measurement, the particles are all coated with a layer of Pt.

3. Results and discussion

We design and fabricate a variant of the T-junction microfluidics to generate sucrose-containing aqueous droplets in a continuous oil phase. As shown in Fig. 1A, carbon/silica precursors, DI water, and HCl solutions are injected from three independent inlets and form aqueous drops in an oil phase. Here, DI water acts as the buffer to prevent the precursors and HCl reacting before the droplet formation. Immediately after the formation of droplets, they appear as coffee beans with three aqueous reagents stratifying from each other. As the drops go through the serpentine mixing channel, the stratified coffee beans turn to homogeneous white beans, implying that the reagents inside the droplets have mixed well with each other. The whole mixing process is conducted on-chip and completed in tens of milliseconds. The rationale of using on-chip mixing is that the hydrolysis process of the precursor solution is very rapid. Consequently, if HCl and the precursor solution are mixed off-chip, gelation will occur rapidly, resulting in a high viscous solution. Formation of emulsion drops using such solution as the disperse phase will be extremely difficult. In addition, mixing of HCl, DI water, and the precursor solution “on-chip” can provide an *in-situ* capability to tune the ratio between the reactants, which is not accessible to other non-microfluidic approaches or bulk reactions.

The obtained drops are then collected and heated at 70 °C or 80 °C to produce solid particles. Fig. 1A-I and A-II are images of collected drops and solidified particles after heating, respectively. Fig. 1A-III shows the polydispersity of the particles. The polydispersity index (PDI) calculated based on the expression of $PDI = (D_{max} - D_{min})/D_{avg}$ where D_{max} is the maximum diameter of the statistic particles, D_{min} is the minimum diameter of the statistic particles, and D_{avg} is the average diameter of the particles, is about

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