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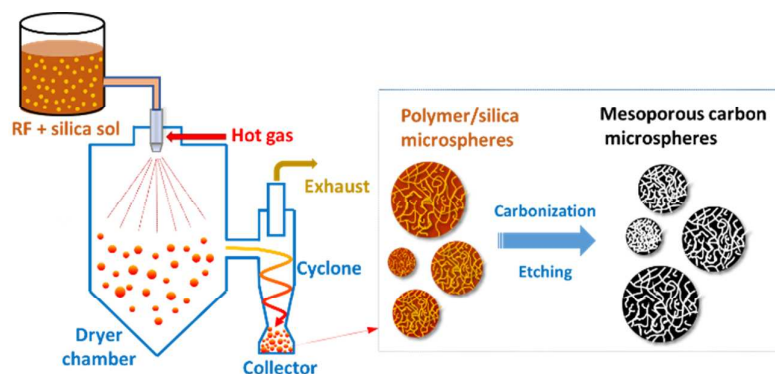
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Large-scale synthesis of mesoporous carbon microspheres with controllable structure and nitrogen doping using a spray drying method



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ARTICLE TYPE

Large-scale synthesis of mesoporous carbon microspheres with controllable structure and nitrogen doping using a spray drying method

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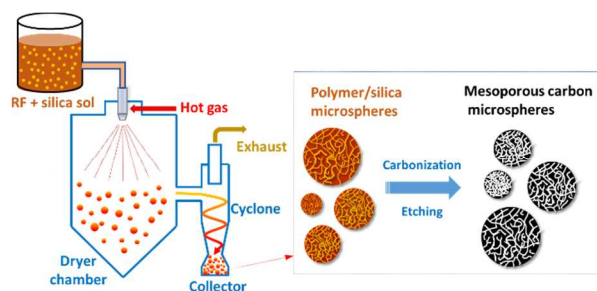
A low-cost and high-throughput spray drying method was developed to produce mesoporous carbon microspheres with controllable structure and nitrogen doping. The obtained microspheres have spherical morphology, controllable nitrogen doping (0-7 wt.%), high specific surface areas (900-1200 m²/g), large pore volumes (1-3 cm³/g), and large mesopores.

Mesoporous carbon materials have recently aroused great research interest due to their well-developed porous structure, good electronic conductivity and excellent thermal and chemical stability,^{1,2} which are extensively applied in gas adsorption and separation, catalysts and supports, and electrode materials.^{3,4} They can be prepared nowadays by the challenging combination of texture and functionality at different length scales.⁵ Interesting textures such as 3D porous structure⁶⁻⁸ and ordered or disordered channels can be generated within the mesoporous size range using the hard templating^{9,10} or self-assembly of block copolymer surfactants^{11,12}, as is well-known now.

However, the obtained mesoporous carbons are usually in the form of powders or irregular particles. The additional control of the morphology may widen the applicability of these materials, such as microspheres, for practical applications, because of their high stacking density, low flow resistance, good mechanical properties and facility in recovering.^{13,14} Recently, several strategies have been developed to synthesize mesoporous carbon microspheres (MCMs).¹⁵⁻¹⁹ For example in our previous work, carbon aerogel spheres were fabricated by an inverse phase suspension polymerization method, followed by supercritical drying and carbonization.¹⁵ In addition, we also prepared ordered mesoporous carbon spheres by an evaporation induced organic-organic self-assembly inside ethanol-in-oil emulsions.¹⁶ Unfortunately, the suspension approach generally generates spheres in the tens of micrometre range, which is too large that limits their electrochemical applications. By an aerosol-assisted evaporation induced self-assembly pathway, ordered mesoporous carbon spheres with much smaller particle diameters from 100 nm to 5 μm can be produced.¹⁷ Using a low-concentration hydrothermal route, highly ordered mesoporous carbon nanospheres can be obtained, however their yield was counted in terms of number of 'milligram'.¹⁸ By using a microfluidic device, uniform-sized carbon microspheres with diameters of several hundreds of microns were obtained.¹⁹ So far, the studies of MCMs are usually carried out as a kind of novel materials owing to the lack of an effective synthesis method with bulk production. As for the potential application of a newly developed

material, the production at large scale with low cost is the last bottleneck. It is highly essential to explore economical and high-throughput methods for the synthesis of MCMs for various applications.

Spray drying is the most widely used industrial process involving particle formation and drying.²⁰⁻²³ The basic idea of spray drying is the production of highly dispersed powders by spraying a particle precursor solution into a high-temperature chamber and removing the solvent from the formed liquid droplets.²⁴ Here, we report a spray-drying technique that can be exploited as a general method for the synthesis of mesoporous carbon particles, which could drastically reduce the production times and costs, and enables continuous and scalable synthesis. The key to our synthesis strategy lies in forming and heating atomized droplets of an aqueous solution containing the carbonaceous precursors and silica sols. This conceptually mimics the emulsions used by chemists to confine the synthesis of spherical materials, but does not require secondary immiscible solvents or surfactants. The resulting dried polymer/silica microspheres are robust and, following carbonization and silica removal, could afford well-dispersed MCMs.



Scheme 1. Formation process of the mesoporous carbon microspheres using the general spray drying strategy

As illustrated in Scheme 1, resorcinol and formaldehyde are firstly pre-polymerized in the presence of inorganic silica sol to generate polymer/silica mixture sol. Then the sol is fed with a peristaltic pump into a high-pressure gas enabled atomizer, in which the solution is atomized into small droplets with a high surface-to-mass ratio. The droplets are carried by a high-pressure air stream through a diffusion dryer at 120 °C, in which most of the water contained in the droplets is removed instantaneously. This process is continuous with a yield of 150 g per hour through a mini commercial spray dryer (90% yield), and can easily amplify on a large scale by an industrial instrument.

The obtained polymer/silica microspheres have a completely spherical shape, smooth surface, dense structure, and non-aggregation characteristics (Fig. 2a). The particle size of the dried microspheres prepared by spray drying method had a relatively narrow distribution from a few microns to ten microns (Fig. S1 EIS), with a mean geometric size of ca. 6.45 μm . It was found that the inlet temperature and precursor concentration are two important operating parameters to produce MCMSSs in the spray-drying process. It was indicated that hollow, mushroom-like deformed and crushed particles were formed when the drying temperature was up to 200 $^{\circ}\text{C}$ (Fig. S2). When high precursor concentration of 15 %w/v was employed, disrupted particles and aggregates were observed (Fig. S3). The other factors (gas flow, flow rate) were of little influence on the particle size and morphology. Thus, by controlling the parameters of the spray-drying method, one can prepare discrete microspheres with good sphericity and yield.

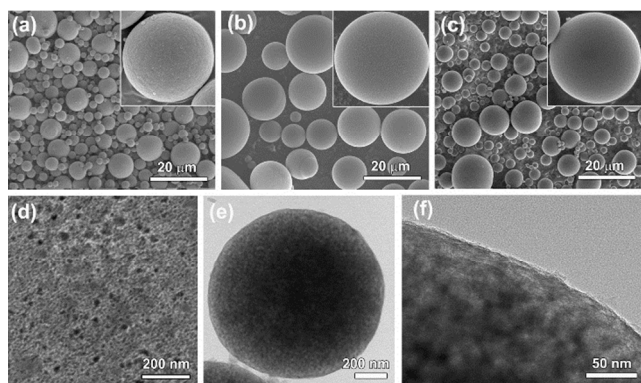


Fig. 1 Typical SEM images of polymer/silica microspheres (a), carbon/silica microspheres (b), mesoporous carbon microspheres (c) and the external surface of mesoporous carbon microspheres (d). TEM images of mesoporous carbon microspheres (e, f)

The obtained microspheres were treated under an N_2 atmosphere at 800 $^{\circ}\text{C}$ to obtain carbon/silica microspheres (Fig. 1b). After a removal of the silica template by NaOH etching, monodispersed carbon microspheres were obtained with discrete spherical morphology (Fig. 1c). The average diameter of the MCMSSs measured from dynamic laser diffraction measurement (DSL) is $\sim 4.7 \mu\text{m}$, a little smaller than that of the polymer/silica microspheres, due to the 21% shrinkage during the high-temperature pyrolysis and 13% shrinkage in silica removal process (Fig. S1). Fig. 1c-f shows the typical SEM image and TEM image of MCMSSs. The MCMSSs inherited well the spherical morphology from the polymer/silica microspheres and their surface have visible macropores and mesopores resulting from the template of silica nanoparticles or their aggregations. TEM image shows that the MCMSSs exhibited a three dimensional wormhole structure in which the pores are linked with each other.

The mesopores of MCMSSs are faithfully replicated from the colloid silica network, thus the pore size and pore volume of the MCMSSs can be freely controlled by controlling the shape, size and/or content of commercially available silica sols to be used.^{25,26} Here we demonstrated that using three kinds of silica sols (7 nm, Ludox SM-30; 12 nm Ludox HS-40; 22 nm, Ludox TM-40) as templates allowed us to prepare MCMSSs with different mesopore sizes. As shown in Fig. 2a, the N_2 adsorption-desorption isotherms of the MCMSSs show a typical IV behaviour with a pronounced H2 hysteresis loop indicating a developed mesoporous structure. The BJH pore size distribution curves (Fig. S) further confirm that the MCMSS-7 (using Ludox SM-30 as templates) and MCMSS-12 (using Ludox HS-40 as templates)

have very uniform mesopore sizes of 7 and 12 nm, respectively, agrees well with the dimensions of the isolated silica nanoparticles. The pore size distribution of MCMSS-22 (using Ludox TM-40 as templates), on the other hand, is very broad, demonstrating that some silica particles are agglomerated together. Furthermore, the porosity of the MCMSSs can also be easily adjusted using different amounts of the Ludox precursor (Fig. 2b). With increasing silica sol contents, the resulting carbons exhibited higher surface area and larger pore volume. The detailed pore structure parameters of each sample are listed in Table S1 in the Supporting Information. Typically, the BET surface areas and pore volume can be easily turned in a relatively wide range of 900- 1200 m^2/g and 1.5-3 cm^3/g , respectively, depending on the kind, size and content of silica sol used. All these MCMSSs have considerable open macropores and mesopores on their external surface (Fig. 2c), facilitating the mass transport of the molecules.

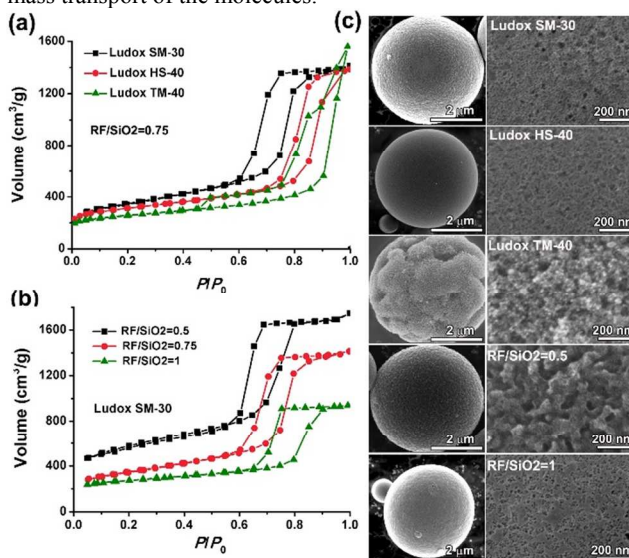


Fig. 2 N_2 adsorption-desorption isotherms of pore size-series (a) and pore volume-series (b) MCMSSs. SEM images of the MCMSSs with different mesoporous structures (c)

Elements in the third or fifth group are usually used as the doping atoms, such as nitrogen atoms into carbon framework, which could alter chemical stability, surface polarity, electric conductivity, and electron-donor properties.²⁷ In this spray drying strategy, nitrogen-doped MCMSSs can be easily prepared by using nitrogen-rich polymer precursors. Herein, melamine was added into resorcinol-formaldehyde system whose nitrogen atoms could be partially inherited to carbon framework.²⁸ This gave rise to rich surface chemistry of N-doped MCMSSs as compared with resorcinol-formaldehyde based MCMSSs having only carbon, hydrogen and oxygen. Except the mesostructure and morphology can be well controlled (Fig. 3c and Fig. S5), the nitrogen content can be easily adjusted by changing the mole ratio of melamine to resorcinol (M/R) in the precursors. As shown in Table S2, the elemental analysis result reveal that about 3.2 and 6.2 wt% nitrogen atoms could be doped into MCMSSs while the M/R ratio is 0.5 and 1, respectively. The X-ray photoelectron spectroscopy (XPS) technique was further used to investigate the chemical nature of the N-doped MCMSSs. In the range of XPS sensitivity, only carbon, nitrogen, and oxygen are detected in the survey scans (Fig. 3a), thus excluding the presence of impurities. The N1s spectra provide the relative atomic ratios of N species (pyridinic N, 398.7 \pm 0.3; pyrrolic N, 400.3 \pm 0.3; graphitic N, 401.4 \pm 0.5 eV, pyridine-N-oxide, 403-403 eV)²⁸. As shown in

Fig. 3b and Table S3, the basic N atoms (pyridinic N and pyrrolic N) are the dominant form representing around 60 %, while graphitic N contribute to ca. 25 %.

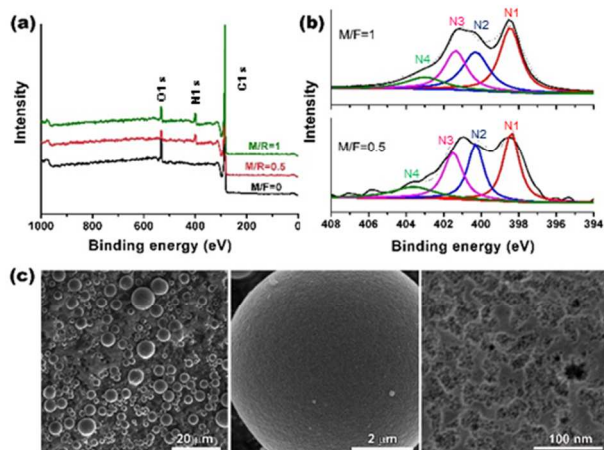


Fig. 3 XPS survey (a) and high-resolution N1s spectra (b) of the MCMs with different M/R ratios. (c) SEM images of the N-doped MCMs with the M/R ratio of 0.5

The discrete spherical morphology and controllable structure of MCMs have considerable advantages in various applications, for example, bio-compound adsorption and in the manufacture of compact electrode films for electrochemical applications (batteries/supercapacitors). Here we give an example of vitamin B₁₂ (VB₁₂, molecular dimension ca. 1.4×1.8×1.1 nm) adsorption over MCMs. VB₁₂ deficiency generally relates to many diseases, thus there is a great interest in the development of a suitable method for their separation and purification.²⁹ Fig. 4 shows the equilibrium adsorption isotherms of VB₁₂ onto MCMs with different mesoporous structures. All isotherms are characterized by a sharp initial rise at lower final solution concentration, suggesting a high affinity between the VB₁₂ and the carbon surface, and slowly increases and reaches a plateau at higher final solution concentration. These isotherms basically obeyed a Langmuir-type isotherm, suggesting monomer coverage of VB₁₂ on the pore surface of the MCMs.³⁰ The equilibrium adsorption capacities of VB₁₂ on the MCMs are in the range of 300-500 mg/g (Table S4). Such high capacity are mainly attributed to their high surface area and numerous large mesopores pore volume. Moreover, it is found that for samples with similar pore sizes, the adsorption capacity increases generally with the increase of pore volume. And for samples with similar pore volumes, the adsorption capacity obviously decreases with the increase of mesopore size, due to stronger adsorption ability of smaller mesopore.

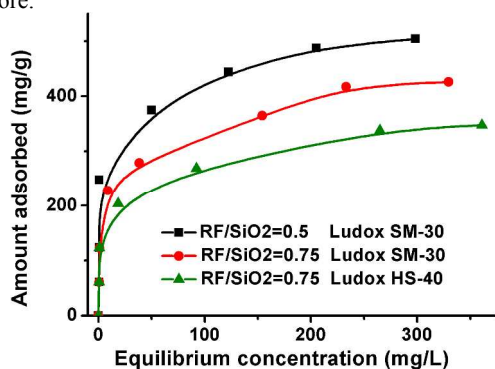


Fig. 4 The equilibrium adsorption isotherms of VB₁₂ onto MCMs with different mesoporous structures

In a conclusion, a spray-drying strategy has been developed for the synthesis of monodisperse mesoporous carbon microspheres. The obtained MCMs have uniform and discrete spherical morphology, controllable nitrogen doping (0-7 wt%), high specific surface areas (900-1200 m²/g), large pore volumes (1.5-3 cm³/g), and highly accessible large mesopores for VB₁₂ adsorption. Given the ever-expanding synthesis methods of mesoporous carbons and the effective morphological control offered by spray-drying, MCMs can now be prepared readily, rapidly and with control over their morphology, mesoporous structure and surface chemistry. This, in turn, should facilitate their development and exploitation for numerous applications, including catalysis, adsorption, electrode materials, drug delivery, packing materials for high performance liquid chromatography and so forth.

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Notes and references

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- † Electronic Supplementary Information (ESI) available: [Experimental details, SEM, DSL particle size distribution, CHN, XPS, N₂ adsorption and Pore size distribution results]. See DOI: 10.1039/b000000x/
- J. W. Lee, J. Kim, T. Hyeon, *Adv. Mater.*, 2006, **18**, 2073-2094.
 - T. Y. Ma, L. Liu, Z. Y. Yuan, *Chem. Soc. Rev.*, 2013, **42**, 3977-4003.
 - C. D. Liang, Z. J. Li, S. Dai, *Angew. Chem. Int. Ed.*, 2008, **47**, 3696-3717.
 - Y. P. Zhai, Y. Q. Dou, D. Y. Zhao, *Adv. Mater.*, 2011, **23**, 4828-4850.
 - A. H. Lu, F. Schuth, *Adv. Mater.*, 2006, **18**, 1793.
 - B. Xu, D. F. Zheng, M. Q. Jia, G. P. Cao, Y. S. Yang, *Electrochim. Acta*, 2013, **98**, 176-182.
 - Q. Li, R. R. Jiang, Y. Q. Dou, Z. X. Wu, T. Huang, D. Feng, J. P. Yang, A. S. Yu, D. Y. Zhao, *Carbon*, 2011, **49**, 1248-1257.
 - F. Yu, S. G. Ge, B. Li, G. Z. Sun, R. G. Mei, L. X. Zheng, *Curr. Inorg. Chem.*, 2012, **2**, 194-212.
 - R. Ryoo, S. H. Joo, S. Jun, *J. Phys. Chem. B*, 1999, **103**, 7743-7746.
 - H. F. Yang, D. Y. Zhao, *J. Mater. Chem.*, 2005, **15**, 1217-1231.
 - C. D. Liang, K. L. Hong, G. A. Guiochon, et al., *Angew. Chem. Int. Ed.*, 2004, **43**, 5785-5789.
 - Y. Meng, D. Gu, F. Q. Zhang et al., *Angew. Chem. Int. Ed.*, 2005, **44**, 7053-7059.
 - A. A. Deshmukh, S. D. Mhlanga, N. J. Coville, *Mater. Sci. Eng. R.*, 2010, **70**, 1-28.
 - Y. Wan, Y. Shi and D. Zhao, *Chem. Mater.*, 2008, **20**, 932.
 - D. H. Long, R. Zhang, W. M. Qiao, L. Zhang, X. Y. Liang and L. C. Ling, *J. Colloid Interface Sci.*, 2009, **331**, 40.
 - D. H. Long, F. Lu, R. Zhang, W. M. Qiao, L. Zhan, X. Y. Liang and L. C. Ling, *Chem. Commun.*, 2008, 2647.
 - Y. Yan, F. Zhang, Y. Meng, B. Tu and D. Zhao, *Chem. Commun.*, 2007, 2867.
 - Y. Fang, D. Gu, Z. X. Wu, F. Y. Li, R. C. Che, Y. H. Deng, B. Tu, D. Y. Zhao, *Angew. Chem. Int. Ed.*, 2010, **49**, 7987-7991.
 - Y. Liu, M. H. Ju, C. Q. Wang, L. X. Zhang, X. Q. Liu, *J. Mater. Chem.*, 2011, **21**, 15049-15056.
 - A. Gharsallaoui, G. Roudaut, O. Chambin, A. Voilley, R. Saurel, *Food Res. Int.*, 2007, **40**, 1107-1121.
 - R. Vehring, *Pharmaceut. Res.*, 2008, **25**, 999-1002.
 - F. Yu, J. J. Zhang, Y. F. Yang, G. Z. Song, *J. Power Sources*, 2010, **195**, 6873-6878.
 - F. Yu, J. J. Zhang, Y. F. Yang, G. Z. Song, *J. Mater. Chem.*, 2009, **19**, 9121-9125.
 - K. Okuyama, I. W. Lenggoro, *Chem. Eng. Sci.*, 2003, **58**, 537-547.
 - S. Han, T. Hyeon, *Chem. Commun.*, 1999, **19**, 1955-1956.

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- 26 S. Han, K. Lee, S. Oh, T. Hyeon, *Carbon*, 2003, **41**, 1049-1056.
- 27 W. Z. Shen, W. B. Fan, *J. Mater. Chem. A*, 2013, **1**, 999-1013.
- 28 H. C. Chen, F. G. Sun, J. T. Wang, W. C. Li, W. M. Q, L. C. Ling and D. H. Long, *J. Phys. Chem. C*, 2013, **117**, 8318-8328.
- 29 A. M. Ramos, M. Otero, A. E. Rodrigues, *Sep. Purif. Technol.*, 2004, **38**, 85-98.
- 30 A. Vinu, V. Murugesan, O. Tangermann, *Chem. Mater.*, 2004, **16**, 3056-3065.