Video Article

Synthesis and Functionalization of Nitrogen-doped Carbon Nanotube Cups with Gold Nanoparticles as Cork Stoppers

Yong Zhao, Yifan Tang, Alexander Star

Department of Chemistry, University of Pittsburgh

Correspondence to: Alexander Star at astar@pitt.edu

URL: <http://www.jove.com/video/50383>

DOI: [doi:10.3791/50383](https://doi.org/10.3791/50383)

Keywords: Physics, Issue 75, Chemistry, Chemical Engineering, Materials Science, Physical Chemistry, Nanotechnology, Metal Nanoparticles, carbon nanotubes (synthesis and properties), carbon nanotubes, chemical vapor deposition, CVD, gold nanoparticles, probe-tip sonication, nitrogen-doped carbon nanotube cups, nanotubes, nanoparticles, nanomaterial, synthesis

Date Published: 5/13/2013

Citation: Zhao, Y., Tang, Y., Star, A. Synthesis and Functionalization of Nitrogen-doped Carbon Nanotube Cups with Gold Nanoparticles as Cork Stoppers. *J. Vis. Exp.* (75), e50383, doi:10.3791/50383 (2013).

Abstract

Nitrogen-doped carbon nanotubes consist of many cup-shaped graphitic compartments termed as nitrogen-doped carbon nanotube cups (NCNCs). These as-synthesized graphitic nanocups from chemical vapor deposition (CVD) method were stacked in a head-to-tail fashion held only through noncovalent interactions. Individual NCNCs can be isolated out of their stacking structure through a series of chemical and physical separation processes. First, as-synthesized NCNCs were oxidized in a mixture of strong acids to introduce oxygen-containing defects on the graphitic walls. The oxidized NCNCs were then processed using high-intensity probe-tip sonication which effectively separated the stacked NCNCs into individual graphitic nanocups. Owing to their abundant oxygen and nitrogen surface functionalities, the resulted individual NCNCs are highly hydrophilic and can be effectively functionalized with gold nanoparticles (GNPs), which preferentially fit in the opening of the cups as cork stoppers. These graphitic nanocups corked with GNPs may find promising applications as nanoscale containers and drug carriers.

Video Link

The video component of this article can be found at <http://www.jove.com/video/50383/>

Introduction

With their inherent inner cavities and versatile surface chemistry, hollow carbon-based nanomaterials, such as carbon nanotubes (CNTs), are considered to be good nanocarriers in drug delivery applications.^{1,2} However, the fibril structure of pristine CNTs has rather inaccessible hollow interiors and may cause severe inflammatory response and cytotoxic effects in biological systems.^{3,4} Nitrogen-doped CNTs, on the other hand, have been found to possess higher biocompatibility than undoped multiwalled carbon nanotubes (MWCNTs)^{5,6} and may have better drug delivery performance. Doping of nitrogen atoms into the nanotube graphitic lattices results in a compartmented hollow structure resembling stacked cups which can be separated out to obtain individual nitrogen-doped carbon nanotube cups (NCNCs) with typical length under 200 nm.^{7,8} With their accessible interiors and nitrogen functionalities which allow for further chemical functionalization, these individual graphitic cups are highly advantageous for drug delivery applications.

Among different synthetic methods for nitrogen-doped CNTs including arc-discharge⁹ and dc magnetron sputtering,¹⁰ chemical vapor deposition (CVD) has been the most prevalent method due to several advantages such as higher yield and easier control over nanotube growth conditions. The vapor-liquid-solid (VLS) growth mechanism is commonly employed to understand the CVD growth process of nitrogen-doped CNTs.¹¹ Generally there are two different schemes to use metal catalyst seeds in the growth. In the "fixed-bed" scheme, iron nanoparticles with defined sizes were first synthesized by thermal decomposition of iron pentacarbonyl and then plated on quartz slides by spin coating for subsequent CVD growth.¹² In the "floating catalyst" scheme, iron catalyst (typically ferrocene) was mixed and injected with carbon and nitrogen precursors, and the thermal decomposition of ferrocene provided *in situ* generation of iron catalytic nanoparticles on which the carbon and nitrogen precursors were deposited. While fixed-bed catalyst provides better size control over the resultant NCNCs, the yield of product is typically lower (<1 mg) compared to the floating catalyst scheme (>5 mg) for the same precursor amount and growth time. As the floating catalyst scheme also provides fairly uniform size distribution of NCNCs, it was adopted in this paper for CVD synthesis of NCNCs.

CVD method affords as-synthesized NCNCs which exhibit fibril morphology comprised of many stacked cups. Although there is no chemical bonding between adjacent cups,⁸ challenges remain in effective isolation of the individual cups because they are firmly inserted into each other's cavities and held by multiple noncovalent interactions and an outer layer of amorphous carbon.⁸ Attempts to separate the stacked cups include both chemical and physical approaches. While oxidation treatments in a mixture of strong acids is a typical procedure to cut CNTs and introduce oxygen functionalities,^{13,14} it can also be applied to cut NCNCs into shorter sections. Microwave plasma etching procedures have been also shown to separate the NCNCs.¹⁵ Compared to the chemical approaches, physical separation is more straightforward. Our previous study showed that by simply grinding with a mortar and pestle individual NCNCs can be partially isolated from their stacked structure.⁷ In addition,

high-intensity probe-tip sonication, which was reported to effectively cut single-walled carbon nanotubes (SWCNTs),¹⁶ was also shown to have a significant effect on separation of NCNCs.⁸ The probe-tip sonication delivers high-intensity ultrasonic power to the NCNC solution that essentially "shakes" the stacked cups and disrupts the weak interactions that hold the cups together. While other potential separation methods are either inefficient or destructive to the cup structure, probe-tip sonication provides a highly effective, cost-efficient and less-destructive physical separation method to obtain individual graphitic cups.

The as-synthesized fibril NCNCs were first treated in concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ acid mixture prior to their separation with probe-tip sonication. The resultant separated NCNCs were highly hydrophilic and effectively dispersed in water. We have previously identified nitrogen functionalities such as amine groups on NCNCs and utilized their chemical reactivity for NCNCs functionalization.^{7,8,17} Compared to our previously reported method of capping NCNCs with commercial nanoparticles,⁸ in this work, gold nanoparticles (GNPs) were effectively anchored to the surface of the cups by citrate reduction from chloroauric acid. Due to the preferential distribution of nitrogen functionalities on the open rims of NCNCs, the GNPs synthesized *in situ* from the gold precursors tended to have better interaction with the open rims and form GNP "cork stoppers" on the cups. Such synthesis and functionalization methods have resulted in a novel GNP-NCNC hybrid nanomaterial for potential applications as drug delivery carriers.

Protocol

1. CVD Synthesis of Nitrogen-doped Carbon Nanotube Cups (NCNCs)

NCNCs were synthesized employing chemical vapor deposition (CVD) technique on quartz substrate using liquid precursors (**Figure 1A**).

1. Place a 3 ft long quartz tube (2.5 cm i.d.) in a Lindberg/Blue tube furnace as the reaction chamber. Place a quartz plate (1" × 12") inside the tube as the substrate for product collection. Seal the quartz tube using homemade stainless steel caps with built-in gas and liquid injection connections/tubes.
2. Make a solution of liquid precursor containing 0.75 wt% ferrocene, 10 wt% acetonitrile and 89.25 wt% xylenes. Before the growth, draw about 5 ml of liquid precursor into a gas tight syringe connected to the inlet to the quartz tube. Place the syringe on a syringe pump.
3. Assemble the CVD system. Connect all gas inlet and outlet. Flow Ar (845 sccm) to purge the CVD system and check leakage using Snoop liquid leak detector. After purging for 20 min, turn on H_2 . Set the flow rate of H_2 to 37.5 sccm and Ar to 127 sccm. Turn on the furnace. Set the temperature of the furnace to 800 °C and wait till it is stable at 800 °C.
4. Use the syringe pump to inject the liquid precursor into the quartz tube. Set the injection rate at 9 ml/hr for 6 min to fill the dead volume of the injector tube. Then turn down the injection rate to 1 ml/hr for the growth of NCNCs. After 90 min of growth, turn off the syringe pump and H_2 gas flow, and shut down the furnace. Keep Ar flowing to maintain an inert atmosphere until the furnace was cooled down to RT.
5. Disconnect all gas inlets and outlets, and the injection system. Disassemble the CVD system and take the quartz plate out. Use a one-sided razor blade to peel off the NCNCs film from the quartz plate. Disperse the collected product in ethanol. Respiratory protection is needed to prevent inhaling possible carbon materials if the work is conducted outside of fume hood.

2. Oxidation of As-synthesized NCNCs by a Mixture of Acids

1. Transfer about 10 mg of as-synthesized NCNCs to a 200 ml round-bottom flask. Add 7.5 ml of concentrated HNO_3 to the flask. Briefly sonicate the mixture in water bath for better dispersion. Then add 22.5 ml of concentrated H_2SO_4 slowly. (**CAUTION:** the strong acid mixture is highly corrosive; carefully handle these acids with safety protection.) Sonicate the reaction mixture in water bath at RT for 4 hr.
2. Dilute the reaction mixture with 100 ml of water while cooling down in ice bath. Filter the mixture through a polytetrafluoroethylene (PTFE) membrane with pore size of 220 nm using a water aspirator.
3. Wash the material on the filter membrane with 200 ml of 0.01 M NaOH solution to remove any acidic residual byproduct.¹⁸ Then wash with 200 ml of 0.01 M HCl solution, followed by copious amount of water until a neutral pH of the filtrate was achieved. Disperse the resultant material (oxidized NCNCs) in water (20 ml) by sonication. The resulted suspension can be stored at RT for further experiments.

3. Physical Separation of NCNCs by Probe-tip Sonication

1. Transfer the suspension of oxidized NCNCs in water to a 100 ml plastic cup placed in ice bath. Fill the plastic cup to the 50 ml mark with water. Set the probe-tip sonicator equipped with a 1/4" diameter titanium microtip at 60% maximum magnitude (12 W). Submerge the microtip to the center of the solution and then process for 12 hr with 30 sec on/off interval. Change the ice every 30 min to prevent overheating.
2. Stop the sonication. Filter the NCNC suspension through a 220 nm pore-size PTFE filter membrane to remove any large particles. The resultant NCNC samples can be store at RT for further applications.
3. (Optional) As a comparison experiment, disperse another sample of as-synthesized NCNCs in DMF and directly sonicate the suspension with probe-tip sonication for 12 hr at the same settings as above.

4. Quantitative Analysis of Amine Functional Groups on NCNCs by Kaiser Test

1. Prepare the reagent A: mix 1 g of phenol and 250 μl of EtOH in 2.5 ml of pyridine, add 50 μl of 0.01 M hydrindantin in H_2O to the mixture. Prepare the reagent B: dissolve ninhydrin (50 mg) in 1 ml of EtOH.
2. Weighed the NCNCs samples (~0.5 mg) on a microbalance and disperse them in 1 ml of 3:2 EtOH/water in small test tubes. Add 100 μl of Reagent A and 25 μl of Reagent B to the sample suspension. Seal the test tubes with parafilms and heat the mixture at 100 °C oil bath for 10 min. Filter the sample through a syringe filter to remove solid particles and collect the filtrate solution.

3. Take the visible spectra on the filtrate for colorimetric analysis with the blank sample made in the same process without adding NCNCs. Record the absorbance of the peak centered at 570 nm and calculate the amine loadings according to the Beer-Lambert law.

5. Functionalization of NCNCs with GNPs

1. Sonicate 4 ml of aqueous suspension containing separated NCNCs (0.01 mg/ml) using a water-bath sonicator for 5 min to achieve a uniform dispersion.
2. Add 1 ml of HAuCl_4 aqueous solution (1 mg/ml) to the NCNC suspension during sonication. Then add 250 μl of 1 wt% trisodium citrate aqueous solution dropwise. Vigorously stir the reaction mixture was at 70 °C on a hot plate for 2 hr.
3. Centrifuge the reaction mixture at 3,400 rpm for 15 min. Collect the NCNCs functionalized with GNPs in the precipitate and wash with water by centrifugation. Disperse the precipitate in water (4 ml).

Representative Results

The as-synthesized NCNCs from CVD growth appeared as a carpet of black material on quartz substrate. Thick films of NCNCs weighing about several mg were obtained by peeling with a razor blade (**Figure 1B**). TEM images show the morphology of as-synthesized NCNCs at different magnifications (**Figure 1**). At the lower magnification (**Figure 1C**), the as-synthesized NCNCs all showed a fibril structure with lengths of typically several micrometers and diameters of 20 - 30 nm. Unlike the continuous tubular structure of undoped CNTs, the NCNC fibers were compartmented with many cup-shaped segments. High-resolution TEM imaging of the tip of a NCNC fiber reveals the curved graphitic structure of nanotube cups that are stacked on top of each other (**Figure 1D**).

Figure 2A shows the TEM images of NCNCs after acid oxidation. The oxidation process cut the long fibers into shorter sections of about 1 μm in length in which the graphitic cups remained stacked. The oxidized NCNCs formed stable suspension in water which was then processed with probe-tip sonication. After 12 hr of sonication and filtration, TEM image shows the significant decrease in the length of NCNCs (**Figure 2B**). Most NCNCs appeared as individual cups with length less than 200 nm. The individual cups isolated from the stacks typically have a semi-elliptical shape with one end sealed and the other open.

The size distribution of NCNCs was based upon ~300 measurements from TEM images. The length distribution histograms (**Figure 3A**) of oxidized NCNCs, NCNCs after 12 hr sonication, and the final product show the effect of probe-tip sonication on separation of stacked NCNCs and obtaining individual cups. The oxidation process resulted in a change in zeta potential of NCNCs from positive to negative (**Figure 3B**), while the inherent amine groups on NCNCs were not affected according to Kaiser test (**Figure 3C**).

The separated NCNCs were then functionalized with GNPs by citrate reduction of HAuCl_4 . The reduction reaction occurred at 70 °C under vigorous agitation. The initially colorless solution started to turn blue after 30 min and gradually changed to wine-red within 2 hr. TEM image of the centrifuge precipitate in **Figure 4A** shows the high coverage of GNPs on NCNCs. Almost all nanotube cups were functionalized with GNPs, and the GNPs were frequently found to be preferentially located at the open rim serving as cork stoppers for the cups. A magnified TEM image (**Figure 4B**) reveals that some GNPs were actually grown into the cup interior forming a "tight" cork. There was a difference in color between the precipitate and the supernatant solution. UV-Vis absorption spectra show that the surface plasmon resonance (SPR) band of GNPs in the precipitate has a red-shift compared to that of the supernatant (**Figure 4C**).

Figure 1. (A) Schematic setup of a tube furnace used for chemical vapor deposition (CVD) synthesis of NCNCs. (B) Photograph of the as-synthesized NCNC film peeled from the quartz substrate. (C) An overview transmission electron microscopy (TEM) image of as-synthesized NCNCs. (D) High-resolution TEM image showing the tip of an individual as-synthesized NCNC.

Figure 2. TEM images of (A) oxidized NCNCs and (B) NCNCs after subsequent 12 hr probe-tip sonication and filtration. Inset shows an individual separated NCNC.

Figure 3. (A) Length distribution histograms for NCNC samples of (1) after 12 hr probe-tip sonication only, (2) after oxidation, (3) after oxidation and 12 hr probe-tip sonication, and (4) the final product after filtration through a 220 nm pore-size membrane. (B) Zeta potentials of as-synthesized, oxidized, and the final NCNC samples. (C) Amine loadings on NCNCs after 12 hr sonication only and after both oxidation and 12 hr sonication.

Figure 4. (A) TEM image of NCNCs functionalized with GNPs by citrate reduction of HAuCl_4 and collected by centrifugation. (B) TEM image showing an individual nanocup corked with GNP. (C) UV-Vis spectra of the reaction mixture, the supernatant solution and the precipitate of the GNP functionalization reaction. The inset photograph shows the color difference between the supernatant (left) and the precipitate (right) solutions. [Click here to view larger figure.](#)

Element (K Shell)	As-synthesized	Final separated
	at %	at %
C (including N)	98.0	95.9
O	0.6	3.8
Fe	1.4	0.1
Ti	-	0.2

Table 1. Elemental analysis of as-synthesized NCNCs and final separated NCNCs based on energy-dispersive X-ray (EDX) spectroscopy.

Discussion

The primary goal of our experiments was to effectively produce graphitic nanocups from nitrogen-doped CNTs. However, nitrogen-doping in the CVD synthesis does not guarantee the formation of the stacked cup-shaped structure. Depending on the chemical composition of the precursor and other growth conditions, the morphology of the resulted product may vary a lot.¹⁹ The concentration of nitrogen source is the primary factor influencing the structure because the compartmented structure results from the incompatibility of nitrogen atoms in the graphitic lattices.²⁰ Generally, the length of the compartments decreases with increasing nitrogen concentration in the precursor. At higher concentrations, the lateral segmentation layers become irregular and corrugated and the uniform cup-shaped compartmented structure is lost.¹⁹ In our procedure, we used 10% MeCN as the precursor which resulted in uniform cup-shaped structure with similar diameters. Carbon source is another pivotal factor for NCNC synthesis. Previous attempts using ethanol as carbon source sometimes formed irregular tear-drop-shaped segments in the resulted NCNCs,¹² presumably due to oxygen defects originated from ethanol. Replacing ethanol with xylenes eliminated formation of any irregular shapes. Moreover, reduced ferrocene concentration (0.75 wt%) helped to form small uniform iron catalyst nanoparticles and relatively low carrier gas flow rate facilitated vertical growth. All these factors resulted in formation of NCNCs with more uniform diameters and higher yield.

The as-synthesized NCNCs are long fibers of stacked cups. High-resolution TEM image (**Figure 1D**) clearly shows the graphitic structure of adjacent stacked cups. The graphitic walls of each cup extend along the direction with a certain angle from the cup axis, having no connections between adjacent cups. The adjacent cups were assumed to be held together by noncovalent interactions between graphitic layers and also by an outer layer of amorphous carbon as observed in **Figure 1D**. The weak interactions that keep the cups together can be disrupted and individual nanocups can be isolated via chemical or physical methods.

In our previous study,⁸ the separation procedure was carried out by physical separation only. The as-synthesized NCNCs were directly sonicated in *N,N*-dimethylformamide (DMF) under probe-tip sonication. 12 hr of sonication significantly reduced the average length of NCNCs from several micrometers to 556.9 ± 256.1 nm and effectively derived individual nanocups, though unseparated NCNCs were still frequently observed. A major drawback for direct ultrasonication was that the as-synthesized NCNC fibers were highly hydrophobic and even poorly suspended in DMF. The efficiency of separation was compromised in this case because the NCNCs were not well dispersed initially. To improve the dispersion of NCNCs in solvent and facilitate the ultrasonic separation, as-synthesized NCNCs were first treated with strong acids. This treatment was widely applied for oxidation of pristine CNTs.¹³ Energy-dispersed X-ray (EDX) spectroscopy shows a significant increase of oxygen concentration in NCNCs after acid treatment (**Table 1**), indicating that oxygen functionalities were introduced to the graphitic structure. The oxidation step not only increased the hydrophilicity of NCNCs, but might have also weakened the interactions between the graphitic layers of the adjacent cups by introducing oxygen lattice defects and removing the outer amorphous carbon. The oxidized NCNCs formed even dispersion in water and thus were more susceptible to the subsequent ultrasonic separation. The average length of oxidized NCNCs measured from TEM images was 770 ± 571 nm. Upon 12 hr of probe-tip sonication, most individual cups were isolated out, and the average length was reduced to 178 ± 94 nm, which was below the 220 nm pore size of the PTFE membranes. A filtration process thus further removed any longer NCNCs and reduced the average length to 110 ± 55 nm, leaving only individual and short stacked nanocups in the filtrate. The final separated NCNCs were well dispersed in water forming stable suspension which showed little precipitation over period of several weeks.

The acid oxidation process greatly altered the surface properties of NCNCs. Due to the existence of nitrogen functionalities that tend to be protonated in solution, the as-synthesized NCNCs were slightly positively charged with a zeta potential of +9 mV. Acid oxidation made NCNCs more suspendable with a negative zeta potential of about -30 mV. It should be noted that the oxidation process did not alter the inherent amine functionalities on the surface of NCNCs as was quantified by Kaiser test. On the contrary, more amine groups were found on separated NCNCs after 4 hr acid oxidation than on the samples separated by sonication only, which indicated that better separation exposed more amine functionalities. The acid oxidation process also effectively removed iron catalyst residues from NCNCs as revealed by the EDX elemental analysis (**Table 1**).

A main problem of the prolonged probe-tip sonication was the wear-out of titanium tips. Long and intensive ultrasonic vibration generates a lot of heat and is abrasive to the microtip. As the tip being worn out, the separation effect was weakened and the titanium particles tended to come off the tip as contamination. To better protect the tip from damage, the sample was processed on 30 sec on/off intervals and the ice bath was replaced every 30 min to prevent overheating. Due to its chemical inertia, the titanium contaminant was hard to be completely removed. The filtration procedure through a 220-nm-pore membrane was effective in removal of any large titanium particles, and small particles could also be mostly removed by brief centrifugation at 3,400 rpm for 4 min, though in the final separated NCNC samples about 0.2 at% of titanium was still present (**Table 1**).

The separated NCNCs have both oxygen and nitrogen functionalities on their graphitic framework, which provide diverse chemical properties essential for drug delivery applications. By thiolation of the amine groups, we were previously able to attach commercial GNPs on to the graphitic nanocups.⁸ Those GNPs, with an average diameter fitting the opening of the cups, tended to seal the cup as cork stoppers. Using the hydrophilic oxidized NCNCs, GNPs can be more effectively anchored on the cups in aqueous phase by direct reduction of chloroauric acid with trisodium citrate as the reduction reagent. GNPs are likely to nucleate on the nitrogen functionalities and continue to grow under the reaction conditions. This bottom-up functionalization approach resulted in strong and specific interaction between GNPs and NCNCs. Due to the preferential distribution of nitrogen functionalities on the open rim of the cups, GNPs had better chance to nucleate at the opening, and the subsequent growth often formed cork-shaped nanoparticles that extended to the interior of the cups. This corking interaction was more frequently observed using the reduction approach compared to our previous method. Free GNPs in solution were also present during the reduction reaction; they can be removed by centrifugation at 3,400 rpm for 15 min. There was distinct difference between the solution colors of the supernatant and the precipitate. The former appeared as wine red with a SPR absorption band at 524 nm and the latter was purple with a SPR band at 540 nm. The red-shift in the SPR band may be attributed to the strong electronic interaction of GNPs on the surface of NCNCs.

In conclusion, we adopted a series of synthetic techniques to obtain individual graphitic nanocups (*i.e.* NCNCs) from their stacking structures. Introduction of the acid oxidation and probe-tip sonication procedures is essential to ensure the high efficiency of separation and the

hydrophilicity of the final nanocups. Through citrate reduction of HAuCl_4 , the NCNCs were then functionalized with GNPs which effectively closed the cups as cork stoppers. This novel GNP-NCNC hybrid nanomaterial may have promising applications as nanoscale containers and drug-delivery carriers.

Disclosures

The authors declare no competing financial interests.

Acknowledgements

This work was supported by an NSF CAREER Award No. 0954345.

References

1. Tasis, D., Tagmatarchis, N., Bianco, A., & Prato, M. Chemistry of carbon nanotubes. *Chem. Rev.* **106** (3), 1105-1136, doi:10.1021/cr050569o (2006).
2. Hilder, T.A. & Hill, J.M. Modeling the loading and unloading of drugs into nanotubes. *Small.* **5** (3), 300-308, doi:10.1002/sml.200800321 (2009).
3. Shvedova, A.A., Kisin, E.R., *et al.* Unusual inflammatory and fibrogenic pulmonary responses to single-walled carbon nanotubes in mice. *American Journal of Physiology - Lung Cellular and Molecular Physiology.* **289** (5), L698-L708, doi:10.1152/ajplung.00084.2005 (2005).
4. Jia, G., Wang, H., *et al.* Cytotoxicity of carbon nanomaterials: Single-wall nanotube, multi-wall nanotube, and fullerene. *Environmental Science & Technology.* **39** (5), 1378-1383, doi:10.1021/es048729l (2005).
5. Carrero-Sánchez, J.C., Elías, A.L., *et al.* Biocompatibility and toxicological studies of carbon nanotubes doped with nitrogen. *Nano Lett.* **6** (8), 1609-1616, doi:10.1021/nl060548p (2006).
6. Zhao, M.L., Li, D.J., *et al.* Differences in cytocompatibility and hemocompatibility between carbon nanotubes and nitrogen-doped carbon nanotubes. *Carbon.* **49** (9), 3125-3133, doi:10.1016/j.carbon.2011.03.037 (2011).
7. Allen, B.L., Kichambare, P.D., & Star, A. Synthesis, characterization, and manipulation of nitrogen-doped carbon nanotube cups. *ACS Nano.* **2** (9), 1914-1920, doi:10.1021/nn800355v (2008).
8. Zhao, Y., Tang, Y., Chen, Y., & Star, A. Corking carbon nanotube cups with gold nanoparticles. *ACS Nano.* **6** (8), 6912-6921, doi:10.1021/nn3018443 (2012).
9. Stephan, O., Ajayan, P.M., *et al.* Doping graphitic and carbon nanotube structures with boron and nitrogen. *Science.* **266** (5191), 1683-1685, doi:10.1126/science.266.5191.1683 (1994).
10. Suenaga, K., Johansson, M.P., *et al.* Carbon nitride nanotubulite - densely-packed and well-aligned tubular nanostructures. *Chem. Phys. Lett.* **300** (5-6), 695-700, doi:10.1016/s0009-2614(98)01425-0 (1999).
11. Chen, H., Yang, Y., *et al.* Synergism of C5N six-membered ring and vapor-liquid-solid growth of CNx nanotubes with pyridine precursor. *J. Phys. Chem. B.* **110** (33), 16422-16427, doi:10.1021/jp062216e (2006).
12. Allen, B.L., Keddie, M.B., & Star, A. Controlling the volumetric parameters of nitrogen-doped carbon nanotube cups. *Nanoscale.* **2** (7), 1105-1108, doi:10.1039/c0nr00043d (2010).
13. Liu, J., Rinzler, A.G., *et al.* Fullerene pipes. *Science.* **280** (5367), 1253-1256, doi:10.1126/science.280.5367.1253 (1998).
14. Zhao, Y., Allen, B.L., & Star, A. Enzymatic degradation of multiwalled carbon nanotubes. *J. Phys. Chem. A.* **115** (34), 9536-9544, doi:10.1021/jp112324d (2011).
15. Wang, Y. & Bai, X. High-yield preparation of individual nitrogen-containing carbon nanobells. *Mater. Lett.* **63** (2), 206-208, doi:10.1016/j.matlet.2008.09.046 (2009).
16. Heller, D.A., Mayrhofer, R.M., *et al.* Concomitant length and diameter separation of single-walled carbon nanotubes. *J. Am. Chem. Soc.* **126** (44), 14567-14573, doi:10.1021/ja046450z (2004).
17. Allen, B.L., Shade, C.M., Yingling, A.M., Petoud, S., & Star, A. Graphitic nanocapsules. *Adv. Mater.* **21** (46), 4692-4695, doi:10.1002/adma.200900851 (2009).
18. Wang, Z., Shirley, M.D., Meikle, S.T., Whitby, R.L.D., & Mikhlovsky, S.V. The surface acidity of acid oxidised multi-walled carbon nanotubes and the influence of *in-situ* generated fulvic acids on their stability in aqueous dispersions. *Carbon.* **47** (1), 73-79, doi:10.1016/j.carbon.2008.09.038 (2009).
19. Liu, H., Zhang, Y., *et al.* Structural and morphological control of aligned nitrogen-doped carbon nanotubes. *Carbon.* **48** (5), 1498-1507, doi:10.1016/j.carbon.2009.12.045 (2010).
20. Mandumpal, J., Gemming, S., & Seifert, G. Curvature effects of nitrogen on graphitic sheets: structures and energetics. *Chem. Phys. Lett.* **447** (1-3), 115-120, doi:10.1016/j.cplett.2007.09.007 (2007).