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Impure Graphene

Metallic Impurities in Graphenes Prepared from Graphite Can Dramatically Influence Their Properties**

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Herein, we wish to demonstrate that graphenes prepared by the top-down exfoliation of graphite contain metallic impurities which might dominate their properties and can have a negative influence on their potential applications.

Graphene and its derivates, such as graphene oxides, have been proposed to play a major role in a wide plethora of applications in physics, chemistry, biomedical, and materials science.[1] Such applications include the fabrication of electronic,[2] sensing, and energy storage devices.[3] Depending on the specific application, several different methods are currently available for graphene preparation. These methods can either be 1) top-down: consisting of the exfoliation of natural or synthetic graphite to single or few layers graphene[4] or 2) bottom-up: consisting of a chemical vapor deposition (CVD) growth of graphene onto metal catalyst substrates.[5] The top-down approach is cost-effective, offers the possibility of a large-scale production, and is preferred when graphene and other graphene-based materials are adopted to fabricate new electrode materials for high-performance sensing and energy storage devices.[6]

The starting material used in the top-down method is typically graphite, which is available at low cost and in large quantities. Graphite is then treated with strong acids and oxidants to yield graphite oxide (GO) which is rich in oxygen-containing groups. Graphite oxide can then be easily exfoliated by various methods, such as thermal exfoliation or ultrasonication.[7] One of the simplest and most commonly used method consists of subjecting GO to thermal shock by rapidly heating to about 1000 °C.[8] This treatment results in both the exfoliation to graphene sheets as well as the reduction of GO by elimination of oxygen-containing groups.[9]

Before continuing our discussion on graphene, we should familiarize ourselves with the properties of another well-known carbon nanomaterial: carbon nanotubes (CNTs). It has been well-documented that CNTs contain a large amount of residual metal-catalyst impurities which are practically impossible to remove even after treatment with strong acid at elevated temperatures.[10] It was also shown that such impurities can completely dominate many properties that were originally attributed to CNTs.

These impurities can alter electrochemical properties,[11] influence redox properties of biomarkers,[12] have effects on adsorption properties[13] and can also cause adverse toxicological effects.[14] Going even further, there is also significant amount of evidence that trace metallic impurities (down to 50 ppb levels) are responsible for some "noble metal catalyst free" synthetic reactions.[15]

Graphenes prepared from graphite do not require the usage of a metal catalyst substrate and thus far, the presence of metallic impurities has not been considered to be an issue. This is highly surprising as it is well known for example that natural graphite contains different metallic impurities such as iron, cobalt and nickel at concentrations that depend on the site of extraction and the specific geomorphologic characteristic of the mine soil.[16]

Herein, we will demonstrate that metallic impurities originating from graphite material are still present even after oxidative treatment, which yields graphite oxide (GO) and also after the thermal exfoliation/reduction of GO to thermally reduced graphene (TR-G; see Figure 1). We will show how the metallic impurities can significantly influence the electrochemical properties of these three materials. We assessed the amount of metallic impurities in all the three materials by using inductively-coupled plasma-mass spectroscopy (ICP-MS), which is able to detect trace amount of metals to ppt levels. The results from the analysis of graphite, graphite oxide, and TR-G are summarized in Table 1.

It is clear that the exfoliated graphene TR-G contains significant amounts of impurities, ranging from 5.2 ppm of Mo

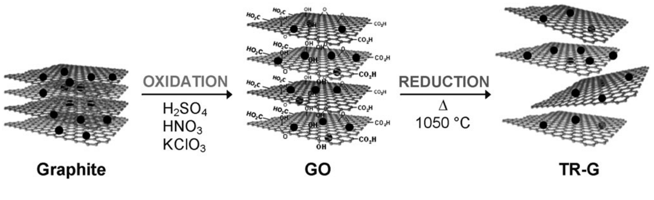

Figure 1. Schematic of the top-down preparation of graphene starting from graphite. The oxidative treatment to obtain graphite oxide (GO) is followed by the thermal exfoliation/reduction to graphene (TR-G). Metallic impurities (black dots) present in graphite, still remain after the treatments.

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Table 1: Metallic impurities content (ppm) in graphite, graphite oxide (GO), and thermally reduced graphene (TR-G) determined by ICP-MS analysis (rounded to 2 significant figures).

Sample	Co	Cu	Fe	Mo	Ni
Graphite	0.37	7.2	2.4×10^2	4.7	1.9×10^2
GO	0.31	7.2	5.6×10^2	3.0	2.2×10^2
TR-G	7.8	59	16×10^2	5.2	2.0×10^2

to 16×10^2 ppm of Fe. It is also interesting to note that in general the amount of impurities determined by ICP-MS increases from the starting material graphite to the final product TR-G. This can be explained by the fact that the microwave acid-based digestion method used to prepare the samples prior to the ICP-MS analysis is able to extract the majority of the impurities only from the completely exfoliated TR-G. Graphite, owing to its inherent nature is hardly completely digested and therefore some of the impurities are well trapped in the crystals and cannot be detected.

It is well recognized that the electrochemical behavior of materials is very sensitive to the presence of heterogeneous impurities.[17] To this point, we will present data that show how trace levels of residual metallic impurities present in the thermally reduced graphene material are capable of dominating its electrochemical properties. Cyclic voltammetry is employed to investigate the redox properties of three molecular probes: cumene hydroperoxide (CHP),[18] L-glutathione (GSH)[11c] and sodium hydrogen sulfide (NaHS).[19] These probes are well known to be very sensitive to presence of metallic impurities, such as Ni and Fe.[11c,18,19]

Before discussing the influence of impurities on the electrochemistry of graphene, we need to introduce the standard material that graphene should be compared to. The electrochemistry of pure graphene as well as thermally reduced graphene resembles that of the edge-plane pyrolytic graphite electrodes (EPPG).[20] This means that any deviation from the electrochemistry of EPPG electrodes can be attributed to the presence of metallic impurities present in the material. We will demonstrate this in the following discussion on the redox properties of cumene hydroperoxide, L-glutathione, and NaHS at graphene electrodes.

Figure 2 A shows the cyclic voltammograms in the presence of 5 mM cumene hydroperoxide. It can be seen that the reduction signal for cumene hydroperoxide at the glassy carbon (GC) and EPPG electrodes starts at about −0.6 V (vs. Ag/AgCl; all potentials stated in this work are vs. Ag/AgCl reference electrode) reaching a maximum at around −0.75 V. TR-G modified electrode presents an intense reduction signal which reaches the maximum at about −0.4 V. For the TR-G material, a clear electrocatalytic effect can be deduced since the reduction of cumene hydroperoxide occurs at more positive potentials than the EPPG and GC electrodes. The graphite-modified electrode exhibits a reduction wave starting at about −0.2 V and reaching maximum at about −0.6 V. GO-modified electrode shows an intense reduction peak starting at about −0.5 V, but this is attributed to the intrinsic reduction of epoxy groups present on the surface of GO.[21] For comparison, CHP reduction was evaluated using Fe_3O_4

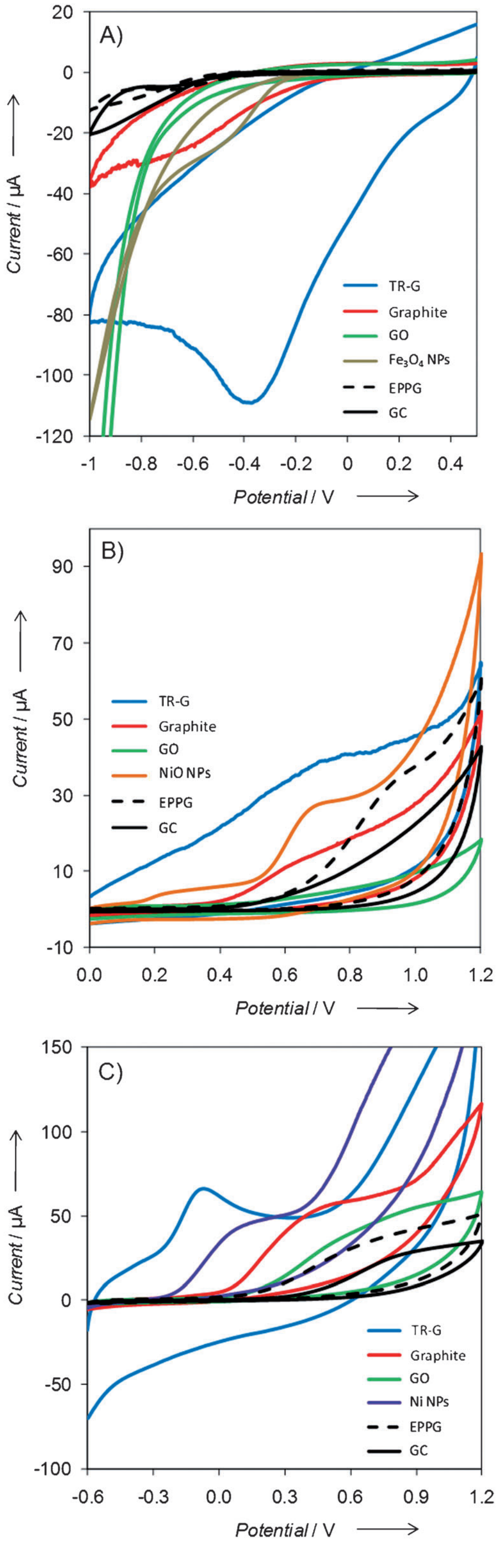

Figure 2. Cyclic voltammograms recorded using electrodes modified with TR-G, graphite, graphite oxide (GO), Ni NPs, NiO NPs, Fe_3O_4 NPs, and using bare GC and EPPG electrodes in the presence of A) 5 mM cumene hydroperoxide; B) 5 mM L-glutathione, and C) 5 mM sodium hydrogen sulfide. Supporting electrolyte, 50 mM phosphate buffered solution at pH 7.2. Scan rate, 0.1 V s^{-1}. Reference electrode: Ag/AgCl.

nanoparticles (Fe_3O_4 NPs) modified electrode which has a well-known catalytic effect on the reduction of hydrogen peroxide[11a] as well as organic peroxides.[18] It appears evident that a catalytic effect is occurring since a reduction signal starts at about −0.2 V with maximum at about −0.5 V, similar to the signals recorded with graphite- and TR-G-modified electrodes. Voltammetric signals resulting from blank solutions and in the presence of cumene hydroperoxide using Co-, Co_3O_4-, Cu_2O-, Ni-, NiO-, MoO_2-, and MoO_3-nanoparticle modified electrodes (data not shown) showed no catalytic effect of these metals/metal oxides to the reduction of cumene hydroperoxide.

Figure 2B shows the cyclic voltammograms investigating the redox behavior of L-glutathione at different electrode materials recorded between 0 and 1.2 V (vs. Ag/AgCl). The EPPG electrode gives a clear oxidative wave starting at about 0.6 V and reaching a maximum at about 0.9 V. There is a significant shift to lower potentials when TR-G or graphite modified electrodes were used. In particular, oxidation of L-glutathione at TR-G resulted in a peak starting at approximately 0.4 V and reaching a maximum at about 0.7 V. Oxidation of L-glutathione at graphite started at about 0.4 V reaching a maximum at about 0.65 V. It is clear that the oxidation of L-glutathione occurs at lower potential when using TR-G or graphite than the EPPG electrode. This effect can be attributed to the presence of NiO metallic impurities present within the TR-G and graphite materials as demonstrated by the fact that the NiO nanoparticles (NiO NPs) modified electrode exhibited a clear main oxidative wave starting at about 0.5 V and reaching a maximum at about 0.65 V, similar to the TR-G and graphite modified electrodes. No clear oxidation wave was recorded using the bare and GO modified GC electrodes. Voltammetric signals resulting from blank solutions and solutions containing L-glutathione at Co-, Co_3O_4-, Fe_3O_4-, Cu_2O-, MoO_2-, and MoO_3-nanoparticle modified electrodes (data not shown) showed no catalytic effect of these metals/metal oxides to the oxidation of L-glutathione.

We also recorded cyclic voltammograms in the presence of 5 mM sodium hydrogen sulfide (NaHS) at glassy carbon electrodes modified with graphite, GO and TR-G and we compared them with the bare GC, EPPG, and Ni nanoparticles (Ni NPs) modified electrodes (Figure 2C). While the EPPG, bare and GO-modified GC electrodes resulted with an oxidative signal starting at about 0.1 V with a maximum at about 0.7 V, the signals recorded with TR-G and graphite shifted towards lower potentials. More precisely, graphite gave a clear oxidative wave starting at about 0 V and reaching a maximum at 0.5 V and the TR-G-modified electrode gave a signal starting at about −0.3 V with a maximum at about −0.1 V. A similar shifting to lower potential for the oxidation of HS^- as compared to the GC or EPPG electrode is also observed when using a Ni NP-modified GC electrode with the signal starting at about −0.2 V with a maximum at about 0.1 V. The catalytic effect toward the oxidation of sulfide ions using TR-G or graphite can therefore be attributed to the presence of Ni impurities which gave a similar oxidative response. Other metals/metal oxides nanoparticles, such as Co, Co_3O_4, Cu_2O, Fe_3O_4, MoO_2, and MoO_3 were tested, but the voltammetric signals resulting from blank solutions and solutions containing NaHS (data not shown) showed no electrocatalytic effect of these metals/metal oxides on the oxidation of NaHS.

It is evident from the experiments performed that metallic impurities present within the graphite starting material still remain after the oxidation treatment to obtain GO, and after the thermal exfoliation/reduction to produce TR-G. These impurities have a profound effect on the electrocatalytic properties of graphenes that were prepared by exfoliation and reduction of graphite, as shown for the oxidation of HS^- and L-glutathione as well as for the reduction of organic peroxides, such as cumene hydroperoxide. This raises an important issue when such graphene-based materials are used to fabricate electrochemical sensing or energy-storage devices. The wider implications are twofold: 1) Even though we have demonstrated that the metallic impurities can dominate the electrochemistry of graphene, it is likely that other properties, such as toxicity will be affected as well. It has been previously demonstrated that graphene grown on Fe–Co nanoparticles exhibited cytotoxicity and this is most likely due to presence of metallic impurities, not graphene itself;[22] 2) We have demonstrated that graphene prepared by top-down method from graphite contains significant amount of impurities. It should thus be highlighted that graphenes grown via the bottom-up methods which requires the use metallic catalyst substrates would most likely face similar issues that are associated with such prepared graphenes.

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