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Graphene Oxide Nanoribbons from the Oxidative Opening of Carbon Nanotubes Retain Electrochemically Active Metallic Impurities

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Graphene nanoribbons are commonly synthesized using carbon nanotubes (CNTs) as a precursor through the oxidative opening of the nanotubes into elongated ribbons. However, CNTs contain significant amounts of metallic impurities even after purification. Herein, we show that these impurities persist at parts-per-billion levels after oxidative opening of CNTs to graphene oxide nanoribbons and heavily influence the electrochemical behavior of the resulting material. This may have negative impacts on the range and effectiveness of potential applications suitable for graphene materials.

Graphene and its derivatives have garnered ever-increasing attention as part of current research, being touted as a new class of "wonder materials" possessing extraordinary chemical, physical, and mechanical properties.[1] These properties lead to graphene materials showing great promise in applications such as sensing,[2,3] energy storage,[4] nanocomposites,[5] and electronics.[6] For practical applications especially in the areas of electronics and electrosensing, bulk quantities of material are necessary for device fabrication, which makes scalable methods of graphene production more favored. To date, methods to synthesize gram-scale quantities of graphene at lower costs generally use the chemical modification of graphite followed by exfoliation and/or reduction to obtain single- or few-layered graphene sheets.[7] For instance, a common route towards the preparation of graphene involves the preliminary oxidation of graphite to varying degrees. This oxidized product (termed graphite oxide) can be subsequently reduced by thermal,[8,9] chemical,[10,11] or electrochemical methods[12,13] to obtain graphene-like materials. Unfortunately, this route is typically hampered by the inevitable introduction of defects (and possibly heteroatoms) into the sp^2 carbon plane, and do not have the same degree of crystallinity as true, pristine graphene.[7]

A variant of the IUPAC defined graphene ("polycyclic aromatic hydrocarbon of quasi infinite size")[14] is the graphene nanoribbon (GNR), which retains the sp^2 carbon plane but has an elongated structure and thus a high aspect ratio. GNRs were found to have adjustable band gaps inversely proportional to their widths, while they can be either semiconducting or metallic based on their edge orientations (zigzag or armchair).[15–17] These properties make them excellent candidates for constructing tuneable semiconducting devices. Although a variety of preparation methods for GNRs exist, carbon nanotubes (CNTs) are convenient precursors since they have intrinsically high aspect ratios to begin with and are easily obtained commercially or grown in a laboratory. Such a route involves the opening of CNTs through several means, for example, plasma etching,[18] intercalation–exfoliation,[19,20] annealing in hydrogen,[21] catalytic metal nanoparticle cutting,[22] and oxidative unzipping.[23,24] The oxidative unzipping method was pioneered by Tour and co-workers[23] and used oxidation by permanganate under acidic conditions. The proposed mechanism shows first the formation of a manganate ester, which then oxidizes further to the dione. Subsequent permanganate oxidation eventually leads to the longitudinally unzipped nanotube. Further optimization and modification of this reaction was carried out in a later work, which showed that the degree of unzipping, exfoliation, oxidation, and the amount of defects could be adjusted as desired.[25] In a step analogous to the reduction of graphite oxide to obtain graphene materials, these graphene oxide nanoribbons (GONRs) then undergo a chemical reduction process to finally obtain GNRs.

Current methods of CNT production require the use of metal catalysts, whether through arc discharge, chemical vapor deposition, or laser ablation methods. These catalysts remain embedded in the CNTs post-production in the form of metallic impurities.[26,27] Furthermore, it is widely acknowledged by the scientific community that these residual impurities are extremely difficult to remove, even though much progress has been made in the purification of CNTs.[27–29] These impurities have tremendous influence on the electrochemical,[30–33] redox,[34] toxicological,[35,36] and electronic[37] properties of CNTs. We have also previously demonstrated that metallic impurities inherent in parent graphite materials persist in the final reduced graphene product, interfering greatly with the electrochemical responses of the materials.[38] It is thus unsettling that, with regard to the GNR synthesis methods using CNTs described above, no effort was made to characterize or quantify any residual metallic impurities present, despite the common knowledge that their parent CNT material typically contains significant amounts of residual metal catalyst.

Herein, we investigate the amount of metallic impurities in multiwalled carbon nanotubes (MWCNTs) as well as the reaction product GONRs after exposure to the oxidative procedure commonly used to open nanotubes. We show that

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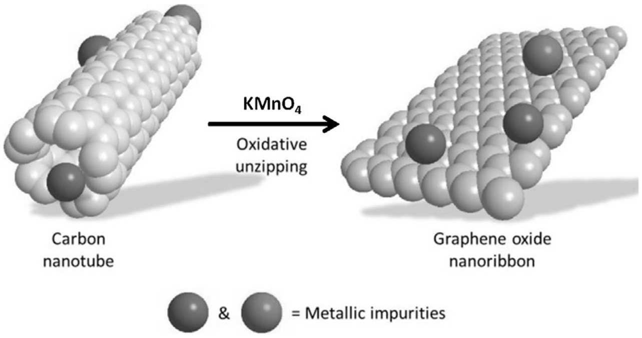

Figure 1. Preparation of graphene oxide nanoribbons through the oxidative unzipping of carbon nanotubes. Metallic impurities inherent in the starting CNTs persist in the resulting GONRs even after chemical treatment.

these impurities persist in the opened nanotubes despite the harsh oxidative conditions used that are typically regarded as being sufficient in eliminating metal-based impurities (Figure 1). Additionally, these impurities are present in amounts that evidently affect the electrochemical properties of the GONRs.

MWCNTs were exposed to oxidative conditions following the procedure laid out by Tour and co-workers.[23] In this method, treatment of MWCNTs with concentrated sulfuric acid is followed by oxidation through $KMnO_4$. The isolated product obtained was highly dispersible in water and DMF because of a large increase in the amount of oxygen-containing groups. X-ray photoelectron spectroscopy (XPS) measurements (Figure 2) affirmed this, showing a significant decrease in the C/O ratio from 8.99 to 2.39 as calculated from the relative C1s and O1s signal intensities.

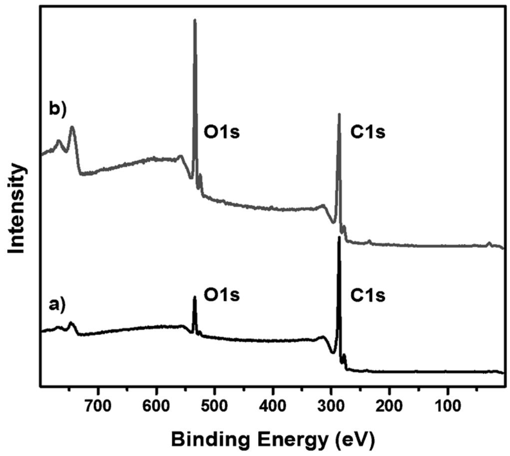

Figure 2. XPS wide spectra of a) MWCNTs before oxidation and b) GONRs. Data shown is normalized to C1s peak intensity.

The morphology of the MWCNTs as observed from scanning electron microscopy was visibly different before and after the treatment, showing a highly expanded material as expected after oxidative treatment (Figure 3a). Scanning transmission electron microscopy uses electron beams of higher intensity and allows the imaging of individual layers of the material. The GONRs exhibit clean, smooth edges (Figure 3b).

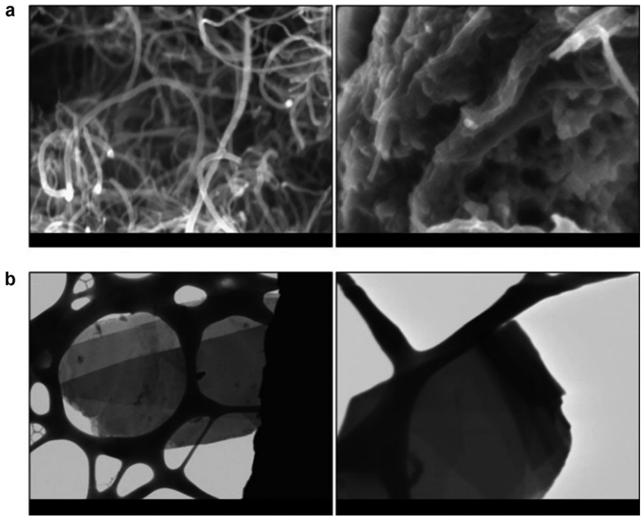

Figure 3. Electron microscopy imaging of materials. a) SEM images of MWCNTs (left) and GONRs (right) with a highly expanded structure. b) STEM images of GONRs, showing smooth and clean edges.

We started our investigation for residual metallic nanoparticles by analyzing the starting MWCNTs and the opened GONRs using inductively coupled plasma mass spectrometry (ICP-MS) for common metallic impurities. The MWCNTs showed the presence of residual metals, particularly Co, Fe, and Ni. This is despite the description of the MWCNTs as already being “cleaned” by the manufacturer. Exposure to the oxidation procedure under acidic conditions decreased the concentrations of all three metals, most notably in Co (1130.9 ppb to 28.6 ppb) and Ni (20.7 ppb to 1.9 ppb). The Fe content showed a more modest decrease from 78.6 ppb to 46.5 ppb. Such levels of decrease in metal contents were similarly observed previously in the oxidation of graphite using the Hummers method, which also used permanganate oxidation in sulfuric acid.[38]

The effect of metallic impurities on the electrochemical properties of carbon nanotubes has been well-documented.[30–33,39] Oxidation of sulfide groups is sensitive towards catalytic metal impurities, and this effect is seen in the lowering of its oxidation potential towards more negative values. We have previously shown that the electrocatalytic oxidation of sulfides at carbon nanotube surfaces can be attributed to the presence of Ni-based impurities.[40] Cyclic voltammetry experiments were conducted in the presence of 10 mM NaHS on MWCNTs, GONRs, and NiO nanoparticle-modified electrodes (Figure 4a). Edge-plane pyrolytic graphite (EPPG, representative of graphitic edge and defect sites in carbon materials)[41] and bare, unmodified glassy carbon (GC) electrodes served as control experiments for comparison. The voltammograms showed that oxidation of the sulfide group on a GC electrode produces a peak at approximately $+0.68$ V, whereas the corresponding value on the EPPG electrode was $+0.51$ V. Experiments with Fe_3O_4- and Co_3O_4-nanoparticle modified electrodes did not show any catalytic activity towards the oxidation of HS^- (data not shown). The

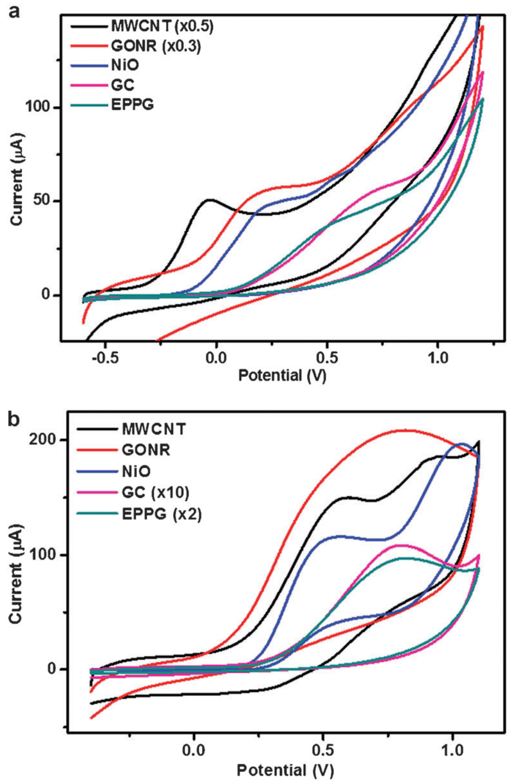

Figure 4. Cyclic voltammetry profiles in the presence of a) 10 mM NaHS, and b) 5 mM hydrazine, on MWCNTs, GONRs, NiO nanoparticle-modified glassy carbon (GC) electrodes as well as bare GC and EPPG electrodes. The suffix "×" denotes the number of times the current values of the CV was scaled for the ease of comparison. Conditions: scan rate, $100\,mVs^{-1}$; background electrolyte, 50 mM phosphate buffer solution (pH 7.4); reference electrode, Ag/AgCl.

MWCNT modified electrode gave a highly electrocatalytic oxidation peak around 0 V, which as previously mentioned arises from residual metallic impurities, even at the ppb level. What is of greater concern is that despite a tenfold decrease in the Ni content to less than 2 ppb after exposure to oxidative treatment, GONRs still showed an electrocatalytic behavior towards the oxidation of HS^-, with both the GONR- and NiO-modified GC electrodes exhibiting oxidative peaks around +0.25 V as well as highly similar voltammetric profiles. This is striking evidence that even the harsh oxidative and acidic conditions used in the unzipping reaction are unable to sufficiently remove metal-based impurities to render them electrochemically inactive.

The electrocatalytic effect of metallic impurities in the oxidation of hydrazine has also been previously reported.[30,42] Since the NaHS experiments were a clear indicator of electrocatalytic activity because of the presence of residual Ni-based impurities, our next course of action was to search for signs of similar activity with hydrazine in both the starting MWCNTs as well as the GONRs obtained. Figure 4b shows cyclic voltammetry measurements in the presence of 5 mM hydrazine using the same electrode setups used in the NaHS investigation. Oxidation of hydrazine on bare GC and EPPG electrodes represented the non-electrocatalytic control case and occurred at similar potentials (+0.80 V). In contrast, the MWCNT-modified electrode gave a first oxidation wave beginning at +0.08 V with a peak at +0.58 V and can be attributed to the presence of Ni-based impurities since it is in the same region as the peak corresponding to first oxidation at a NiO-modified electrode (beginning at +0.12 V, peak at +0.53 V). The second oxidation peak in both cases arises from the underlying GC electrode surface; such behavior is typical of heterogeneous electrode surfaces and could arise from incomplete coverage of the GC electrode with the deposited materials. As for the electrode modified with GONRs, a much broader peak with oxidation commencing at +0.03 V was observed, and constituted both Ni-catalyzed oxidation of hydrazine as well as the uncatalyzed reaction on the underlying GC surface. This may conceivably be due to the lowered Ni content in the nanoribbons as compared to the MWCNT starting material.[38] Nevertheless, it is evident and paramount that the lowered Ni content in GONRs after oxidative treatment under acidic conditions, once again, manifests itself in the electrocatalytic oxidation of hydrazine.

In conclusion, we have demonstrated that the oxidative opening of multiwalled carbon nanotubes cannot eliminate metallic impurities despite the relatively harsh conditions used, although the metal content is indeed lowered. For the MWCNTs used as well as the GONRs derived from them, residual metals (demonstrated in the form of Ni-based impurities) still heavily influence the electrochemical behavior of the materials as shown in the oxidation of HS^- and hydrazine. This phenomenon occurs even at the extremely low (ppb) detected level. It is likely that the presence of metallic impurities affects more than just the electrochemical properties of opened nanotubes, which would be of concern when the purity of the material is important in its applications, for example in biomedical uses and the fabrication of nanoscale electronic devices. It is reasonable to propose that all reports on the applications of graphene-based materials should also include accurate measurements of the existing levels of metallic impurities.

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