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Simple silica-particle template synthesis of mesoporous carbons

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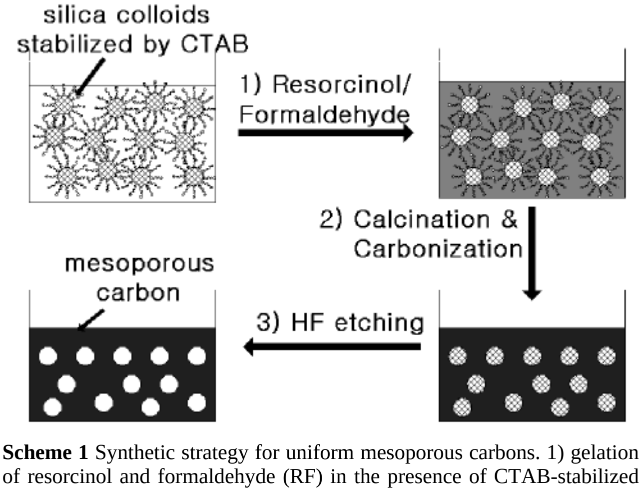
A simple preparative method for mesoporous carbons with high pore volumes using surfactant stabilized silica particles as templates is reported.

The synthesis of mesoporous M41S silica materials by Mobil researchers has stimulated explosive research on the preparation of inorganic porous materials through template approaches.[1] A large variety of mesoporous inorganic materials have been prepared using various types of organic templates including surfactant self-assemblies and block copolymers.[2] Uniform sized polymer latex spheres and emulsions have also been utilized to produce mesoporous inorganic materials with larger pores of >10 nm.[3]

Porous carbons have been extensively used as adsorbents in many separation and purification processes.[4] These porous carbons are generally microporous and the production of mesoporous carbons is extremely important for their applications in the separation and adsorption of bulky organic materials. Inorganic templates have been used to tune the pore size of carbon materials.[5] Recently, we have developed a new synthetic method to generate porous carbon materials with pores of >50 nm using commercial silica sol as a template.[6] Here, we report the fabrication of mesoporous carbon with narrow pore size distribution and high pore volume through surfactant stabilized silica particles as templates.

In previous work, we simply added carbon precursor, resorcinol and formaldehyde (RF) into Ludox HS-40 silica sol solution.[6] The resulting RF–silica composite was carbonized and etched with HF solution to obtain carbon materials with pores ranging in size from 10 to 60 nm [Fig. 1(a), dashed line]. The average particle size of HS-40 silica sol was reported to be 12 nm, and obviously the aggregates of silica particles are acting as templates. In order to obtain a more uniform pore size distribution, isolated silica particles stabilized by surfactant were applied as templates. The overall synthetic procedure is shown in Scheme 1. In a typical synthesis, 5 g of cetyltrimethylammonium bromide (CTAB) was added to 100 mL of an aqueous Ludox HS-40 silica sol solution (40 wt% silica with average particle size of 12 nm), and the mixture was stirred for 20 min at 50 °C, resulting in a muddy slurry. The stabilized silica particles were then collected by filtration under vacuum, and washed with double-distilled water to remove un-adsorbed surfactant. Resorcinol–formaldehyde gel (RF gel) was used as a carbon precursor.[7] A solution of 1 resorcinol: 2 formaldehyde: 0.014 Na_2CO_3 (catalyst): 5.62 H_2O with pH 7.3 was added dropwise under mild suction to be infiltrated into the CTAB-stabilized silica particles. The resulting yellow RF–silica composite was aged at 85 °C for three days to obtain a red RF gel–silica composite. The composite was carbonized at 850 °C for 3 h under nitrogen to yield a silica–carbon composite. To remove the silica template, the carbon–silica composite was stirred in 48 wt% aqueous HF solution for 12 h. The BET surface area was found to be 1512 $m^2\ g^{-1}$. The N_2 adsorption isotherm shown in the inset of Fig. 1(a) (continuous line) exhibited type IV behavior (hysteresis at high relative pressure), indicating the presence of mesopores. The BJH (Barrett–Joyner–Halenda) cumulative pore volume (corresponding to pores >2 nm) was extremely high (3.6 $cm^3\ g^{-1}$). The pore size distribution of the carbon material was narrow with an average pore size of 12 nm along with a shoulder around 15 nm [continuous line in Fig. 1(a)]. The overall pore size distribution is similar to the reported particle size distribution of Ludox HS-



Scheme 1 Synthetic strategy for uniform mesoporous carbons. 1) gelation of resorcinol and formaldehyde (RF) in the presence of CTAB-stabilized silica particles; 2) carbonization of RF gel–silica composite at 850 °C to obtain carbon–silica composite; HF etching of silica templates to obtain mesoporous carbons.

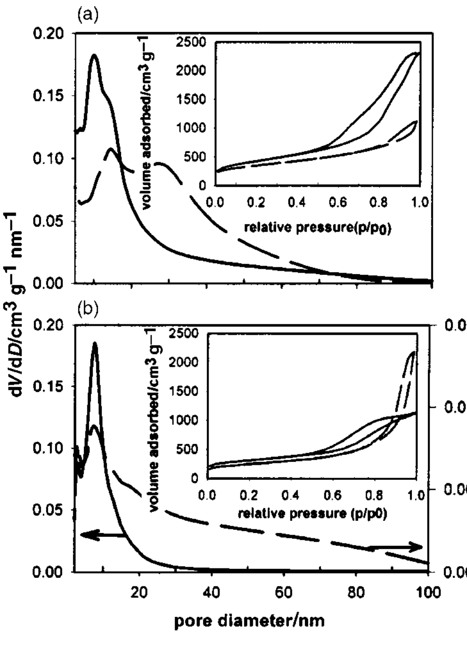


Fig. 1 The pore size distributions calculated from the adsorption branch of the nitrogen isotherm by the BJH method and the corresponding N_2 adsorption and desorption isotherms (insets) of mesoporous carbons. (a) (—) carbon prepared with CTAB-stabilized Ludox HS-40 silica sols as template and (----) carbon prepared with Ludox HS-40 silica sol aggregates as template. (b) (—) carbon prepared with CTAB-stabilized Ludox SM-30 silica sols as template and (----) carbon prepared with Ludox SM-30 silica sol aggregates as template. The isotherms were collected at 77 K on a Micrometrics ASAP2000 Gas Adsorption Analyzer after the carbon materials were degassed at 200 °C at 10 μTorr for 5 h.

30 silica sol (30 wt% silica).[8] By contrast, a carbon xerogel derived from the sol–gel polymerization of resorcinol–formaldehyde (RF) at pH 8 without silica templates was nearly non-porous. These results clearly demonstrate that the stabilized silica particles are acting as a true template for the formation of mesopores.

We have also produced carbon material using CTAB-stabilized Ludox SM-30 silica (30 wt% of silica with average particle size of 8 nm) particles as templates. The resulting carbon material revealed a very narrow pore size distribution centered at 8 nm [Fig. 1(b), continuous line]. The pore volume of the carbon material was high (1.69 $cm^3 g^{-1}$) and the BET surface area of the material was found to be 1089 $m^2 g^{-1}$. Carbon materials produced through SM-30 silica sol without a surfactant stabilization exhibited a relatively broad pore size distribution ranging from 8 to 100 nm [Fig. 1(b), dashed line]. Our present results demonstrate that uniform mesoporous carbons with pore size around 10 nm and very high pore volume can be easily fabricated by using surfactant-stabilized silica sol particles as templates.

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