

# PREPARATION AND PHYSICOCHEMICAL MODIFICATION OF ELECTRIC ARC-PREPARED CARBON NANO-ONIONS

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## Introduction

Carbon nano-onions (CNOs) are made up of multilayered fullerene shells, which arrange themselves concentrically. These are the least studied carbon allotropes, with great potential in composite materials and biomedical applications [1]. We are studying CNOs with ca. 30 nm diameters, prepared by the underwater electric arc method introduced by Sano *et al.* [2]. We have optimized the synthetic conditions of arc-prepared carbon nano-onions (A-CNOs). These highly hydrophobic nano-onions are solubilized through functionalization of their outer layers via Billups reductive alkylation and oleum-assisted carboxylation. We have also modified the A-CNO synthesis in order to prepare nano-onions with B<sub>4</sub>C cores.

## Experimental

**Preparation of A-CNOs.** An automated arc-discharge apparatus was designed to control the plasma formed during synthesis. Power was supplied from a Dual MIG 151T/2 welder. The apparatus was programmed to operate at 50% duty cycle and to maintain a narrow voltage fluctuation ( $\pm 5$  V) during synthesis. In a typical experiment, high-purity, a 6.4-mm graphite anode and a 12.7-mm cathode were plugged into the automated arc apparatus, which was immersed in distilled water (3 L) in a 4 L Pyrex beaker. N<sub>2</sub> was continuously purged through the water and the temperature was maintained at 45 °C by using a jacket of continuously flowed cold water surrounding the beaker. CNOs were prepared at various arc powers while keeping other parameters constant.

**Functionalization of A-CNOs.** In a typical Billups reductive alkylation, ammonia (50–60 mL) was condensed into a round-bottom flask and CNOs (0.200 g) were added under N<sub>2</sub>. Excess lithium was added to the suspension, which was stirred for 30 min at -78 °C. An electrophile (800 mg 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 warmed to room temperature. After the ammonia evaporated, the residue was quenched with water (30 mL). The product was repeatedly washed with water, acetone and dichloromethane followed by drying in a vacuum oven at 45 °C overnight.

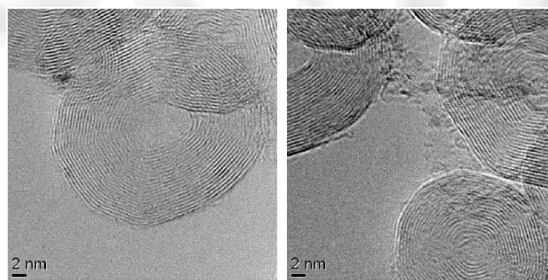
In an oxidative approach, CNOs were dispersed in oleum (20% SO<sub>3</sub>) followed by addition of mixed acid (2:3 HNO<sub>3</sub>: H<sub>2</sub>SO<sub>4</sub>, 1 h, 80 °C). After filtration and drying, the material was treated with oxalyl chloride and a drop of DMF under N<sub>2</sub>. An alcohol or 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.

**Boron-containing CNOs.** In a typical experiment, a 3.2-mm diameter hole was cored through the center of 15.2-cm long, 6.4-mm diameter graphite rod. A paste of 57 wt% B<sub>4</sub>C/FurCarb resin LP-340 was prepared by using a mortar and pestle, injected into the core of the graphite rod from a plastic syringe, and annealed at 1000 °C for one hour under N<sub>2</sub>. The annealed rod was used as an anode for underwater arc discharge at 1327 W. The resulting black solid was collected on a 0.2  $\mu$ m pore membrane filter, washed with distilled water and vacuum dried overnight at 45 °C to give B<sub>4</sub>C@A-CNOs.

## Results and Discussion

**Preparation of A-CNOs.** From thermogravimetric analysis (TGA) and high-resolution transmission electron microscopic (HRTEM) data, we found that with increasing arc power, amorphous and graphite particles in the samples increase. Although polygonal particles were observed at all arc powers (465 W, 825 W, 1327 W, 2016 W) used, 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  $\sim 3.4$  Å between lattice fringes (**Fig. 1**). A-CNOs prepared under our experimental conditions are not always spherical, with polygonal shapes commonly observed. The irregular hollow cores of these A-CNOs are up to 10–12 nm in diameter. Because of their tighter size distribution and fewer graphite impurities, A-CNOs synthesized at 825 W are preferred over other arc power used.

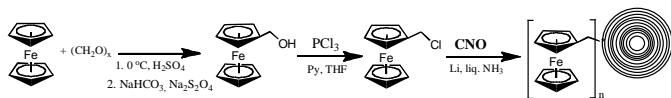


**Fig. 1** HRTEM of A-CNOs prepared at 825 W arc power.

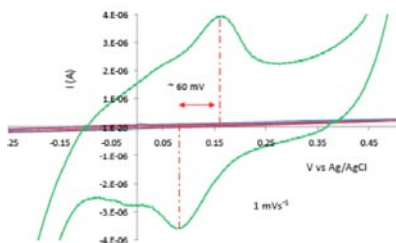
**Table 1.** Oxidative stability,  $d$  spacing and  $L_c$  values of A-CNOs

Sample	A-CNO	A-CNO	A-CNO	A-CNO	Anode
Arc power	465 W	825 W	1327 W	2016 W	---
Combustion Stability	623 °C	652 °C	662 °C	678 °C	753 °C
$d_{002}$ (Å)	3.412	3.413	3.409	3.394	3.363
$L_c$ (nm)	19.40	22.03	21.24		---

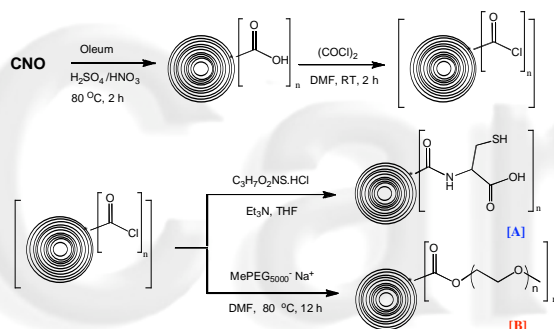
**Functionalization of A-CNOs.** We e functionalized A-CNOs by using both Billups reductive



**Scheme 1.** Ferrocenemethyl-functionalized CNOs via Billups reductive alkylation.



**Fig. 2** Cyclic voltammogram of ferrocenylmethyl-functionalized A-CNOs

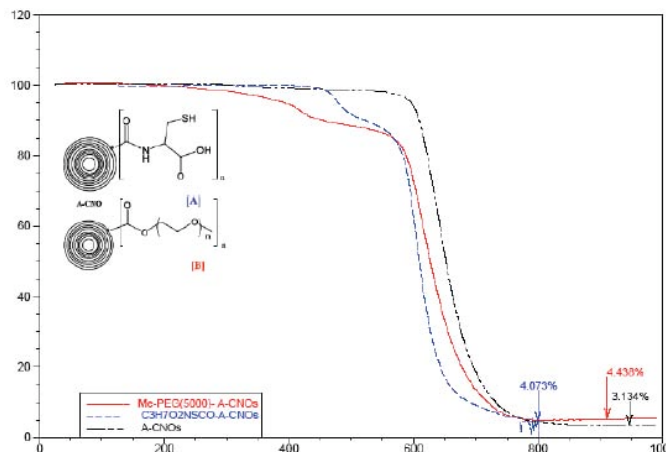


**Scheme 2** Oleum-assisted carboxylation of CNOs followed by ester or amide formation.

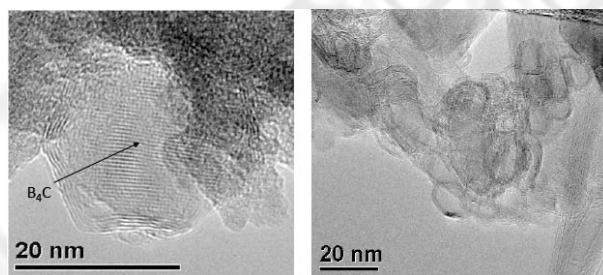
alkylation (**Scheme 1**) and oleum oxidation (**Scheme 2**) methods. A cyclic voltammogram of the ferrocenylmethyl-functionalized CNO sample (**Fig. 2**) has coupled oxidation and reduction waves with peak separation  $\sim 60$  mV at a sweep rate of 1 mV/s. Thermogravimetric analysis of functionalized A-CNOs under dry air (**Fig. 3**) showed two main mass losses. Initial mass loss at  $\sim 400$  °C corresponds to surface functional groups, while mass loss at  $\sim 600$  °C corresponds to combustion of A-CNOs. ICP analysis of cysteine-functionalized CNOs showed sulfur content that corresponded to approximately 1.5% surface coverage. These attached groups improved the solubility of functionalized A-CNOs in organic solvents. The high zeta potential values of these functionalized CNOs in ethanol accounted for their kinetic stability in suspension.

**Boron-containing CNOs.** TGA analysis of boron-incorporated CNOs showed higher thermal stability (786 °C) and higher residue (24.5%) than A-CNOs, attributed to the high combustion stability of boron and formation of

$B_2O_3$  during air oxidation, which remains as residue at 1000 °C. Powder X-ray studies showed typical peaks corresponding to boron carbide ( $B_4C$ ). HRTEM studies of boron incorporated CNOs showed nearly spherical structures with 3-4 concentric carbon shells surrounding the inner  $B_4C$  core (**Fig 4**). EDX studies also revealed the presence of boron inside these carbon shells.



**Fig. 3** TGA compilation of [A], [B] and A-CNOs



**Fig. 4** HRTEM image showing  $B_4C$  cored CNO

## Conclusions

Control of the plasma power produces purer, more homogenous A-CNOs. From the study of the thermal stability and the morphology of A-CNOs produced at various arc powers, we found that arc power in the range of 800 W produces the highest yield of the most homogeneous A-CNOs. Billups reductive alkylation and oleum-assisted functionalization can be effectively used to solubilize and add functionality to carbon nano-onions.  $B_4C$ -cored A-CNOs, which can be used as radiation shielding, were prepared under arc-discharge conditions.

## References

- [1] Palkar, A.; Kumbhar, A.; Athans, A. J.; Echegoyen, L. Pyridyl-functionalized and water-soluble carbon nano onions: first supramolecular complexes of carbon nano onions Chem. Mater. 2008; 20:1685-1687.
- [2] Sano, N.; Wang, H.; Chhowalla, M.; Alexandrou, I.; Amaratunga, G. A. J. Nanotechnology: Synthesis of carbon 'onions' in water Nature 2001; 414: 506-507.