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A general approach towards hierarchical porous carbon particles

J. Eric Hampsey, Qingyuan Hu, Lynn Rice, Jiebin Pang, Zhiwang Wu and Yunfeng Lu*

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A general, aerosol-based, one-step approach was explored to synthesize microporous and mesoporous spherical carbon particles with highly porous foam-like structures from aqueous sucrose solutions containing colloidal silica particles and/or silicate cluster templates.

Mesoporous carbon particles are of great interest in column packing, filler, hydrogen storage, supercapacitors, catalyst supports, and other applications.[1] One frequently used technique to synthesize these porous carbon materials is a two-step templating approach, which involves infiltration of carbon precursor molecules into the pores of a preformed inorganic framework (*e.g.*, mesoporous silica), carbonization of the precursor, and removal of the inorganic template. To date, mesoporous carbon particles with rod, fiber, plate, and donut-like morphologies were prepared by using mesoporous silica templates with the corresponding geometric shapes.[2] Spherical carbon particles such as hollow mesoporous particles and microporous nanospheres have also been synthesized from core–shell structured silica particle templates or a naphthalene derived pitch, respectively. Recently, we reported the synthesis of spherical mesoporous carbon particles using mesoporous silica particle templates synthesized from an aerosol-assisted surfactant self-assembly process.[3]

Although this two-step templating technique allows for precise control of pore sizes and pore structures, it has several limitations such as incomplete infiltration of the carbon precursor, formation of nanoporous carbon on the exterior of the template, and requiring many tedious and time consuming infiltration steps. As an alternative approach, many researchers have focused on direct one-step methods that can eliminate the preformed template and tedious infiltration steps. For example, mesoporous carbons can be synthesized by mixing silicates with carbon precursors resulting in silica/precursor gels, followed by carbonization of the precursor and removal of the silica template.[4] Other one-step techniques include carbonization of organic aerogels made from supercritical CO_2 drying and carbonization of polymers or polymeric mixtures made from a blend of carbonizing and pyrolyzing polymers.[5] These methods generally lead to the formation of porous carbon in the form of monoliths or powders. Direct synthesis of mesoporous carbon particles still remains challenging. Here, we report, for the first time, a general approach towards the synthesis of mesoporous carbon particles from sucrose and silica building blocks using a direct one-step aerosol process. As shown in Fig. 1, aqueous solutions of sucrose and silicate templates (*e.g.*, colloidal silica particles, silicate clusters, or their mixture) are sent through an atomizer using nitrogen as a carrier gas. The atomizer disperses the solution into aerosol droplets, which are then passed through a glass tube that is heated to 400 °C. Continuous solvent evaporation at the air/liquid interface of the aerosol droplet enriches the sucrose and silica, resulting in the formation of spherical silica/sucrose nanocomposite particles. The particles are then collected on a membrane filter in a press, and subsequent carbonization of the sucrose followed by silica removal results in the formation of spherical porous carbon particles.

This general approach allows for the precise control of pore structures by using different templates, as shown in Fig. 2. In route I, beginning with aerosol droplets containing sucrose and silicate clusters that are prepared by hydrolysis and condensation reactions of an alkoxysilane, nanocomposite particles with a bicontinuous structure are formed from the co-assembly of sucrose and silicate clusters. Subsequent carbonization followed by silica removal results in carbon particles with a microporous network

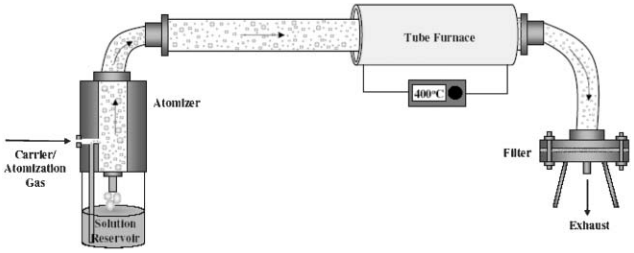


Fig. 1 Schematic of the aerosol process used to synthesize spherical porous carbon particles.

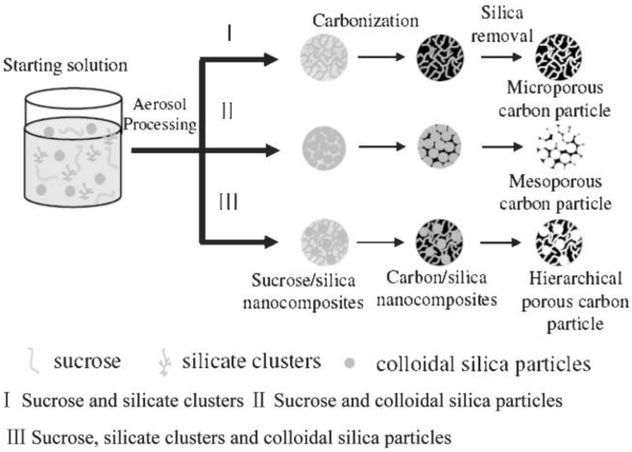


Fig. 2 Proposed formation of porous carbon particles with micro-, meso-, and hierarchical pore structures from aqueous solutions containing sucrose and silicate clusters and/or colloidal silica particles.

Department of Chemical and Biomolecular Engineering, Tulane University, New Orleans, LA 70118. E-mail: ylu@tulane.edu
*ylu@tulane.edu

templated by the silica network.[6] In route II, mesoporous carbon particles can be synthesized from a precursor solution containing sucrose and colloidal silica particles that are commercially available in different sizes and shapes. Route III assembles both colloidal silica particles and silicate clusters with sucrose and results in carbon particles with hierarchical bimodal pore structures (*i.e.* micropores templated by the silicate clusters and mesopores by the colloidal silica particles). This general approach provides an efficient, scalable route to continuously synthesize spherical, porous carbon particles with hierarchical pore structures and is suitable for manufacturing scale-up.

For the synthesis of microporous carbon particles, 4.2 g of tetraethyl orthosilicate (TEOS) was added to a solution of 5.5 g of ethanol, 2 g of 0.1 M HCl, and 10 g deionized water. After stirring for 30 minutes, 1.8 g of sucrose was added until completely dissolved. The solution was then sent through the aerosol atomizer (TSI model 3076) to produce aerosol droplets using 40 psi nitrogen as the carrier gas. The resulting particles were heated to 900 °C at a rate of 3 °C min^{-1} and held for 4 h under nitrogen flow. A black powder was then collected and immersed in a 5 M NaOH solution and stirred for 48 h. The solution was then filtered, rinsed several times with deionized water, and dried in an oven at 100 °C. For the synthesis of bimodal carbon particles, 0.6 g of colloidal silica solution (20–30 nm diameter, 50% silica) was added to the above formulation and the subsequent steps were repeated. In the synthesis of the highly porous carbon particles, 2–3 g of sucrose and 4 g of colloidal silica solution were added to 10 mL of 0.1 M HCl until completely dissolved, and the same subsequent steps were repeated. The samples were characterized using field emission scanning electron microscopy (FESEM, LEO 1550 VP operated at 10 kV), transmission electron microscopy (TEM, JEOL 2011 operated at 120 kV), and nitrogen sorption techniques (Micromeritics ASAP 2010 operated at 77K).

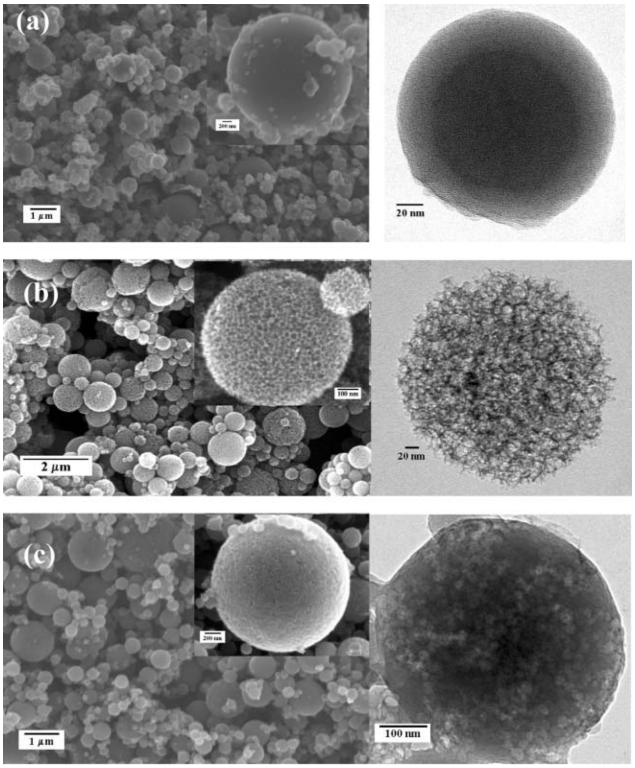
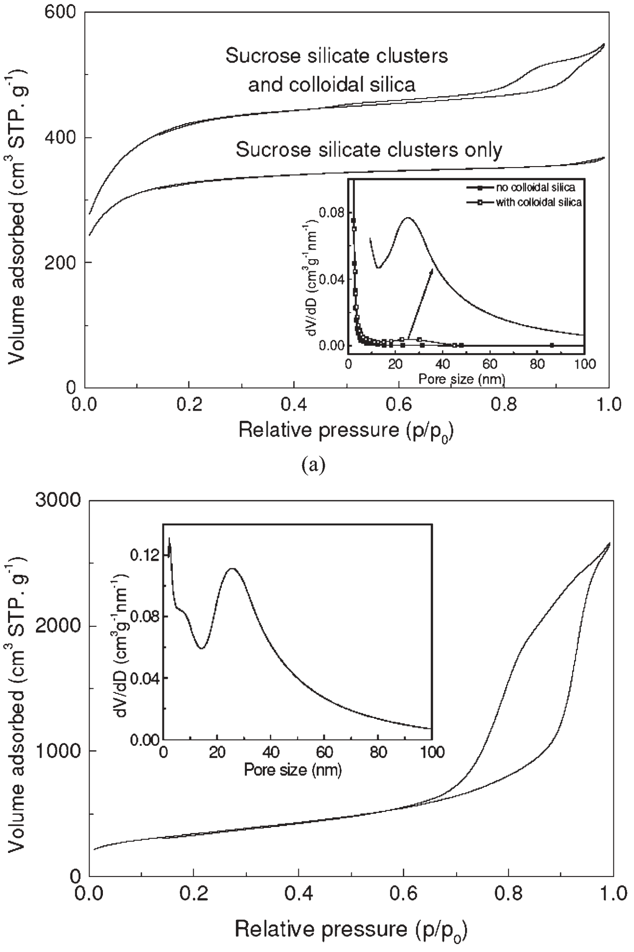


Fig. 3 Representative FESEM (left) and TEM (right) images of porous carbon particles synthesized by a general aerosol approach: (a) microporous carbon particles templated from silicate clusters, (b) highly porous mesoporous carbon particles templated from 20–30 nm colloidal silica particles, and (c) hierarchical bimodal carbon particles templated from silicate clusters and 20–30 nm colloidal silica particles.

Fig. 3 shows representative field emission scanning electron micrographs (FESEM) and transmission electron micrographs (TEM) of carbon particles synthesized using this general approach. As seen in the images, the aggregated particles are spherical in morphology with polydisperse particles sizes that range from less than 50 nm to greater than 1 μm. Monodisperse particles with diameters in the micron range can also be achieved using a Vibrating Orifice Aerosol Generator (VOAG) instead of the general atomizer used in these experiments.[7] Fig. 3a shows carbon particles assembled from sucrose and silicate clusters formed from the hydrolysis and condensation of TEOS. These particles have a smooth surface morphology with no visible large pores or defects as seen in the FESEM image (left) and a microporous structure as seen in the TEM image (right). The microporous structure is templated from the silica network formed by the condensation of the silicate clusters.[6] In Fig. 3b, solutions containing sucrose and colloidal silica particles are used in the synthesis of the carbon particles. A highly porous sponge- or foam-like pore structure with 20–30 nm mesopores sizes is observed in both the SEM (left) and TEM (right) images. This unique pore structure results from the removal of the colloidal silica particles uniformly distributed within the carbon framework. Fig. 3c displays the carbon particles assembled from sucrose, silicate clusters, and 20–30 nm colloidal silica particles. As shown in the SEM image (left), the carbon particles exhibit a rough surface morphology with large pores templated from the colloidal silica particles. The TEM image (right) clearly shows the formation of carbon particles with bimodal pore sizes. The large pore diameters are around 20–30 nm, consistent with the sizes of the silica particles added.

The porosity of the carbon particles was characterized using a nitrogen sorption technique. Nitrogen adsorption–desorption isotherms and the resulting pore size distributions are shown in Fig. 4. The particles assembled with sucrose and silicate clusters only (bottom curve in Fig. 4a) display a typical type I isotherm indicating a microporous structure. The calculated BET surface area and pore volume is 1121.0 m^2 g^{-1} and 0.56 cm^3 g^{-1}, respectively. The particles also display a unimodal pore size distribution centered at approximately 20 Å (see inset of Fig. 4a). When sucrose, silicate clusters, and 20–30 nm colloidal silica particles are used in the starting solution (top curve of Fig. 4a), the resulting carbon particles display an isotherm with two uptake steps. The first adsorption step at a relative pressure below 0.2 is contributed by the micropores templated from the silica network and the second adsorption step at a relative pressure above 0.9 is contributed by the mesopores templated the colloidal silica particles. The resulting pore size distribution of the particles also shows a bimodal distribution centered as approximately 20 Å and 250 Å. Such a bimodal pore structure is advantageous for applications that require rapid mass transport or pore accessibility to larger molecules. The calculated BET surface area and pore volume of the bimodal carbon particles is 1478.5 m^2 g^{-1} and 0.83 cm^3 g^{-1}, respectively.



(a)

(b)

Fig. 4 Nitrogen adsorption–desorption isotherms and pore size distribution (insets) of carbon particles synthesized from various amounts of sucrose, silicate clusters, and colloidal silica particles: (a) particle synthesized with silicate clusters and (b) particles synthesized without silicate clusters. The pore size distribution was derived from the adsorption branch.

The adsorption–desorption isotherms and resulting pore size distribution of the carbon particles synthesized from only sucrose and 20–30 nm colloidal silica particles are displayed in Fig. 4b. The isotherms are similar to type IV isotherms with a hysteresis in the desorption loop and a steep adsorption step at a relative pressure of 0.9. The non-parallel hysteresis reflects a non-uniform pore connectivity that is due to the nature of a collodal-silica-based templating approach. The resulting pore size distribution also has a narrow unimodal pore size distribution centered at 25 nm (see inset in Fig. 4b), which is consistent with the size of the colloidal silica template. The pore size distribution also show the presence of smaller pores that may be created during the carbonization of the precursors. The particles exhibit a BET surface area of 1219.4 m^2 g^{-1} and an extremely high pore volume of 4.01 cm^3 g^{-1}. Assuming the density of amorphous carbon to be ∼2.0 g cm^{-3} (ref. 8), the porosity of these foam-like carbon particles is calculated to be nearly 90%. Adding different amounts of colloidal silica particle templates can control the pore volume. For example, when the sucrose : silica starting weight ratio is increased to 1.5 : 1, the surface area increases to 1401.5 m^2 g^{-1} and the pore volume decreases to 3.71 cm^3 g^{-1} (data not shown). However, use of a high silica content may weaken the carbon framework and collapse the pore structure upon removal of the silica template. These highly porous carbon particles are very similar to carbon aerogels in surface area and pore volume.[9] However, aerogels are typically synthesized using an energy intensive supercritical drying process while these highly porous carbon particles are synthesized using the aerosol technique at ambient conditions.

In summary, we have demonstrated a general, aerosol-based, one-step approach to synthesize spherical porous carbon particles from aqueous sucrose solutions containing colloidal silica particles and/or silicate cluster templates. Microporous and mesoporous carbon particles with highly porous foam-like structures are synthesized using silica clusters and colloidal silica particles as templates, respectively. A mixture of silicate cluster and colloidal silica particle templates leads to the formation of carbon particles with a hierarchical bimodal pore structure. The carbon particles have large surface areas (1121–1479 m^2 g^{-1}) and tunable pore volumes (0.6–4.0 cm^3 g^{-1}), depending on the amounts of templates used. This novel, general process provides carbon particles with controlled pore structures for applications such as adsorbents, column packing, nanocomposite fillers, hydrogen storage, and supercapacitors.

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