



On the possibility of electrochemical unzipping of multiwalled carbon nanotubes to produce graphene nanoribbons



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ABSTRACT

Multiwalled carbon nanotubes (MWCNTs) with different geometrical characteristics and chemical doping have been synthesized and electrochemically oxidized to study the possibility of unzipping, and creating graphene nanoribbon (GNR) nanostructures. Modified glassy carbon electrodes of the MWCNTs have been tested in an aqueous electrolyte *via* anodic scans in a wide range of potentials, followed by keeping at the maximum potential for different times. The microstructural features, structural defects, and functional groups and their elements have been then studied using high resolution transmission electron microscopy (HRTEM), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS), respectively. All results have confirmed that no successful unzipping occurs in the MWCNTs after electrochemical oxidation, even for the nitrogen-doped MWCNTs (CN_x-MWCNTs) with reactive nitrogen groups and defective bamboo structures. In contrast to the report by Shinde et al. (J. Am. Chem. Soc. 2011, 133, 4168–4171), it has been concluded that the electrochemical oxidation in aqueous electrolytes is very unlikely to facilitate sufficient incorporation of the intercalated molecules among the walls of the MWCNTs. These molecules are, however, responsible for unzipping of MWCNTs.

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1. Introduction

Graphene nanoribbons (GNRs), narrow elongated strips of graphene with ultra-high aspect ratios and abundant edges, have recently attracted much interest due to their versatile properties, particularly if synthesized by unzipping of multiwalled carbon nanotubes (MWCNTs). GNRs have been investigated for the fabrication of composites [1–3] and for use in batteries [4], supercapacitors [5] and fuel cells [6,7] owing to the high available surface area and active edge sites, high mechanical strength and electrical conductivity, and the scalability of the synthesis.

Prior to the reports of unzipping of MWCNTs [8–10], GNRs had been typically synthesized with minute yields and with limited width control [11]. Now, GNRs can be synthesized by unzipping of MWCNTs through chemical oxidation [8], etching catalytic nanoparticles [12], electron beam etching [13], potassium vapor-induced splitting [14], and sodium/potassium intercalation [15]. Although extensive studies have been conducted to produce graphene nanosheets *via* electrochemical exfoliation of graphite [16], Pillai and co-workers are the only group who claimed the

longitudinal unzipping of MWCNTs [17] and SWCNTs [18] in aqueous electrolytes using an electrochemical oxidation and reduction method. They proposed alignment of MWCNTs induced by the interfacial electric field led to the carbon-carbon cleavage, which is essentially based on the previous reports of chemical unzipping mechanism through protonation of manganate ester and ketone formation [8,19]. However, our recent experimental studies [1,2,20–22], in close agreement with the findings by Tour and co-workers [23–25], showed that the unzipping of MWCNTs is most probably due to the intercalation of the oxidizing molecules among the defective carbon nanotube walls.

In the present study, the possibility of electrochemical unzipping of various types of MWCNTs is investigated. The MWCNTs are NC7000 from Nanocyl™, and un-doped (Un-MWCNTs) and nitrogen-doped (CN_x-MWCNTs) in-house synthesized MWCNTs *via* a catalytic chemical vapour deposition (CCVD) technique. The MWCNTs were electrochemically oxidized in 0.5 M H₂SO₄ electrolyte from the open circuit potential (OCP) to a wide range of anodic potentials (1–5 V), and for different times (3 min to 6 h). High resolution transmission electron microscopy (HRTEM) images, Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) results show no evidence of successful unzipping, but slight oxidation of the MWCNTs was observed.

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2. Experiments

2.1. Chemicals and materials

Sulfuric acid (H_2SO_4 , 95%) and ethanol (denatured, reagent) were purchased from Sigma-Aldrich, Canada. NC7000 from Nanocyl™ with average length of 1–2 μm and diameter of 10 nm.

2.2. Catalytic CVD Synthesis of MWCNTs

Alumina-supported iron catalyst ($\text{Fe}/\text{Al}_2\text{O}_3$) was prepared by incipient wetness impregnation of iron nitrate (iron(III) nitrate nonahydrate, Baker Analyzed[®] ACS Grade) on an aluminum oxide support (Sasol Catalox SBA-200), followed by drying, calcination and reduction [21]. The iron loading was set at 20 wt.%. The catalyst was dried at room temperature for 24 h and at 100 °C for 2 h. The calcination was done at 350 °C under air flow, with a flow rate of 100 sccm for 4 h, to transform the iron nitrate precursor into its corresponding oxide. It was then ground and sieved with a small sieve to obtain a fine powder. The catalyst was further reduced in hydrogen (Praxair HY 5.0UH-T) flow, with a flow rate of 100 sccm at 400 °C for 1 h, to obtain metallic iron supported on alumina.

CN_x -MWCNTs and Un-MWCNTs were synthesized *via* a CVD method using a mixture of ethane, ammonia and argon, according to the protocol of Zehrab Yazdi et al. [21] Ethane (Praxair ET 2.0-K) was used as a source of carbon and ammonia (Praxair AM 4.5-K) as a source of nitrogen. The alumina-supported iron catalyst was placed inside a quartz boat located inside a quartz tubular reactor, with an inner diameter of 4.5 cm, then placed inside a tube furnace (Thermo Scientific–Lindberg Blue M). The flow rates of the gases were controlled by gas flowmeters (Cole Parmer 150-mm 316 SS). The synthesis temperature, time, catalyst mass and gas total flow rate were kept constant at 750 °C, 2 h, 0.6 g and 150 sccm, respectively. Un-MWCNTs were synthesized by replacing the ammonia gas (source of nitrogen) with hydrogen; the other synthesis parameters were similar to the CN_x -MWCNTs' synthesis.

2.3. Electrochemical measurements

All electrochemical properties were measured using a three-electrode system, where a modified glassy carbon electrode was used as working electrode, Pt wire as counter electrode and silver/silver chloride filled by 4 M of KCl solution as reference electrode. Modified glassy carbon electrodes were typically prepared by drop casting 40 μL of the sample suspension every 10 min for a total of 4 mL onto a glassy carbon electrode with an active diameter of 3 mm. The electrode was then dried for 12 h before electrochemical measurements. The sample suspension is a mixture of the MWCNTs and ethanol (3 mg/2 mL ratio) continuously bath sonicated during the drop-casting process. Prior to the deposition of the suspension, the glassy carbon electrode was mechanically polished by a 1.0, 0.3 and 0.05 μm alumina slurry and washed with distilled water and ethanol to obtain a mirror-like surface. All electrochemical measurements were performed in 0.5 M solution of H_2SO_4 electrolyte using an Autolab PGSTAT (Metrohm, UK) machine.

2.4. Characterization techniques

The overall microstructural features of MWCNTs were studied by HRTEM. The HRTEM was carried out in a Tecnai TF20 G2 FEG-TEM (FEI, Hillsboro, Oregon, USA), at 200 kV acceleration voltage, with the standard single tilt holder. The images were captured by a Gatan UltraScan 4000CCD (Gatan, Pleasanton, California, USA) at 2048 \times 2048 pixels. To prepare the sample for electron microscopy after electrochemical oxidation, the modified glassy carbon

electrode was taken out of the reaction cell, and dried at room temperature for 4 h. Note that the aqueous acid electrolyte was completely clear after the electrochemical reactions, indicating no displacement of carbon nanoparticles occurred inside the electrolyte during the electrochemical oxidation. The solid carbon nanomaterial was then removed from the surface of the electrode, and washed twice by deionized water, and vacuum filtered using a PTFE 0.2 μm filter membrane. Finally, the black carbon powder was collected for analysis. 1 mg of the sample was suspended in 10 mL ethanol, and sonicated in an ultrasonic bath for 30 min. A drop of this suspension was placed on the carbon side of a standard TEM grid that was covered with a \sim 40 nm thin holey carbon film (EMS, Hatfield, Pennsylvania, USA) and placed on a filter paper to quickly dry. In order to comprehensively check the possibility of unzipping, 3 samples of each reaction conditions were prepared, and several spots in each sample were checked at low and high magnifications using HRTEM. To measure the elemental composition, a Physical Electronics PHI VersaProbe 5000-XPS was used to record XPS spectra. The spectra were taken using a monochromatic aluminum source, at 1486.6 eV and 49.3 W, with a beam diameter of 200.0 μm . The samples were pressed on a piece of an indium foil and, a double neutralization – a low energy electron beam and low energy Ar⁺ beam – were used during spectrum acquisition. The binding energies were reported relative to C1s at 284.8 eV. The chamber analysis pressure was 2.0×10^{-7} Pa during acquisition. The take-off angle was 45°. For each sample, a high sensitivity mode spectrum was taken with a wide binding energy range of 0–1350 eV (survey) to determine the surface elemental composition of the samples at a pass energy of 140 eV. Then, a narrower binding energy window, with a pass energy of 26 eV, was used to get high energy resolution spectra of the elements present in the sample to determine its chemical environment and quantification. The structural defects of the samples were investigated using Raman spectroscopy. The Raman spectra were recorded by a Thermo Nicolet Dispersive XR Raman Microscope with a laser radiation of 532 nm, integration of 50 s, \times 10 objective and a laser power of 24 mW.

3. Results and discussions

The electrochemical oxidation of the MWCNTs were studied in 0.5 M H_2SO_4 electrolyte *via* a linear sweep voltammetry technique (LSV) with a scanning rate of 100 mV/s (Fig. 1). The MWCNTs were different in length, diameter and chemical doping, as shown in Table 1. In particular, the distribution and type of the nitrogen functional groups (pyridinic, pyrrolic and quaternary) found through the CN_x -MWCNTs will increase their reactivity during oxidation [20,21] and thus, electrochemical unzipping is more probable to occur than the usual MWCNTs (*i.e.* NC7000, Un-MWCNTs). The anodic scans were performed from the OCP to a maximum potential (1–5 V), followed by keeping the sample at that potential for a desired time (3 min to 6 h) to observe if any sign of oxidation/unzipping could be detected. Shinde et al. [17] previously claimed that by keeping the potential for 6 h, the oxidation and unzipping of the MWCNTs generated an enormous number of oxygen functionalities leading to an increase in the potential of 60 mV. In contrast to their findings, as shown in Fig. 1 a–f, no visible increase in potential can be detected in any of the MWCNTs samples. Note that increasing the maximum potential to 5 V even for the highly reactive CN_x -MWCNTs sample only generated some oxygen species, which resulted in detachment of the sample from the electrode after 3 min (Fig. 1 d, inset) and thus, the measurement stopped at that time.

Microstructural features of the MWCNTs after electrochemical oxidation were studied using HRTEM method, and shown in Fig. 2. All MWCNTs were scanned from the OCP to 2 V, and then kept at

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