

INVESTIGATING CHEMISTRY OF NITROGEN DOPED MULTIWALLED CARBON NANOTUBES (N-MWCNTs)

Aman Preet Kaur, Mark S. Meier and Dali Qian

Department of Chemistry and Center for Applied Energy Research, University of Kentucky, Lexington, KY 40506

Introduction

Carbon nanotubes have many potential applications including advanced composites, electrochemical devices, hydrogen storage media, field emission devices, microelectronics, sensors and probes because of their unique electronic and mechanical properties and aspect ratio[1]. These layered sp^2 carbon nanosystems, open up potential possibilities of tailoring electronic, structural (in which we are interested) and mechanical properties by ‘doping’ at varying concentrations (from parts per million to small weight percentages)[2]. Considerable changes in mechanical, electrical and chemical properties can be envisaged by doping with nitrogen (N-MWCNTs), which has been supported by theoretical and experimental studies [3]. N-MWCNTs have a ‘bamboo’ structure in which the axes of the graphene planes are not parallel to the tube axis and the core is periodically bridged. Their surface is therefore a set of graphene edges, and this led us to investigate their chemistry.

Experimental

N-MWCNTs are produced at the UK Center for Applied Energy Research from a pyridine feedstock containing dissolved ferrocene as catalyst, at 800°C using N_2 as the carrier gas in a 4 inch tube diameter reactor[4]. Annealing/graphitization of these materials is done by heating to a temperature of $\sim 2800^\circ\text{C}$ in a helium-purged vertical electric resistance tube furnace[5]. The dissolving metal reduction followed by alkylation is done under classical Birch reduction conditions, with little modification[6]. The alkylating agents used are either commercially available or synthesized by following known procedures. The sulfur-containing α -halo esters and amides were characterized using NMR spectroscopy (^1H , ^{13}C) measured on 400MHz Varian Inova spectrometer. SEM studies are carried out on Hitachi S-4800 FE-SEM operated at 5-10 kV. STEM observations are made on S-4800 FE-SEM, equipped with a transmitted electron detector and an Oxford EDS system, operated at 30 kV. HRTEM, STEM, EDS, EELS are conducted using JEOL 2010F field-emission TEM operated at 200 kV. Surface area analysis of the samples is done using nitrogen physisorption at 77 K using ASAP 2020 V3.00H instrument.

Results and Discussion

When graphitized material (g-N-MWCNT) is subjected to dissolving metal reduction in anhydrous ammonia followed by alkylation with various alkylating agents, it fractured into tight spirals. We observed single (either right- or left-handed) as

well as double thread helicity.

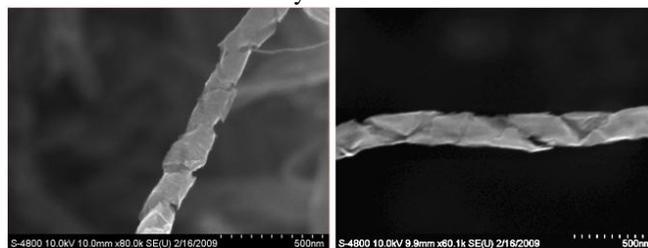


Fig. 1 Spiral fractures resulting from Li/ NH_3 reduction of g- N-MWCNTs.

With reduction/alkylation of these g-N-MWCNTs in ethylene diamine (EDA), linear fractures are observed. Curiously when g-N-MWCNTs were first subjected to reduction / alkylation in EDA, isolated, and followed by another reduction/alkylation step in ammonia, the initially formed linear fractures opened up significantly.

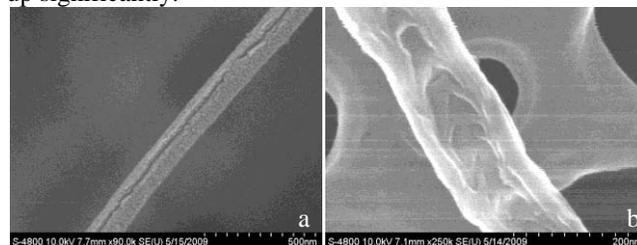


Fig. 2 a) Linear fractures resulting from Li/EDA reduction of g- N-MWCNTs; b) g-N-MWCNT, reduced and alkylated in EDA, followed by a second reduction/alkylation in NH_3 .

The surface area analysis is consistent with impressions developed from SEM images. g-N-MWCNTs that have been converted into spirals have greater surface area (Table 1) and a higher fraction of macropore surface area than g-N-MWCNTs with linear fractures. The total surface area in doubly-reduced material does not increase as much as seen in single-step reduction, but the micropore fraction decreases significantly (from 2.21 % to 0.92%) and the macropore fraction increases (from 45% to 59%). The changes in the porosity distribution are consistent with the size of the fractures formed in respective materials, as suggested by SEM images.

Table 1. Surface Area Analysis of Fractured g-N-MWCNTs

Sample	Surface Area ^a (m ² /g)	Micro pore ^b (< 2 nm)	Meso pore ^b (2-50 nm)	Macro pore ^b (> 50 nm)
g-N-MWCNTs	34	4.46	46.26	49.28
g-N-MWCNTs alkylated ^c in NH_3	91	1.33	46.92	51.75
g-N-MWCNTs alkylated ^c in EDA	69	2.21	52.85	44.94
g-N-MWCNTs alkylated ^c in EDA and then in NH_3	86	0.92	40.39	58.69

^a Measured by N_2 physisorption at 77K, BET model, average of 3 runs. ^b Percentage of total pore volume. ^c CH_3I was used as the alkylating agent.

The observation of differences in morphology of fractures within the same sample of g-N-MWCNTs by merely changing solvent in reduction process put forward interesting questions about the structure of these materials. Then, we attempted to unroll the fractured materials (Fig. 1 and Fig. 2b) all the way to graphite platelets. To achieve this, these materials were subjected to high power sonication in an aqueous surfactant solution. SEM reveals that after 15 minutes of sonication, the nanotubes started unrolling (Fig. 3a). After 25 minutes of sonication, though some nanotubes are still recognizable along with few partially unrolled, we also observed two new forms of graphene: a bundled form (Fig. 3b) composed of very narrow filaments and graphite platelets (Fig. 3c) with one dimension matching the length of tube and the other being far greater than the circumference of tube.

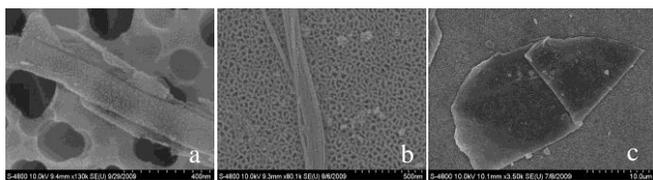
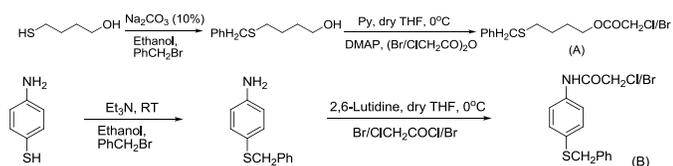


Fig. 3 SEM images (Au coated) on porous alumina. a) Incompletely unrolled nanotube; b) A bundle of filaments; c) Graphite platelets.

We also tried to develop methods to functionalize the graphene edges formed during the course of channeling reaction. To demonstrate that the new chemistry has occurred on these specific structural targets, we designed a chemical transformation at the reduction step of synthesis. We introduced ligands that can bind metals, which can later be used as probes in imaging technique to prove desired functionalization. The recipe followed here involved synthesizing thiol containing ligands (Scheme 1) to use in the reduction/ alkylation step and then binding 10 nm Au particles to the thiol groups. Not surprisingly the benzyl thioether is also deprotected under reductive conditions.



Scheme. 1 Synthesis of (A) 4-(benzylthio)butylchloro/bromoacetate (B) N-(4-(benzylthio)phenyl)-2-chloro/bromoacetamide.

The STEM images (Fig. 4) of Au-complexed g-N-MWCNTs show presence of black spots and EDS and HRTEM further confirmed that these black spots are Au particles that are 10 nm in size. We observed in STEM and TEM images of these materials that the Au nanoparticles are concentrated at the edges of the newly formed fractures and the original outer surface seems unaffected. This was also confirmed by imaging the samples simultaneously in SEM and STEM mode (Fig. 5).

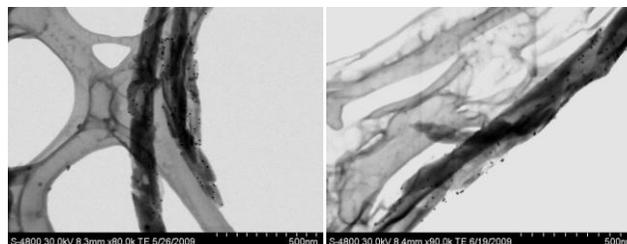


Fig. 4 STEM (operated at 30 kV) photograph of thiol functionalized g-N-MWCNTs in ammonia and then complexed with 10 nm Au particle.

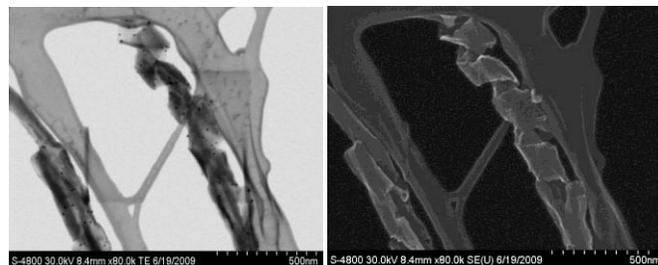


Fig. 5 STEM and SEM of Thiol functionalized graphitized N-MWCNTs complexed with Au nanoparticles.

Conclusions

With such results in hand, we believe that the structure of g-N-MWCNTs is more complex than simple bamboo or stacked cups or coiled ribbons. This observation that only the newly formed edges during reduction are the reactive sites for functionalization to take place and not the outer surface (being a set of edges) inspire detailed investigation of these materials.

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