

Homogeneous Incorporation of Metal Nanoparticles into Ordered Macroporous Carbons

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The synthesis of periodic macroporous solids¹ is currently an active area of research since materials of this type are being investigated for a range of applications including catalysis, separations, photonic crystals, and nanoelectronics. A common method for the preparation of three-dimensionally ordered macroporous solids utilizes close-packed arrays of monodisperse spheres (typically silica or polystyrene) as templates. In this approach, the interstitial regions of these colloidal crystals are infused with a reaction solution of the material that will eventually comprise the replicate structure. Once the composite has formed, the template is then removed, either chemically or thermally, yielding the macroporous replicate solid with periodic voids in the 0.1–1 μm size range. A variety of macroporous materials have been prepared by this method, including silica,² metal oxides,³ metals,⁴ carbon,⁵ and polymers.⁶ A promising extension of the template approach toward

ordered porous materials of higher complexity is the development of methods that allows one to tailor composition and porosity of the wall structure defining the macropores. Such an advance will be extremely important in the design of new ordered macroporous materials for catalysis, separations, and sensor applications.

In this communication, we present the first examples of ordered macroporous carbons (OMC) that contain distributions of metal ($M = \text{Co}, \text{Ni}, \text{Cu}$) nanoparticles. Our approach to the template-assisted preparation of these novel materials utilizes our recently developed sol–gel technique for the synthesis of metal-doped carbon aerogels.⁷ This technique, which involves the sol–gel polymerization of resorcinol derivatives containing ion-exchange moieties, was shown to be an effective method to uniformly incorporate metal ions into the aerogel matrix. For example, the base-catalyzed polymerization of formaldehyde with potassium salt of 2,4-dihydroxybenzoic acid produces a K^+ -doped hydrogel. The potassium ions in the hydrogel can then be replaced with the desired metal ion through ion exchange and the metal-doped hydrogels can then be processed and carbonized to generate a metal-doped carbon aerogel. We also noted that certain metal ions are reduced during the carbonization process, leading to the formation of nanometer-sized metallic particles that are distributed throughout the carbon matrix. When this same sol–gel technique is used, novel ordered porous carbons can be prepared that not only contain homogeneous distributions of metallic species but also possess a hierarchical pore structure due to the mesoporosity in the wall structure. This feature is important as the mesopores allow access to the metal particles and serve as interconnections between the large ordered macropores. To demonstrate the utility of this approach, this communication describes the synthesis and physical characterization of novel OMC containing Co, Ni, and Cu nanoparticles.

The synthesis of the metal-doped OMCs is summarized in Scheme 1. The colloidal crystal template was prepared by filtration of a dilute solution of monodisperse polystyrene (PS) particles (300 or 450 nm) through a narrow-pore membrane, resulting in the accumulation of 3-D ordered layers of the PS spheres on the membrane surface. An organic sol, produced from the base-catalyzed polymerization of potassium 2,4-dihydroxybenzoate with formaldehyde,⁸ was infused into the void

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(1) For recent reviews, see: (a) Kulinowski, K. M.; Jiang, P.; Vaswani H.; Colvin, V. L. *Adv. Mater.* **2000**, *12*, 833. (b) Stein, A. *Micropor. Mesopor. Mater.* **2001**, *44–45*, 227.

(2) (a) Velev, O. D.; Jede, T. A.; Lobo, R. F.; Lenhoff, A. M. *Nature* **1997**, *389*, 447. (b) Velev, O. D.; Jede, T. A.; Lobo, R. F.; Lenhoff, A. M. *Chem. Mater.* **1998**, *10*, 3597. (c) Holland, B. T.; Abrams, L.; Stein, A. *J. Am. Chem. Soc.* **1999**, *121*, 4308. (d) Holland, B. T.; Blanford, C. F.; Do, T.; Stein, A. *Chem. Mater.* **1999**, *11*, 795. (e) Zeng, F.; Sun, Z.; Wang, C.; Ren, B.; Liu, X.; Tong, Z. *Langmuir* **2002**, *18*, 9116. (f) Zhou, Y.; Yu, S. H.; Thomas, A.; Han, B. H. *Chem. Commun.* **2003**, 2662. (g) Gu, Z. Z.; Uetsuka, H.; Takahashi, K.; Nakajima, R.; Onishi, H.; Fujishima, A.; Sato, O. *Angew. Chem., Int. Ed.* **2003**, *42*, 894.

(3) (a) Holland, B. T.; Blanford, C. F.; Stein, A. *Science* **1998**, *281*, 538. (b) Wijnhoven, J. E.; Vos, W. L. *Science* **1998**, *281*, 802. (c) Yang, P.; Deng, T.; Zhao, D.; Feng, P.; Pine, D.; Chmelka, B. F.; Whitesides, G. M.; Stucky, G. D. *Science* **1998**, *282*, 2244. (d) Yan, H.; Blanford, C. F.; Holland, B. T.; Parent, M.; Smyrl, W. H.; Stein, A. *Chem. Mater.* **2000**, *12*, 1134. (e) Wijnhoven, J. E. G. J.; Bechger, L.; Vos, W. L. *Chem. Mater.* **2001**, *13*, 4486. (f) Carreon, M. A.; Gulians, V. V. *Chem. Mater.* **2002**, *14*, 2670. (g) Kuai, S.; Badilescu, S.; Bader, G.; Bruning, R.; Hu, X.; Truong, V. V. *Adv. Mater.* **2003**, *15*, 73. (h) Dong, W.; Bongard, H. J.; Marlow, F. *Chem. Mater.* **2003**, *15*, 568. (i) Wang, D.; Rogach, A. L.; Caruso, F. *Chem. Mater.* **2003**, *15*, 2724.

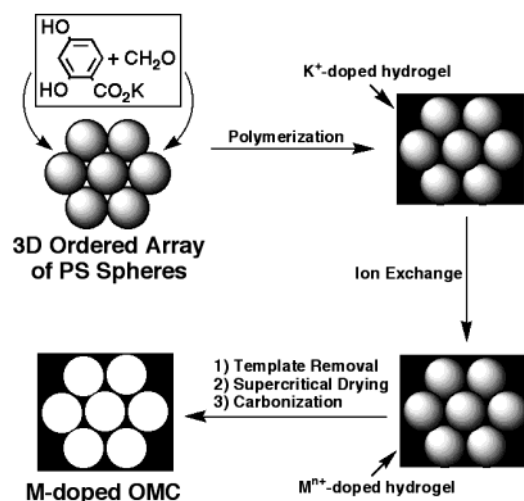
(4) (a) Jiang, P.; Cizeron, J.; Berone, J. F.; Colvin, V. L. *J. Am. Chem. Soc.* **1999**, *121*, 7957. (b) Velev, O. D.; Tessier, P. M.; Lenhoff, A. M.; Kaler, E. W. *Nature* **1999**, *401*, 548. (c) Yan, H.; Blanford, C. F.; Holland, B. T.; Parent, M.; Smyrl, W. H.; Stein, A. *Adv. Mater.* **1999**, *11*, 1003. (d) Xu, L.; Zhou, W. L.; Frommen, C.; Baughman, R. H.; Zakhidov, A. A.; Malkinski, L.; Wang, J. Q.; Wiley, J. B. *Chem. Commun.* **2000**, 997. (e) Yan, H.; Blanford, C. F.; Smyrl, W. H.; Stein, A. *Chem. Commun.* **2000**, 1477. (f) Wijnhoven, J. E. G. J.; Zevenhuizen, S. J. M.; Hendriks, M. A.; Vanmaekelbergh, D.; Kelly, J. J.; Vos, W. L. *Adv. Mater.* **2000**, *12*, 888. (g) Yan, H.; Blanford, C. F.; Lytle, J. C.; Carter, C. B.; Smyrl, W. H.; Stein, A. *Chem. Mater.* **2001**, *13*, 4314. (h) Bartlett, P. N.; Baumberg, J. J.; Birkin, P. R.; Ghanem, M. A.; Netti, M. C. *Chem. Mater.* **2002**, *14*, 2199. (i) Sumida, T.; Wada, Y.; Kitamura, T.; Yanagida, S. *Langmuir* **2002**, *18*, 3886. (j) Feng, M.; Puddephatt, R. J. *Chem. Mater.* **2003**, *15*, 2696.

(5) (a) Zakhidov, A. A.; Baughman, R. H.; Iqbal, Z.; Cui, C.; Khayrullin, I.; Dantas, S. O.; Marti, J.; Ralchenko, V. G. *Science* **1998**, *282*, 897. (b) Yu, J. S.; Yoon, S. B.; Chai, G. S. *Carbon* **2001**, *39*, 1421. (c) Yu, J. S.; Kang, S.; Yoon, S. B.; Chai, G. S. *J. Am. Chem. Soc.* **2002**, *124*, 9382. (d) Kang, S.; Yu, J. S.; Kruk, M.; Jaroniec, M. *Chem. Commun.* **2002**, 1670.

(6) (a) Park, S. H.; Xia, Y. *Chem. Mater.* **1998**, *10*, 1745. (b) Park, S. H.; Xia, Y. *Adv. Mater.* **1998**, *10*, 1045. (c) Johnson, S. A.; Ollivier, P. J.; Mallouk, T. E. *Science* **1999**, *283*, 963. (d) Jiang, P.; Hawang, K. S.; Mittleman, D. M.; Bertone, J. F.; Colvin, V. L. *J. Am. Chem. Soc.* **1999**, *121*, 11630. (e) Deutsch, M.; Vlasov, Y. A.; Norris, D. J. *Adv. Mater.* **2000**, *12*, 1176. (f) Qian, W.; Gu, Z. Z.; Fujishima, A.; Sato, O. *Langmuir* **2002**, *18*, 4526. (g) Yi, D. K.; Kim, D. Y. *Nano Lett.* **2003**, *3*, 207.

(7) Baumann, T. F.; Fox, G. A.; Satcher, J. H.; Yoshizawa, N.; Fu, R.; Dresselhaus, M. S. *Langmuir* **2002**, *18*, 7073.

Scheme 1. Preparation of Metal-Doped Ordered Macroporous Carbons



spaces of the template using filtration. After formation of the K^+ -doped hydrogel within the template, the resulting PS/sol-gel composite, isolated as thin monolithic disks, was soaked in a 0.1 M aqueous solution of $M(NO_3)_2$, where $M = Co^{2+}$, Ni^{2+} , or Cu^{2+} , for 48 h to exchange the potassium ions for the desired metal ion. The template was then dissolved from the M^{2+} -doped sol-gel replica using toluene. After solvent exchange with acetone, the sol-gel replica was dried using supercritical carbon dioxide ($T_c = 31.1^\circ C$, $P_c = 7.4$ MPa) to afford the metal-doped ordered macroporous organic aerogel. The metal-doped OMC was obtained through pyrolysis of the organic aerogel at $800^\circ C$ under nitrogen.⁹

Examination of the metal-doped OMCs by scanning electron microscopy (SEM) shows that their macropore structure consists of hexagonally ordered domains of spherical cavities with different crystal orientations, reflecting the symmetry of the original PS template. In the pre-carbonized samples, the sizes of the voids are close to the size of the original latex spheres, indicating that template removal through dissolution with toluene does not significantly perturb the overall void network. Following carbonization, the sizes of the macropores are 40–50% smaller than the sizes of the voids in the uncarbonized material (Figure 1a). The shrinkage of the ordered lattices in the carbon material is related to the carbonization process. During pyrolysis of organic aerogels, significant mass loss occurs, leading to volumetric shrinkage and densification in the resulting carbon aerogels.¹⁰ Interestingly, the shrinkage of the carbon matrix in the metal-doped OMCs occurs in a uniform fashion and does not alter the spherical shape of the

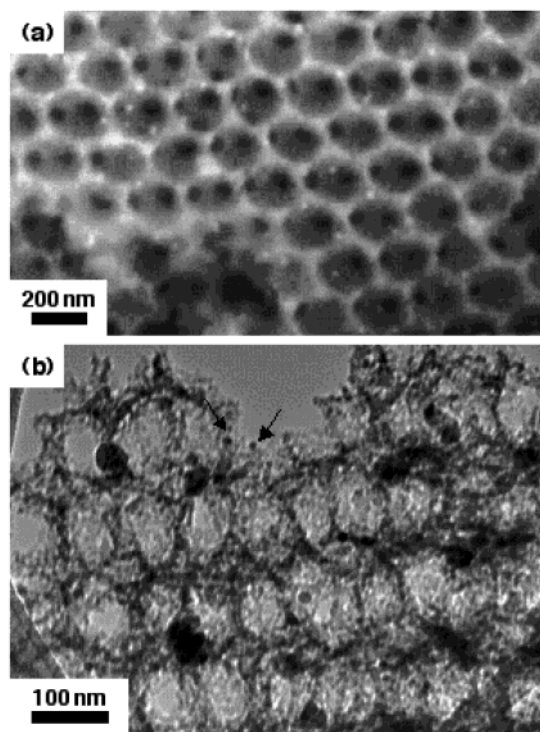


Figure 1. Micrographs of metal-doped OMCs: (a) an SEM image of a Co-doped OMC prepared using an ordered array of 450 nm PS spheres as a template and (b) a TEM image of a Ni-doped OMC prepared using an ordered array of 300 nm PS spheres as a template.

voids. The SEM images also show that the sol-gel material completely fills the void spaces between the PS spheres, resulting in the formation of volume-templated structures. Within each void are smaller circles that represent interconnections to neighboring spherical voids, similar to those observed in other replicate solids prepared using colloidal crystal templates.

The ordered macropore network is also clearly visible in the transmission electron micrographs of the metal-doped OMCs (Figure 1b). In addition, the TEM images reveal the dense networks of interconnected carbon particles that define the meso- and microporosity in the wall structure. This porosity is an important aspect of these materials since these mesopores provide access to the metal sites and serve as interconnections between the ordered macropores. The mesoporosity of the metal-doped OMCs was examined using nitrogen adsorption/desorption techniques. In general, these materials exhibited a nitrogen isotherm of Type II, consistent with a macroporous adsorbent.¹¹ The isotherms also show a hysteresis loop at higher relative pressures, a feature that is typically associated with capillary condensation within mesopores, indicating that textural mesoporosity exists within the wall structure. The average BJH pore diameter of the carbon matrix was 6 nm, giving rise to an average BET surface area of $530\text{ m}^2/\text{g}$.

The SEM and TEM images of the metal-doped OMCs show the presence of metal nanoparticles throughout the carbon framework, ranging in size from 5 to 60 nm.

(8) A suspension of 2,4-dihydroxybenzoic acid (1.45 g, 9.4 mmol) in distilled water (12 mL) was treated with K_2CO_3 (0.78 g, 4.7 mmol) with vigorous stirring. Once the acid was neutralized, formaldehyde (1.5 g, 18.8 mmol) was then added to the solution, followed by the catalyst, K_2CO_3 (37 mg, 0.26 mmol). Gelation of this particular sol-gel formulation typically occurs within 48 h at room temperature.

(9) Elemental analyses (wt %) for the M-doped OMCs: $M = Co$, C (83.19), H (<0.5), Co (9.93); $M = Ni$, C (81.61), H (<0.5), Ni (9.20); $M = Cu$, C (81.88), H (<0.5), Cu (9.57). Analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

(10) Pekala, R. W.; Alviso, C. T.; LeMay, J. D. In *Chemical Processing of Advanced Materials*; Hench, L. L., West, J. K., Eds.; J. Wiley & Sons: New York, 1992.

(11) Rouquerol, F.; Rouquerol, J.; Sing, K. *Adsorption by Powders and Porous Solids: Principles, Methodology and Applications*; Academic Press: London, 1999.

The metal particles are formed through reduction of the M^{2+} ions during pyrolysis of the organic aerogel since there are no visible metal particles or precipitated metal salts in the micrographs of the pre-carbonized metal-doped materials. While the larger metal particles are visible as bright spots in the SEM images (Figure 1a), the smaller nanoparticles can be seen dispersed throughout the carbon matrix in the TEM images, as indicated by the arrows in Figure 1b. The X-ray diffraction patterns of the metal-doped OMCs indicate that the metal particles have a cubic crystalline structure and that the crystallite size of the Co particles is smaller than those for the Ni and Cu particles.

This report describes the template-assisted synthesis of novel OMCs containing metal nanoparticles and a hierarchical pore structure. This approach is general and, as a result, can be used to prepare OMCs with a wide variety of metal species and different wall porosities. In addition, we noted from our work with the untemplated metal-doped carbon aerogels that we can control the size of the metal particles through the

carbonization temperature.¹² We are currently investigating the catalytic and transport properties of these ordered macroporous metal-doped carbon aerogels and the results will be the subject of a future report.

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Supporting Information Available: SEM image of a pre-carbonized metal-loaded ordered macroporous organic aerogel ($M = Ni^{2+}$), XRD patterns for the metal-doped OMCs, and a representative nitrogen adsorption/desorption isotherm for M-doped OMC ($M = Co$) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(12) Baumann, T. F.; Satcher, J. H.; Fu, R.; Dresselhaus, G.; Dresselhaus, M. S. *J. Non-Cryst. Solids* **2003**, submitted.