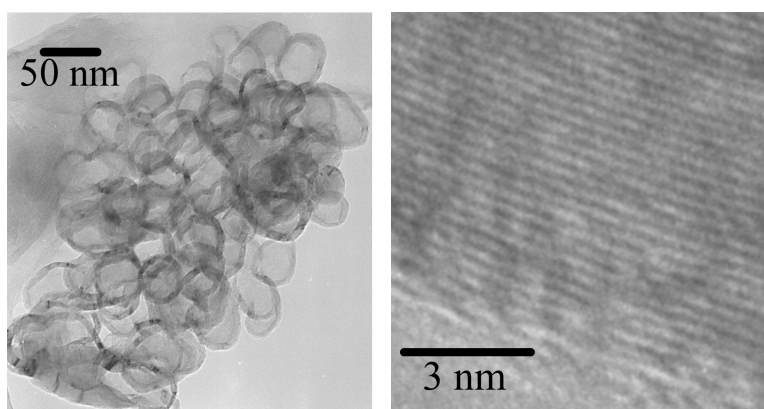Communication

A Novel Method for the Templated Synthesis of Homogeneous Samples of Hollow Carbon Nanospheres from Cellulose Chars

Andrew M. Herring, J. Thomas McKinnon, Bryan D. McCloskey, Jonathan Filley,
Keith W. Gneshin, Ryan A. Pavelka, Hans-Joachim Kleebe, and Darin J. Aldrich

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 8 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

A Novel Method for the Templated Synthesis of Homogeneous Samples of Hollow Carbon Nanospheres from Cellulose Chars

Andrew M. Herring,*,† J. Thomas McKinnon,† Bryan D. McCloskey,† Jonathan Filley,†
Keith W. Gneshin,† Ryan A. Pavelka,† Hans-Joachim Kleebe,‡ and Darin J. Aldrich‡

*Department of Chemical Engineering and Department of Metallurgical and Materials Engineering,
Colorado School of Mines, 1500 Illinois Street, Golden, Colorado 80401*

Received March 6, 2003; E-mail: aherring@mines.edu

Here, we report a novel method for the production of homogeneous samples of hollow carbon nanospheres, HCNS, from doped cellulose char in a three-step process: charring, high-temperature pyrolysis, and acid digestion. The spheres are derived via the template synthesis of an intermediate structure, a graphitic open Ni-core shell, ONCS. HCNS have been observed previously,[1] but not in readily available large quantities of high purity nor via a facile closure of an open graphitic structure under mild conditions.

There is an immense interest in the fabrication of new carbon-based nanomaterials with highly curved graphitic structures. The interest in these materials stems from their unique structural, mechanical, and electronic properties and hence their potential for use in important commercial products. These materials, which include the open and closed nanotubes, carbon onions, and graphitic nanocones, are mostly synthesized, in low yield, via laser vaporization, resistive heating, or arc discharge methods, usually under high vacuum.[2] Furthermore, the products of such syntheses are often heterogeneous and difficult to purify.[3] Novel methods for the fabrication of carbon nanoparticles are especially welcome if they can produce samples of both high purity and yield from readily available and inexpensive starting materials.

Cellulose is unique among biopolymers in that when it is charred below 400 °C and above its decomposition temperature of 280 °C it produces an aromatic structure in which domains of polycyclic aromatic hydrocarbon, PAH, anneal into larger ensembles containing five- and six-membered aromatic rings.[4] Other biopolymers such as pectin, xylan, and lignin, while producing chars containing aromatic structure, do not show this PAH annealing behavior to the same extent. The extensive hydrogen-bonding network between the decomposing cellulose strands almost certainly plays a part in this behavior. Aromatic and PAH molecules and carbon soot have been used to produce carbon nanoparticles, via catalyzed or templated routes.[5] These methods are not well understood, but are strongly influenced by the presence or absence of either a catalyst or a template species.

It would seem reasonable that we could influence the chemistry of cellulose charring by the addition of metal salts which could also act as a template for the charring material. Furthermore, these metal particles embedded in the char could influence any subsequent pyrolysis chemistry used to produce samples of carbon nanoparticles. The 3d transition metals are known for their efficient production of single- and multiwall nanotubes,[6] and so nickel was initially chosen. The amorphous carbon produced on charring cellulose becomes graphitic above 2000 °C.[7] We employed laser pyrolysis to rapidly pyrolyze the cellulose char and produce graphitic nanostructures. Carbon dioxide lasers operated at 10.6 μm in continuous-wave mode have been used to produce carbon nanotubes

Scheme 1. Preparation of Carbon Nanospheres from Nickel Chloride Doped Cellulose
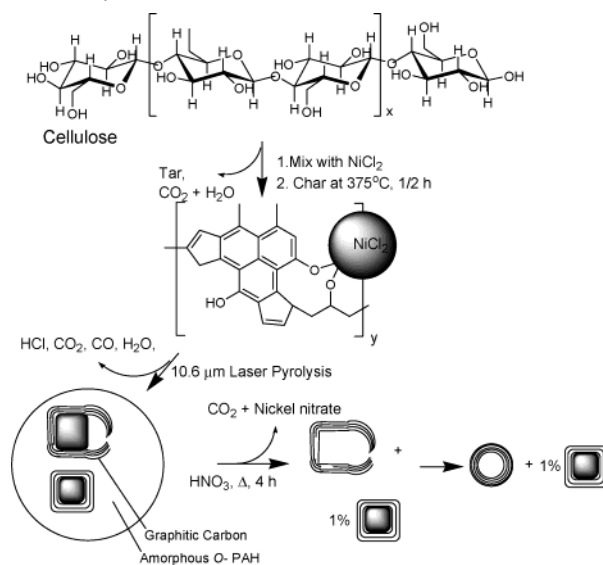
from graphite/bimetallic targets,[8] and this method would enable the easy scale-up of the process using a continuously fed char stream.

Avicel cellulose was ground with $NiCl_2 \cdot 6H_2O$ in a 4:1 ratio by weight and charred at 375 °C for 0.5 h, Scheme 1. The ground Avicel cellulose/nickel chloride powder is initially composed of nickel particles of ca. 30 μm; on charring the powdered mixture at 375 °C for 0.5 h, the nickel chloride is broken down into crystallites of 10−20 nm surrounded by an amorphous carbonaceous material, Figure 1a, which may be regarded as a continuum of oxygenated PAH, O-PAH.

The diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of this char, Figure S1, is very similar to that of undoped cellulose charred under identical conditions, Figure S2, with the exception that the ν(C=O) band, 1709 cm^{-1}, is reduced and a new sharp aromatic γ(CH) band appears at 764 cm^{-1}, indicating that the aromatic ring structure is less substituted than in pure cellulose char. As expected, the XRD pattern, Figure 2a, is of a mixture of $NiCl_2$ (confirmed by EDX analysis) Figure S3 and amorphous carbon.

This charred material was laser-pyrolyzed using a carbon dioxide laser with a power of 58.5 W, Scheme 1.[9] The temperatures achieved by this process are estimated to be 2250 °C, far in excess of the temperature of sublimation of anhydrous $NiCl_2$, 973 °C. The major products from this reaction at lower laser powers, 6.5 W, as detected by molecular beam mass spectroscopy are HCl, CO, and CO_2. A plausible reaction is that the $NiCl_{2(g)}$ would oxidize the amorphous O-PAH, producing carbon, Ni(0), and HCl; the CO and CO_2 are simply byproducts of pyrolysis of the char. At low laser
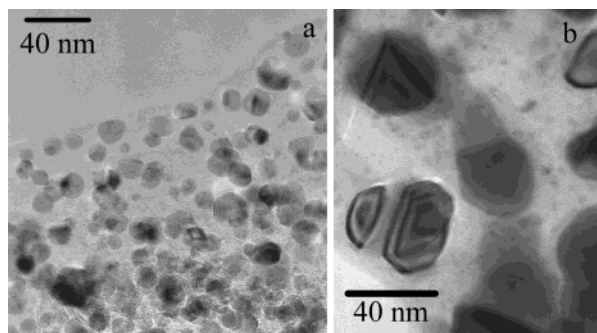
Figure 1. TEM images of 1:4 nickel chloride/cellulose (a) after charring for 0.5 h at 375 °C and (b) after laser pyrolysis of the resultant char.
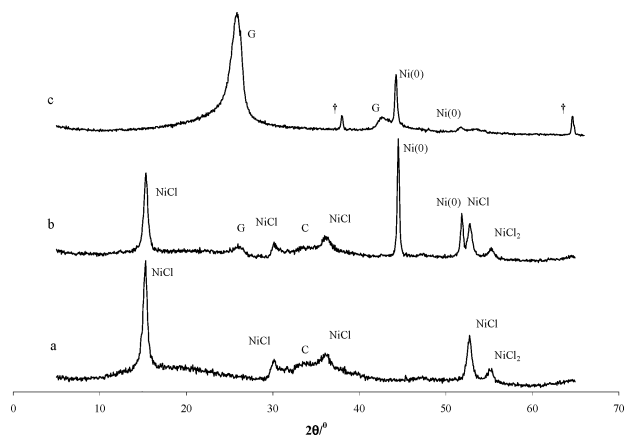

Figure 2. Normalized XRD patterns of (a) charred cellulose/NiCl$_2$, (b) laser pyrolyzed char, and (c) HNO$_3$ digested laser pyrolyzed char. C, amorphous carbon; G, graphitic carbon; †, unidentified phase.

powers, 6.5−50 W, this gray material is amorphous carbon containing intercalated Ni. This reaction at high laser power, 58.5 W, resulted in the appearance of new peaks in the XRD patterns assigned to nickel metal and graphitic carbon, Figure 2b. Examination of the material by TEM reveals 30 nm particles of pure Ni, confirmed by EDX analysis, Figure S4, surrounded by a 5−10 nm shell of graphitic carbon, Figure 1b; these graphite encapsulated Ni particles are surrounded by amorphous carbon. Each larger Ni particle formed is clearly the result of the reduction of several of the adjacent smaller NiCl$_2$ particles in the original char. Close examination of a number of the graphitic encapsulated Ni particles reveals that the majority of these structures comprise irregular graphitic ONCS, Figure S5, similar to initial growth models for nanotubes on Fe particles.[1a] This material was digested in refluxing concentrated nitric acid for 4 h, and the resultant material was washed in deionized water, yielding 100 mg of a black powder on drying.

Control experiments using pure Avicel cellulose and no metal salts, charred in a way identical to that of the metal doped material, produce no insoluble material after nitric acid digestion.

The XRD of the black powder, Figure 2c, is dominated by peaks assigned to graphitic carbon, some residual nickel metal, and a small amount of an as yet unidentified phase. The only impurities observed by TEM (approximately 1%) are HCNS filled with nickel metal. Line width analysis of the XRD using the Debye−Shearrer equation gives crystallite sizes for the graphite and Ni of 5.2 and 29.4 nm, respectively. Individual TEM imaging of random samples of this material from multigram batches have all revealed extremely homogeneous samples of clumps of 40−50 nm diameter HCNS with a wall thickness of 5 nm, Figure 3. The shells of the nanospheres are composed of highly ordered layers of up to 60 concentric curved graphitic sheets. The spacing of the graphite layers, 0.341 nm, correlates with a temperature of formation of 2250
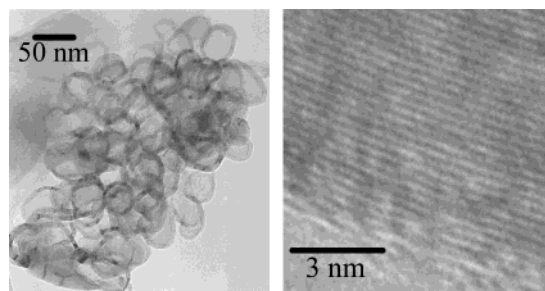
Figure 3. Representative TEM images of a group of hollow carbon nanospheres and details of one individual sphere.

°C.[10] The DRIFTS of this material reveals weak features assigned to surface carbonyl and hydroxyl, 1764 and 3181 cm^{-1}, Figure S6.

Previously, HCNS of different diameters have all been prepared at high temperature, by annealing Na-doped carbon onions or Fe-bearing nanoparticles at 1400 or 1100 °C, respectively, as well as by lasing carbon soot at temperatures well in excess of 1650 °C.[1] While the graphitic ONCS are formed at 2250 °C, the conversion to HCNS occurs at 120 °C in refluxing nitric acid. At this time, the detailed mechanism of the ONCS−HCNS conversion under these mild thermal conditions is not fully understood. The dissolution of exposed metallic nickel from the irregular graphitic ONCS is presumably a facile process. What is less well understood is the mechanism of conversion of the now-empty nanoshells to the lower energy closed spheres. Once formed, the HCNS are stable to the refluxing nitric acid as these structures possess no edge carbons,[1c] which would be expected to be oxidized under these conditions.[2] As the size of the ONCS will depend on the size of the NiCl$_2$ crystallites, the charring conditions, and the laser residence time, it should be possible to produce homogeneous samples of HCNS of controlled and varied sizes.

Supporting Information Available: DRIFTS of cellulose char, NiCl$_2$ doped cellulose char, and HCNS; TEM of representative ONCS and EDX analyses, Figures S1−6 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Hu, G.; Ma, D.; Cheng, M.; Liu, L.; Bao, X. *Chem. Commun.* **2001**, 8630. (b) Huo, H.; Schaper, A. K.; Weller, F.; Greiner, A. *Chem. Mater.* **2002**, *14*, 3990. (c) Vander Wal, R. L.; Tomasek, A. J.; Ticich, T. M. *Nano Lett.* **2003**, *3*, 223.

(2) (a) Iijima, S. *Nature* **1991**, *354*, 56. (b) Ugarte, D. *Nature* **1992**, *359*, 707. (c) Krishnan, A.; Dujardin, E.; Treacy, M. M. J.; Hugdahl, J.; Lynum, S.; Ebbesen, T. W. *Nature* **1997**, *388*, 451.

(3) Georgakilas, V.; Voulgaris, D.; Vázquez, E.; Prato, M.; Guldi, D. M.; Kukovecz, A.; Kuzmany, H. *J. Am. Chem. Soc.* **2002**, *124*, 14318.

(4) Herring, A. M.; McKinnon, J. T.; Petrick, D. E.; Gneshin, K. W.; Filley, J.; McCloskey, B. D. *J. Anal. Appl. Pyrolysis* **2003**, *66*, 165.

(5) (a) Boese, R.; Matzanger, A. J.; Volhardt, K. P. C. *J. Am. Chem. Soc.* **1997**, *119*, 2052. (b) Goel, A.; Hebgen, P.; Vander Sande, J. B.; Howard, J. B. *Carbon* **2002**, *40*, 177. (c) Hou, H.; Schaper, A. K.; Weller, F.; Greiner, A. *Chem. Mater.* **2002**, *14*, 3990. (d) Gherghel, L.; Kübel, C.; Lieser, G.; Räder, H.-J.; Müllen, K. *J. Am. Chem. Soc.* **2002**, *124*, 13130.

(6) Colomer, J.-F.; Bister, G.; Willems, I.; Kónya; Fonseca, A.; Van Tendeloo, G.; Nagy, J. B. *Chem. Commun.* **1999**, 1343.

(7) Kim, D.-Y.; Nishiyama, Y.; Wada, M.; Kuga, S. *Carbon* **2001**, *39*, 1051.

(8) Maser, W. K.; Munoz, E.; Beito, A. M.; Martinez, M. T.; de la Fuente, G. F.; Naniette, Y.; Anglaret, E.; Sauvajor, J.-l. *Chem. Phys. Lett.* **1998**, *292*, 587.

(9) The charring process and laser pyrolysis were performed under Ar$_{(g)}$ and He$_{(g)}$, respectively. Avicel (2.5 g) and nickel chloride (2.5 g) were ground together in a mortar and pestle and pressed into a 3 cm diameter circular pellet under 100 000 psi in a stainless steel die press. The pellet was subsequently charred for 0.5 h at 375 °C. The charred pellet was laser-pyrolyzed while being spun at 1.2 rpm in the path of a 2 mm diameter beam of 10.6 μm radiation, residence time, 1.2 s, produced by a Synrad duo-lase carbon dioxide laser operating at 58.5 W under 0.5 Torr of He$_{(g)}$.

(10) Mantel, C. *Carbon and Graphite Handbook*; Wiley and Sons: New York, 1968.

JA035031J