

## Nanostructured Carbons Prepared by Ultrasonic Spray Pyrolysis

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Activated carbon materials (ACMs) have important large-scale applications including water treatment, air purification, gas separations, and pollutant remediation. Current commercial ACMs are produced from coal and biomass (e.g., wood, nutshells, etc.) in a two-stage process: initial carbonization and subsequent activation (i.e., physical or chemical improvement of porosity), and typically have surface areas of 500–1500 m<sup>2</sup>/g.<sup>1</sup> There has been a recent surge in interest in new methods for making porous carbon materials with surface areas as high as 3000 m<sup>2</sup>/g. Carbonization of block copolymers<sup>2,3</sup> or resorcinol-formaldehyde resin aerogels<sup>4</sup> can produce ACMs with a variety of properties, although such starting materials are exceedingly expensive relative to most applications. Templating with silica<sup>5</sup> or zeolites<sup>6</sup> can yield high-surface-area materials with a narrow pore size distribution, but such ex situ templating methods are both expensive and inefficient, requiring tedious etching with HF or KOH to remove the template.<sup>7</sup>

Aerosol methods are well-suited for large-scale, continuous synthesis of materials<sup>8,9</sup> and have been applied to ACMs. The precursors reported for aerosol synthesis of ACMs have included block copolymers,<sup>10</sup> sucrose with silicate templates,<sup>11</sup> or in situ salt templates formed from the decomposition of alkali carboxylates,<sup>12</sup> but again these precursors are expensive or cumbersome.

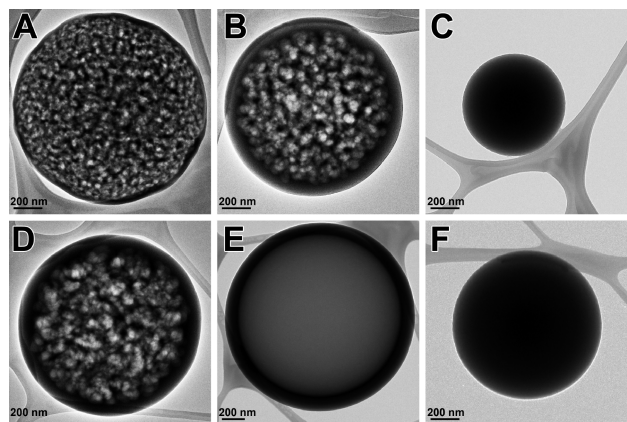
Here, we present a facile synthesis of a new class of ACMs using ultrasonic spray pyrolysis (USP) of low-cost, environmentally friendly materials without the use of a sacrificial template. An aqueous solution containing sucrose and sodium carbonate or bicarbonate is ultrasonically nebulized and a flow of argon carries the droplets through a heated tubular reactor where solvent evaporation and precursor decomposition occur. The pyrolysis product is collected in a series of water bubblers at the reactor outlet where the salt byproduct dissolves leaving porous carbon. A schematic of the USP system is shown in the Supporting Information (Figure S1).

Sodium carbonate or bicarbonate in the precursor solution plays two important roles in the production of these carbon materials. First, the salt is a base catalyst for the decomposition of sucrose: spray pyrolysis of a sucrose-only solution does not produce carbon products because the residence time of the droplet in the reactor is too short for complete decomposition to occur, even at high temperatures and decreased flow rates. Second, the gaseous decomposition products from the salt create high porosity, i.e., they act as porogens in the carbon material. The TEM images in Figure 1 show that the morphology of the carbon products varies depending on the choice of salt and its concentration in the precursor solution; SEM and TEM images of the porous carbons before and after removal of the salt are presented in the Supporting Information, Figure S2. The surface area and pore structure of the carbons were studied by N<sub>2</sub> adsorption; Table 1 summarizes the total surface area (*S*<sub>BET</sub>), micropore surface area (*S*<sub>mic</sub>), total pore volume (*V*<sub>t</sub>), and micropore volume (*V*<sub>mic</sub>) for each carbon. When other basic salts (e.g., NaOH or KOH) are used to catalyze the

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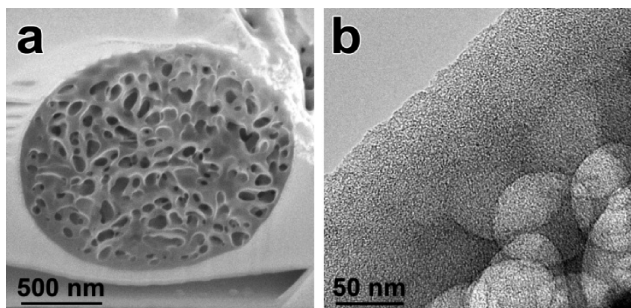


**Figure 1.** TEM images of carbons prepared by ultrasonic spray pyrolysis from 0.5 M sucrose and (A) 1.0 M  $\text{Na}_2\text{CO}_3$ , (B) 0.5 M  $\text{Na}_2\text{CO}_3$ , (C) 0.1 M  $\text{Na}_2\text{CO}_3$ , (D) 1.0 M  $\text{NaHCO}_3$ , (E) 0.5 M  $\text{NaHCO}_3$ , and (F) 0.1 M  $\text{NaHCO}_3$ . Furnace residence time is 9 s at 800 °C.

**Table 1. Surface Area and Pore Volume of Porous Carbons<sup>a</sup>**

porogen conc. (M)	code <sup>b</sup>	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$S_{\text{mic}}$ ( $\text{m}^2/\text{g}$ )	$V_{\text{t}}$ ( $\text{cm}^3/\text{g}$ )	$V_{\text{mic}}$ ( $\text{cm}^3/\text{g}$ )
$\text{Na}_2\text{CO}_3$					
1.0	A	540	350	0.50	0.16
0.5	B	710	540	0.39	0.24
0.1	C	350	300	0.17	0.13
$\text{NaHCO}_3$					
1.0	D	610	580	0.33	0.26
0.5	E	830	680	0.40	0.31
0.1	F	480	470	0.23	0.21

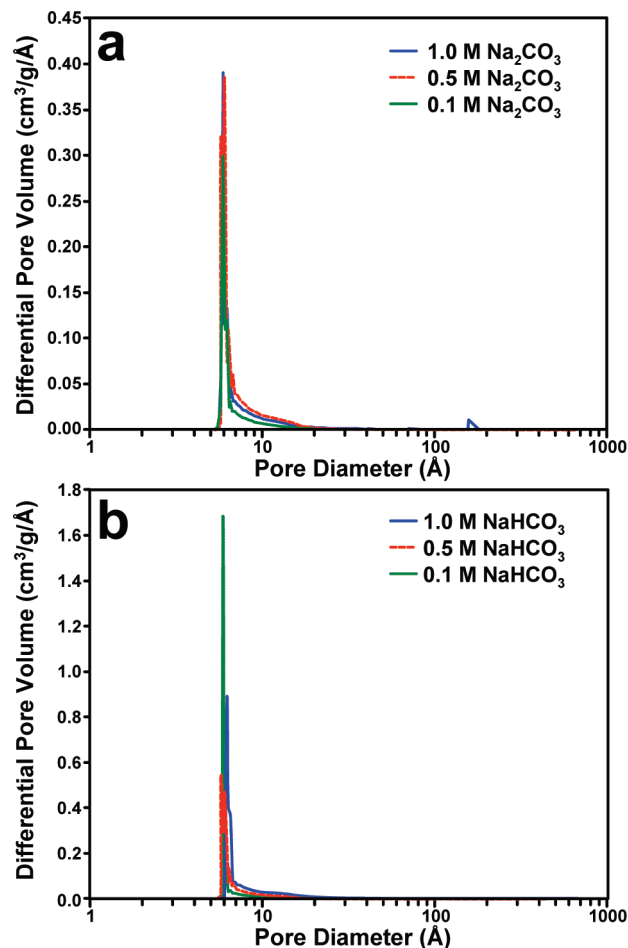
<sup>a</sup>  $S_{\text{BET}}$ , total surface area;  $S_{\text{mic}}$ , micropore surface area;  $V_{\text{t}}$ , total pore volume;  $V_{\text{mic}}$ , micropore volume. <sup>b</sup> Code designation corresponds to the images in Figure 1.



**Figure 2.** (a) Focused ion beam image of interior of 1.0 M  $\text{Na}_2\text{CO}_3$  product, and (b) TEM image of outer shell of 0.5 M  $\text{Na}_2\text{CO}_3$  product.

decomposition of sucrose and produce carbon materials, they do not yield any gaseous decomposition products to create the internal pores and the resulting carbons do not have the hollow interior morphology (see the Supporting Information, Figure S3).

Carbons prepared from 1.0 or 0.5 M  $\text{Na}_2\text{CO}_3$  or 1.0 M  $\text{NaHCO}_3$  (Carbons A, B, and D, respectively) have an outer shell and a macroporous interior (Figure 1A–B, D). Hierarchical pore structure is revealed by further investigation of the morphology: focused ion beam etching reveals the spongelike nature of the internal macropores and high-resolution TEM shows the microporous fine-structure of the outer shell of Carbon A (Figure 2).



**Figure 3.** Pore size distributions of porous carbons prepared from USP of (a) 0.5 M sucrose plus  $\text{Na}_2\text{CO}_3$  and (b) 0.5 M sucrose plus  $\text{NaHCO}_3$ , as labeled.

Carbons B and D have a thicker shell than Carbon A (100 nm, 100 nm, and 30 nm, respectively) and a higher surface area, suggesting that the majority of the surface area comes from the microporosity of the shell. The walls of the internal pores may also contribute to the total surface area. The type IV isotherms displayed by these carbons (see the Supporting Information, Figure S4) show that gas is able to permeate the outer shell. The carbon prepared from 0.1 M  $\text{Na}_2\text{CO}_3$  or 0.1 M  $\text{NaHCO}_3$  (Carbons C and F, respectively) appear solid under TEM (Figure 1C, F), but the substantial surface areas indicate that they are in fact microporous.

The carbon products prepared from 0.5 M  $\text{NaHCO}_3$  (Carbon E) are hollow shells approximately 100 nm thick (Figure 1E). These carbons have the highest surface area, further supporting the idea that the majority of the surface area of these carbons comes from the microporosity of the outer shell.

All of the carbons have very narrow pore size distributions, with the majority of the pores being  $< 10$  Å in diameter (Figure 3). It is unusual to obtain such narrow

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distributions in porous carbons, which are generally only observed in carbon materials created from templating methods (e.g., carbonization of zeolites).<sup>7a</sup>

FTIR spectra of the carbons are typical of ACMs,<sup>13</sup> and show the expected oxygenate functionalities (see the Supporting Information, Figure S5). Powder XRD shows these carbon materials to be amorphous both before and after annealing at 900 °C (see the Supporting Information, Figure S6).

The order of the decomposition of the sucrose/carbonate precursor (as shown in TGA studies, see the Supporting Information, Figure S7) can explain the origins of the observed morphology. After solvent evaporation is completed, sucrose is the first component to decompose (~200 °C) and evolves CO, CO<sub>2</sub>, H<sub>2</sub>, and H<sub>2</sub>O vapor,<sup>14</sup> leaving a composite of carbon and Na<sub>2</sub>CO<sub>3</sub>, with some likely porosity at this stage from the sucrose derived gases. As heating continues, the Na<sub>2</sub>CO<sub>3</sub> will then decompose and evolve CO<sub>2</sub> (which has been shown<sup>15</sup> to occur around 400 °C in the presence of H<sub>2</sub>O), and the release of the CO<sub>2</sub> creates additional porosity in the resulting carbon material. The Na<sub>2</sub>O byproduct is easily washed away (as aqueous NaOH) in the water bubblers, leaving the final ACM. If bicarbonate is used in place of carbonate, it will first decompose at ~60 °C to form Na<sub>2</sub>CO<sub>3</sub>, CO<sub>2</sub>, and H<sub>2</sub>O, and the same scheme then follows.

The internal porosity is created both from the evolution of gases (notably CO<sub>2</sub>, but also those from decomposition of the sucrose) and from the eventual removal of the temporary salt template. As the concentration of Na<sub>2</sub>CO<sub>3</sub> in the precursor mixture is decreased, the particle size decreases because less CO<sub>2</sub> is being evolved and therefore less expansion of the carbon results. When the Na<sub>2</sub>CO<sub>3</sub> concentration is decreased to 0.1 M (Carbons C and F), there are no internal macropores formed because the amount of Na<sub>2</sub>CO<sub>3</sub> in the precursor is so small that the CO<sub>2</sub> evolved is small in comparison to the amount of carbon produced. The low carbonate carbons C and F

still have significant surface area because of the microporosity created from the escape of gaseous products from the decomposition of sucrose. This suggests that shell porosity derives mostly from the decomposition of sucrose, whereas core porosity derives from the decomposition of the carbonate.

If the same precursors are decomposed in bulk, rather than as a spray, porous carbon monoliths are formed (see the Supporting Information, Figure S8) with variable surface areas and no microspheres. The monolith is fragile and powders formed from it are nonuniform in size. The USP method is necessary for formation of the hollow shell morphology: ultrasonic nebulization creates micrometer-sized droplets that act as microreactors and confine the decomposition gases within the spherical microparticle. Additionally, USP has the advantage of preparing a nonagglomerated powder as opposed to the monolith formed by thermal decomposition.

We have shown that nanostructured carbon materials can be produced from simple precursors such as sucrose and sodium carbonate or bicarbonate using a facile, one-step USP process without the need for sacrificial templates. The high surface areas and unique hierarchical pore structures of these materials suggest that they may find use as adsorbents and catalyst supports. The hollow interior provides a low-density, free-flowing microsphere morphology that may prove especially useful for any applications requiring a fluidized bed reactor or packed chromatographic column.

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**Supporting Information Available:** A schematic of the USP setup and additional materials characterization (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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