

EXPLORING THE MECHANISM OF LONGITUDINAL CUTTING IN NITROGEN-DOPED MULTIWALLED CARBON NANOTUBES (N-MWCNTS)

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Introduction

Carbon nanotubes are boosting research activity in several fields because of unique electronic and mechanical properties [1]. These materials are broadly classified as single walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs) and are often drawn as perfect cylinders of graphene [2]. Doping carbon nanotubes with nitrogen is a method for tuning the properties of nanotubes.

The morphology of nitrogen doped MWCNTs (N-MWCNTs) is best described as ‘bamboo’ or ‘nesting cups’, rather than as a true tubular structure. We have recently discovered that treatment of stacked cup N-MWCNTs with lithium in liquid ammonia (the Birch reduction) results in a dramatic ripping open of the nanotubes. To explore different possible mechanisms, we prepared aligned arrays N-MWCNTs, and infiltrated these arrays with different polymers. This technique allowed the end of the N-MWCNTs open, so that chemistry is performed on the open ends alone.

Experimental

N-MWCNTs were synthesized on quartz plates by a floating catalytic chemical vapor deposition (CVD) method. This CVD process produced well-aligned arrays of nanotubes by pyrolysis of pyridine-ferrocene mixtures in a four-inch tube diameter reactor. Ferrocene, the catalyst for CVD carbon nanotubes synthesis, was dissolved into pyridine at a 0.75 at. % Fe:C ratio. The CVD reaction was carried out at 800°C for 2h with N₂ as carriage gas [3]. Birch reductive methylation was done in 250 ml three neck round bottom flask. Anhydrous liquid ammonia was condensed using a Dewar condenser and dry ice-acetone. Li metal was added and stirred for 10 mins. To this solution, N-MWCNTs were added and the mixture was stirred for 30 mins. Methyl iodide was added by syringe, the cooling bath was removed, and mixture was stirred under nitrogen until all of the ammonia had evaporated. The resulting N-MWCNTs were subsequently washed with water, ethanol and methylene chloride. N-MWCNT arrays were coated with poly (methyl methacrylate) (PMMA) by immersing an array of N-MWCNTs, grown on small substrates, in 20 % PMMA-toluene solution for 12 hrs. The array was then air dried for 4 hrs and then dried in a vacuum

oven for 12 hrs. N-MWCNTs were then removed from quartz by scratching with sharp razor blade. Scotch tape was pressed onto the surface of N-MWCNTs array and carefully removed to clean the top surface of the arrays. This process removed a thin layer of disordered nanotubes on the top surface of the array. PMMA was removed from the tubes by sonicating the PMMA-coated N-MWCNTs in toluene for 15 mins and then filtered on 0.2- μ m nylon membrane filters. This process was repeated three times.

TGA experiments were performed on TA 2950 with a standard heating rate of 10°C/min from ambient temperature to 1000°C. Microscopy was done using a scanning electron microscope (SEM) Hitachi S-4800 operated at 5-10 kV. Surface area analysis of the samples were measured using nitrogen physisorption at 77 K using a Micromeritics ASAP 2020 V3.00H instrument.

Results and Discussion

Floating catalyst CVD process produced well-aligned arrays of nanotubes, with the carbon nanotubes growing vertically from the substrate surface. An interesting characteristic of these materials is that the graphene planes within the nanotubes are not parallel to the tube axis and that there are periodic septa within the central core of the nanotube.

We have recently discovered that treatment of stacked cup N-MWCNTs with lithium in liquid ammonia (the Birch reduction) results in a dramatic ripping open of the nanotubes (Fig. 1) [4]. The resulting channels in the nanotubes reach all the way from the outer surface to the core and can be microns in length, exceeding our ability to follow a given feature in either TEM or SEM instruments. Essentially every nanotube in the sample is torn open in this process. In some cases, the channel is quite nicely parallel to the long axis of the nanotube. Surface area analysis of the channeled material reveals that the channeling reaction is not limited to a few individual nanotubes, but substantially changes the bulk material. We also found that when tubes are only treated with liquid ammonia, the tubes are not ripped open. These results suggest that lithium intercalation is a likely reason for channeling reaction [5]. It is possible that intercalation of lithium and ammonia into graphene sheets generate enough pressure to cause channeling in tubes.

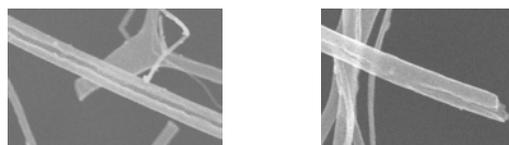


Fig. 1 SEM images of fractures on reduced/alkylated N-MWCNTs.

We believe that it is extremely important to know the mechanism of channeling reaction. This study will provide insight into details of the structure of the nanotubes. To explore different possible mechanisms, we prepared aligned arrays N-MWCNTs. These arrays of N-MWCNTs behave in the same manner as loose nanotubes. The arrays were infiltrated with PMMA by the dip coating technique. This technique prevents the tubes from reacting with Li/NH₃. When the coated tubes are treated with Li/NH₃ they do not show evidence of longitudinal cuts. Our aim was to expose only the ends of tubes to Li/NH₃. So to do this we detached the tubes from the quartz by scratch, allowed the end of the N-MWCNTs open, so that chemistry is performed on the open ends alone. We found that when the bottom end of the tubes is exposed to Li/ NH₃, longitudinal cuts are not formed. In SEM images of the bottom end we found a speck at the end of each tube, and most likely these are catalyst particles. Energy dispersive spectroscopy (EDS) confirmed that the specks are iron and it perhaps this interferes with the reaction that leads to the channeling of tubes. We removed this catalyst by treating those tubes with 5% HF solution so that bottom end is open. After treatment, SEM image of these tubes clearly showed that the specks are gone and that a few tubes were open (Fig. 2b). We further confirmed these results by EDS, which showed that the iron content is reduced to 0.57 % after HF treatment. Then these HF-treated nanotube arrays were treated with Li/NH₃, we found that the nanotubes were ripped open.

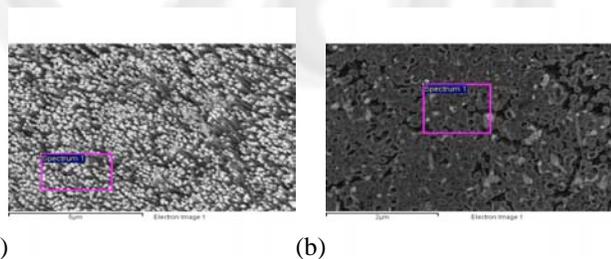


Fig. 2 SEM images (a) Bottom ends of N-MWCNTs with catalyst; (b) Bottom ends of N-MWCNTs after treatment of 5% HF solution, with a lesser amount of catalyst.

Table 1. Energy dispersive spectroscopy (EDS) analysis of bottom end (substrate side) of N-MWCNTs.

Elements	Atomic %	Atomic %
Carbon	89.61	98.02
Iron	9.17	0.57
Oxygen	1.20	1.39
Silicon	0.02	0.01

We have attempted to expose the top ends of the nanotube arrays to Li/NH₃. To start this, we first took SEM image of top

end of the tubes (Fig. 3a). Images show some amorphous carbon particles on the surface and the tips of the nanotubes were not visible. We used a simple but very effective technique to clean the top surface of N-MWCNTs. The arrays were cleaned by pressing scotch tape onto the surface of N-MWCNTs, then removing the tape along with poorly adhere carbon particles and nanotubes. This was repeated several times until all of the debris was removed from the surface. This is very selective technique - the adhesive surface of tape must remove weakly adhered material and the N-MWCNTs remain intact. SEM images clearly showed the tips of tubes after cleaning with tape (Fig. 3b). With the top surface of the arrays cleaned with scotch tape, we are going to coat it with PMMA and we will remove top surface polymer by UV-ozone surface cleaning. UV-Ozone treatment will only clear polymer from the surface and it will not influence N-MWCNTs.

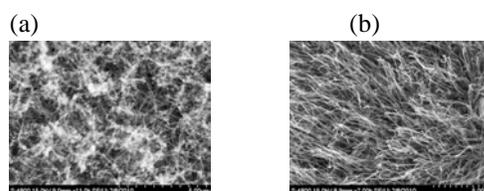


Fig. 3 SEM image (a) Top end of the N-MWCNT; (b) Top end of N-MWCNT after cleaning with tape.

By doing this only top ends of the top will be exposed to Li/NH₃. This study will explore different possible mechanisms of channeling reaction.

Conclusions

In these processes, Birch reduction of N-MWCNTs when bottom of tubes are open results into channeling reaction. This result insight that intercalation of lithium and ammonia is most likely reason for channeling reaction. We are currently investigating how this process can be used to affect the electrical properties of these materials.

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