

CARBON NANO-ONIONS FROM ARC DISCHARGE AND NANODIAMOND GRAPHITIZATION: COMPARISON OF THEIR PROPERTIES AND CHEMISTRY

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Introduction

Carbon nano-onions (CNOs), concentrically multilayered fullerenes, are prepared by several different methods. We are comparing the properties of A-CNOs, obtained from an underwater arc discharge between two carbon electrodes, with those of N-CNOs, obtained from the high-temperature graphitization of commercial nanodiamond. In general, A-CNOs are larger than N-CNOs (ca. 30 nm vs. 6 nm diameter). A-CNOs are more difficult to disperse in solvents and much less reactive than N-CNOs. We are functionalizing both types of nano-onions by using (a) Birch/Billups reductive alkylation with lithium and an organic electrophile in ammonia; (b) harsh oxidation with $\text{H}_2\text{SO}_4/\text{HNO}_3$ followed by conversion of the resulting carboxylic acid groups to esters and amides; and (c) Friedel-Crafts acylation under a variety of conditions. The functionalized CNOs are characterized by using a variety of spectroscopic and physical methods, including thermogravimetric analysis (TGA), electron microscopy, titrimetry, pyrolysis mass spectroscopy, electrochemistry and solid-state ^{13}C nuclear magnetic resonance spectroscopy.

Experimental

Preparation of N-CNOs. Nanodiamond (Dynalene Inc.) was graphitized by heating from room temperature to 1650 °C under flowing helium 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.

Preparation of A-CNOs. A 6.4-mm anode and a 12.7-mm cathode of high-purity graphite were subjected to arc discharge while immersed in nitrogen-purged distilled water (3 L) maintained at 45 °C in a 4 L Pyrex beaker. Power was supplied to the custom-built apparatus with a Dual MIG 151T/2 welder.

Billups reductive alkylation. In a typical procedure, lithium (25–50 mg, 3.6–7.2 mmol) was dissolved in ammonia (50–60 mL) in a three-necked, round-bottom flask at –78 °C. A-CNOs or N-CNOs (100–200 mg) were added and the suspension was stirred for 30 min at –78 °C. An electrophile (4–6 mmol of iodomethane, ethyl bromoacetate, lauroyl chloride or chloromethylferrocene) was added slowly. 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 mixture was quenched with water. (~30 mL). The black suspension was filtered

through a 0.2- μm nylon membrane filter and the resulting solid was washed with water until the pH of the filtrate was neutral, further washed with appropriate organic solvents, and finally dried in a vacuum oven overnight at 45 °C.

Oleum oxidation. To A-CNOs or N-CNOs (100–200 mg) was added oleum (H_2SO_4 with 20% SO_3 , 20–30 mL) and the suspension was stirred for 24 h under N_2 at room temperature. A 2:3 mixture of HNO_3 and H_2SO_4 (~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 100 mL of ice-cold distilled water. The suspension was centrifuged for 2 h to precipitate the oxidized solid. The centrifugate was diluted with distilled water and filtered on a 0.2- μm nylon membrane filter. The black solid was washed with ~15 mL of methanol, ~10 mL of ethyl ether and dried under vacuum at 60 °C.

Oleum-oxidized CNOs were treated with oxalyl chloride and a drop of DMF under N_2 . An alcohol or amine plus excess triethylamine were charged to the reaction mixture, which was stirred overnight at room temperature. The product was washed with dichloromethane and ethanol in a Soxhlet extractor for 24 h.

Friedel-Crafts acylation of N-CNOs. Lauroyl chloride (5.0 mL, 22 mmol) and air-cleaned N-CNOs (50 mg) were added to a molten mixture of NaCl (1.4 g, 24 mmol) and AlCl_3 (3.2 g, 24 mmol) at 160 °C. The suspension was stirred for 4 h at 180 °C, cooled to 40 °C and stirred with 5% 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- μm nylon membrane, washed several times with methanol and dried under vacuum.

Results and Discussion

Preparation of A-CNOs. We have designed and constructed an automated arc-discharge apparatus similar to Echegoyen's [1] that allows the preparation of A-CNOs under controlled conditions (Fig. 1). The device operates at 50% duty cycle, maintaining a narrow voltage fluctuation (± 5 V) by controlling the feed rate of the cathode, allowing variation of the power supplied to the plasma while keeping other parameters constant. Minimizing contact between the water bath and metal parts, especially the electrode holders, results in A-CNOs with low metal content (i.e., low TGA combustion residue). From TGA and high-resolution transmission electron microscopic (HRTEM) data, we find that the quality of A-CNOs varies with arc power. At low power (465 W), carbon recovery is lower and the samples contain a higher fraction of polygonal carbon particles. More amorphous carbon and graphite particles are present in samples prepared at the highest powers (up to 2016 W). Arc power in the range of 825 W to 1327 W produces A-CNOs with less impurities and higher yields. These A-CNOs are well formed with an average diameter of 20–40 nm, consisting of about 25–35 graphitic

layers with a spacing of ~ 3.4 Å between lattice fringes (Fig. 2) Discharge at 825 W produces A-CNOs with optimal size distribution and fewer graphite impurities. Even the best A-CNOs require purification to remove carbon and non-carbon impurities. We have surveyed several purification schemes, including “air-cleaning”, acid treatments and precipitation with phosphotungstic acid.

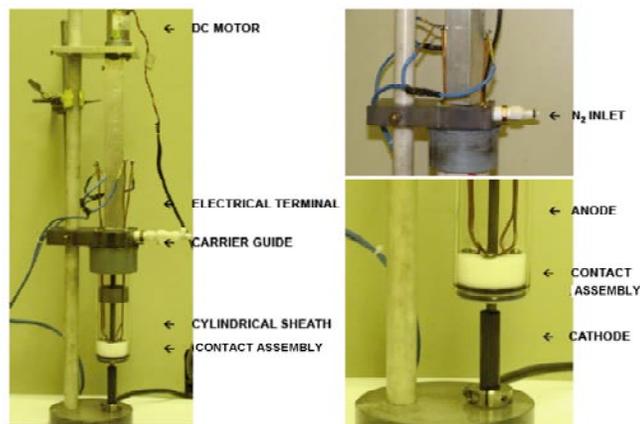


Fig. 1 Automated arc-discharge apparatus used to prepare A-CNOs.

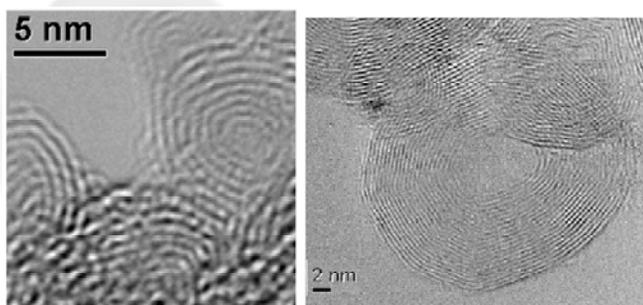


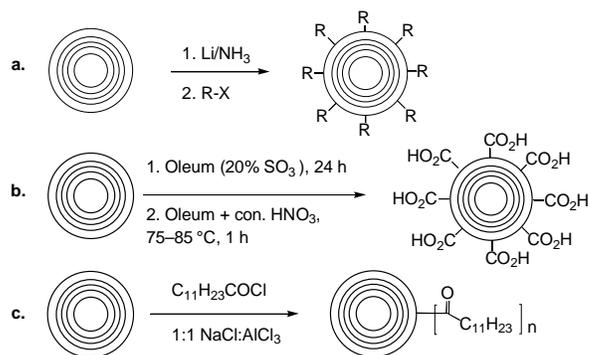
Fig. 2 HRTEM images of N-CNOs (left) and A-CNOs prepared at 825 W arc power (right).

Carbon nano-onions derived from the graphitization of nanodiamond (N-CNOs) as described by Echegoyen *et al.* [2] have a narrow size distribution from 6 to 10 nm with 7 to 10 graphitic layers (Fig. 2). Although they benefit from “air-cleaning,” N-CNOs require less purification than A-CNOs.

Consistent with the findings of Echegoyen *et al.*, N-CNOs are generally more reactive than A-CNOs, their smaller size, high curvature and perhaps density of surface defects. [1-3] We find that both types of nano-onions can be functionalized by a variety of reactions, including Billups reductive alkylation, oleum oxidation and Friedel-Crafts acylation (Scheme 1).

Billups alkylation proceeds similarly using lithium in liquid ammonia for both types of nano-onions. The properties of N-CNOs, especially dispersibility, are more affected than those of A-CNOs by Billups alkylation. This may reflect a higher degree of alkylation of N-CNOs. We have introduced

both alkyl and acyl groups by using this method. Alkylation with chloromethylferrocene gives electroactive CNOs whose surface coverage can be assayed by using cyclic voltammetry.



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

Oxidation of both types of nano-onions with oleum (H_2SO_4 with 20% SO_3) followed by mixture of HNO_3 and H_2SO_4 coats their surfaces with carboxylic acid groups. Thermal desorption experiments and MALDI-MS suggest that some of the carboxylates of oleum-oxidized CNOs are actually bonded to adsorbed CCFs (carboxylated carbonaceous fragments). Regardless of where they are attached, the carboxylic acid groups can be converted to acid chlorides by treatment with oxalyl chloride. Subsequent reactions with alcohols and amines lead to esters and amides with a variety of functionality.

Friedel-Crafts reactions proceed more readily with N-CNOs than A-CNOs. We have carried out these reactions under conventional Friedel-Crafts conditions, as well as in molten NaAlCl_4 and ionic liquids. N-CNOs functionalized with lauroyl chloride form particularly stable suspensions in organic solvents.

Conclusions

Both A-CNOs and N-CNOs can be functionalized under a variety of reaction conditions. N-CNOs are generally more reactive. We are pursuing potential applications of modified CNOs in electronics, biology and composite materials.

References

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