

FUNCTIONALIZATION AND CHARACTERIZATION OF NANODIAMOND-DERIVED MULTI-LAYERED FULLERENES (CARBON NANO-ONIONS)

Mahendra K. Sreeramoju and John P. Selegue

Department of Chemistry, University of Kentucky, Lexington, KY 40506

Introduction

Carbon nano-onions (CNOs), discovered by Ugarte in 1992, are multi-layered fullerenes that are spherical analogs of multi-walled carbon nanotubes with a broad range of diameters. [1] CNOs synthesized by graphitization of nanodiamonds (N-CNOs) with diameters from 6 to 10 nm and 7-10 graphitic layers are the subjects of our research. During graphitization of nanodiamonds, the preferential exfoliation of (111) and (110) planes takes place to form (001) graphitic planes. [2] Typical N-CNOs with varying numbers of graphitic layers and their corresponding surface area and number of carbon atoms are shown in **Fig. 1**. N-CNOs are more reactive than other CNOs due to their smaller size, high curvature and perhaps density of surface defects. We are exploring potential applications in electronics, biology and polymer composites.

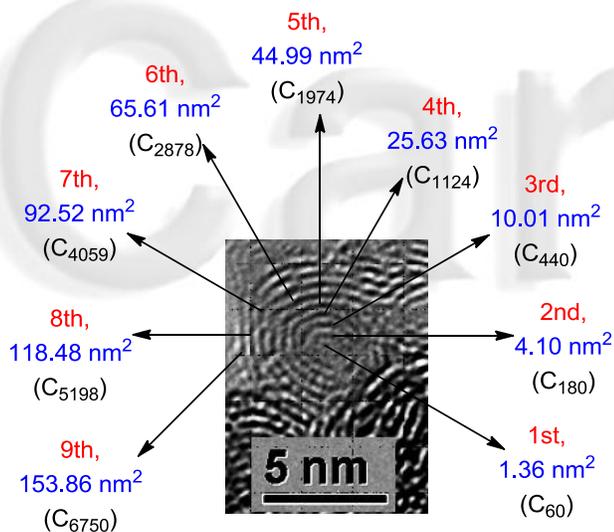


Fig. 1 TEM image of N-CNO with calculated surface areas and numbers of carbon atoms for each graphitic layer.

Experimental

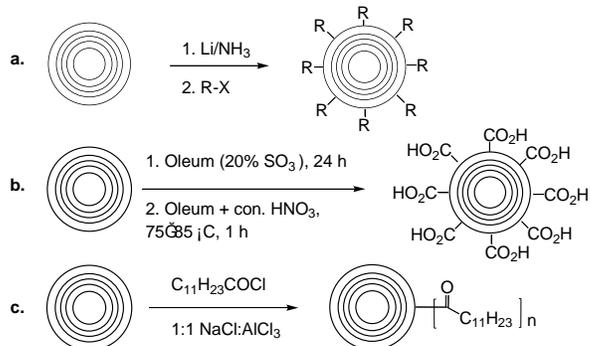
N-CNOs. Nanodiamond (Dynalene Inc.) was graphitized by heating from room temperature to 1650 °C under helium flow at 20 °C/min, followed by cooling to room temperature at 50 °C/min. The resulting N-CNOs were air-cleaned to remove amorphous carbon by heating the material in a tube furnace at 400 °C under flowing air for 4 h. Billups reductive alkylation, oleum oxidation and acylation under Friedel-Crafts conditions were used to functionalize N-CNOs.

Billups reductive alkylation. In a typical procedure, ammonia (~60 mL) was condensed into a round-bottom flask

and lithium (24.3 mg, 3.50 mmol) was dissolved in it. Air-cleaned N-CNOs (100 mg) were added and the suspension was stirred for 30 min at -78 °C. The electrophile (4.5 mmol of iodomethane, ethyl bromoacetate or lauroyl chloride) was added slowly and the reaction mixture was stirred for another 15 min at -78 °C and then brought to room temperature. After the ammonia had completely evaporated, the reaction was quenched with water. The black suspension was filtered through a 0.2- μ m nylon membrane filter and the resulting solid was washed with water until the pH of the filtrate was neutral, followed by ethanol and dichloromethane, and finally dried in a vacuum oven overnight at 45 °C.

Oleum oxidation. To air-cleaned N-CNO (100 mg) was added oleum (20 mL, 20% SO₃) and the suspension was stirred for 24 h under N₂ at room temperature. A mixture of oleum and conc. HNO₃ 2:3, 25 mL) was added slowly at 0 °C and stirred for 15 min. The mixture was heated gradually to 75–85 °C and stirred for 1 h. After cooling to room temperature, the reaction mixture was poured into a beaker containing 100 mL of ice-cold distilled water. The solution was transferred into polycarbonate centrifuge tubes and centrifuged for 2 h to precipitate the oxidized solid, leaving the acid solution above. The precipitate from all of the tubes was combined in a beaker, diluted 10-fold with distilled water and filtered through a 0.2- μ m nylon membrane filter. The solid was washed with ~15 mL of methanol, followed by 10 mL of ethyl ether. The black product was dried under vacuum at 60 °C.

Friedel-Crafts Acylation of N-CNOs. To a molten mixture of NaCl (1.4 g, 24 mmol) and AlCl₃ (3.2 g, 24 mmol) at 160 °C were added lauroyl chloride (5.0 mL, 22 mmol) followed by air-cleaned N-CNOs (50 mg). The suspension was stirred for 4 h at 180 °C, cooled to 40 °C and stirred with 5% v/v HCl solution for 12 h. The aqueous layer was decanted and the residual black slurry was treated with aqueous sodium hydrogen carbonate. The aqueous layer was again decanted after stirring for 2 h. The remaining material was treated with methanol to dissolve organic byproducts. The black solid that settled from methanol was filtered on a 0.2- μ m nylon membrane, washed several times with methanol and dried under vacuum. The product was highly dispersible in non-polar solvents.



Scheme 1 N-CNOs modification by (a) Billups reductive alkylation, (b) oleum oxidation and (c) Friedel-Crafts acylation.

Results and Discussion

N-CNOs were modified by three methods shown in Scheme 1a–c. Considerable surface modification with Billups reductive alkylation is evident from TGA results (Fig. 2). As the complexity of electrophile increased, the combustion temperature of N-CNOs decreased. Reductive alkylation also caused a tremendous increase in the bulk density of N-CNOs – i.e., the functionalized powder was considerably less flocculent than untreated N-CNOs. Billups alkylation and Friedel-Crafts acylation both improved the dispersibility of N-CNOs in organic solvents.

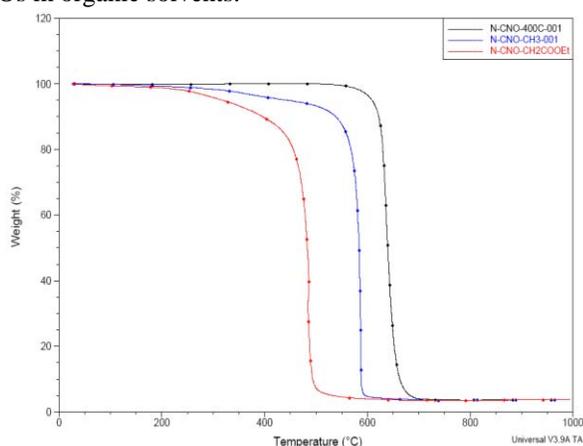


Fig. 2 Thermograms under dry air of air-cleaned N-CNOs, methyl-functionalized and ethyl 2-bromoacetate-functionalized N-CNOs.

Oleum-oxidized N-CNOs (ON-CNOs) were highly dispersible in highly polar solvents like DMSO, DMF and basic water due to the incorporation of acidic functional groups. A pH titration (Fig. 3) indicated the presence of mainly carboxylic acids with pK_a similar to that of benzoic acid. The broad titration curve may indicate either a range of functional groups including phenols, or slow heterogeneous deprotonation kinetics.

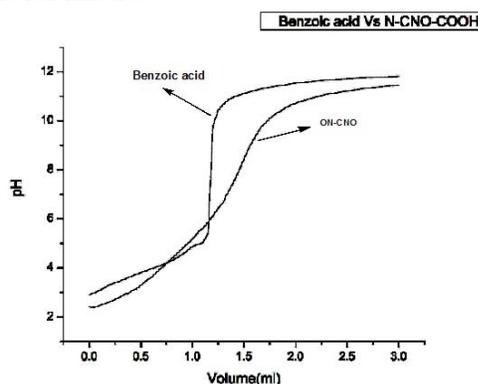


Fig. 3 pH titration of ON-CNOs compared to benzoic acid

TGA analysis of ON-CNOs shows significant mass losses at about 200 °C and 430 °C (Fig. 4). Based on previously reports that much of the carboxylic functionality of oxidized carbon nanotubes is actually bonded to adsorbed

CCFs (carboxylated carbonaceous fragments),[3] we suggest that the mass loss at 200 °C is due to the desorption of CCFs formed during the oxidation, and the mass loss at 430 °C is due to the decarboxylation of CNO-bound COOH groups. Thermal desorption of ON-CNOs under vacuum at 200 °C causes the disappearance of most of the 200 °C mass loss and some of the 430 °C mass loss. MALDI-MS of ON-CNOs shows carboxylated polyaromatic fragments. The graphitic structure of the N-CNO was preserved after the vigorous oxidation and thermal desorption (Fig. 5).

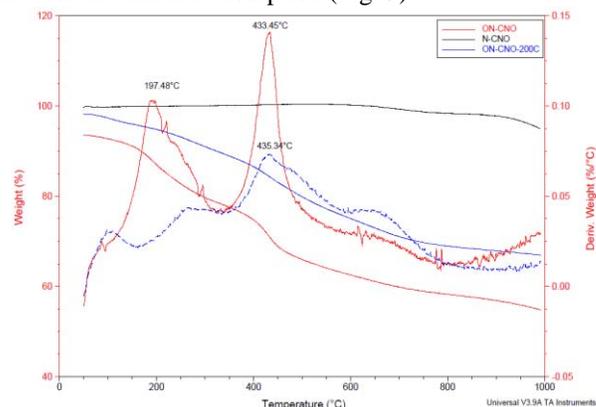


Fig. 4 Thermograms under dry air of ON-CNOs before (red) and after (blue) thermal desorption at 200 °C

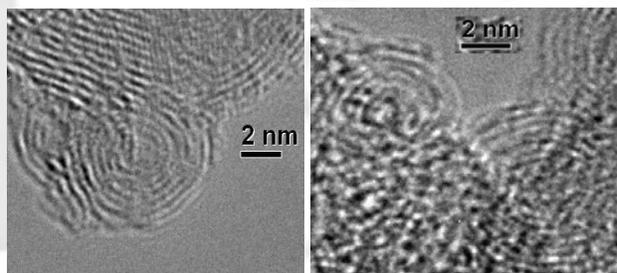


Fig. 5 HRTEM images of ON-CNOs before (left) and after (right) the thermal desorption

Conclusions

Although several synthetic approaches induce surface modifications, oleum oxidation is the most effective functionalization technique as it introduces many carboxylic acid groups on the surface of N-CNOs. Some of the carboxylates may actually be attached to adsorbed CCFs. Alkylated and acylated N-CNOs both show good dispersion properties in organic solvents.

References

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- [2] Kuznetsov VL, Zilberberg IL, Butenko YV. Theoretical Study of Formation of Closed Curved Graphite-Like Structures During Annealing of Diamond Surface. *J. Appl. Phys.* 1999; 86: 863-870.
- [3] Salzmann CG, Llewellyn SA, Tobias G, Ward MAH, Huh Y, Green MLH. The role of carboxylated carbonaceous fragments in the functionalization and spectroscopy of a single-walled carbon-nanotube material. *Advanced Materials* 2007; 19(6): 883-887.