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"Metal-Free" Catalytic Oxygen Reduction Reaction on Heteroatom-Doped Graphene is Caused by Trace Metal Impurities**

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Abstract: *The oxygen reduction reaction (ORR) is of high industrial importance. There is a large body of literature showing that metal-based catalytic nanoparticles (e.g. Co, Mn, Fe or hybrid Mn/Co-based nanoparticles) supported on graphene act as efficient catalysts for the ORR. A significant research effort is also directed to the so-called "metal-free" oxygen reduction reaction on heteroatom-doped graphene surfaces. While such studies of the ORR on nonmetallic heteroatom-doped graphene are advertised as "metal-free" there is typically no sufficient effort to characterize the doped materials to verify that they are indeed free of any trace metal. Here we argue that the claimed "metal-free" electrocatalysis of the oxygen reduction reaction on heteroatom-doped graphene is caused by metallic impurities present within the graphene materials.*

The oxygen reduction reaction (ORR) is of utmost technological importance as it is a key reaction in fuel cells and next-generation Zn batteries.[1] The most efficient and widely used catalyst for the ORR is platinum. However, its limited accessibility at large scale encouraged an intensive search for alternative non-Pt catalysts that are more easily available at low costs and demonstrate comparable catalytic properties for the ORR. There is a large body of literature showing, for example, that metal-based catalytic nanoparticles (e.g. Co, Mn, Fe or hybrid Mn/Co-based nanoparticles) supported on graphene or carbon nanotubes act as efficient catalysts for the ORR.[2–9] A significant research effort is also directed to the so-called "metal-free" oxygen reduction reaction on heteroatom-doped carbon surfaces,[10,11] and more recently on graphene surfaces.[12–18] In these instances, graphene doped with nitrogen, boron, sulfur or in combinations (i.e. nitrogen/sulfur or nitrogen/boron) provided significant electrocatalytic effects for the ORR.[12–18] While such studies on the ORR with heteroatom-doped (nonmetallic) graphene are advertised as "metal-free", there is typically no sufficient effort to characterize the doped materials to verify that they are indeed free of any trace metal. Characterization techniques for trace metals such as ICP-MS/OES, X-ray fluorescence or neutron activation analysis would easily provide the actual material composition with the types and levels of impurities present, but are never employed.[12–18] This is striking since it is already well-known that similar to carbon nanotubes,[19,20] graphene materials, especially those prepared using graphite as a starting material, contain a significant amount of metallic impurities which influence their electrochemical properties.[21]

Graphene used as "metal-free" electrocatalyst for the ORR in the aforementioned studies are prepared from graphite and it is important to note that the Hummers oxidation method is usually applied.[22] This involves the use of permanganate oxidant to obtain an intermediate material, graphite oxide, prior to a reduction/doping step to give graphene.[12–18] It is known for decades that graphite contains large varieties of metallic impurities with a contribution up to 2 wt% of the material.[23–31] These impurities consist of Fe, Ni, Co, Mo, Mn, V, and Cr.[24] It has been previously shown by Compton and others that these metallic impurities within sp^2 carbon nanomaterials dramatically influence the electrocatalytic properties of the nanomaterials and that they can, in some cases, dominate the electrochemistry of the materials even when present at only trace levels.[19,32–36] It was shown that even impurities within known impurities, such as clusters of tens of iron atoms in large Co/Mo-based nanoparticle impurities, are able to catalyze important reduction reactions.[37] From a broader perspective, one should also mention that traces of Cu impurities at low parts per million levels in $FeCl_3$ were found to be responsible for cross-coupling synthetic reactions;[38,39] and 50 ppb of Pd impurities were the source of catalysis in supposedly transition-metal-free Suzuki-type cross-coupling reaction.[40,41] Recently there was an important report showing that trace metal residues were responsible for the electrocatalytic effect in the ORR at amorphous carbon surfaces.[42]

Here we wish to highlight that residual manganese-based metallic impurities in graphene play an extremely active role in the electrocatalysis of the oxygen reduction reaction on supposedly metal-free graphene electrodes. Manganese-based impurities are present abundantly in graphene prepared by the Hummers oxidation method which applies a large amount of permanganate oxidant.[43,44]

In this work, we employed natural graphite (from a single source) as a starting material to prepare two different graphene materials. One of the graphene materials was prepared employing the Hummers oxidation method[22] (permanganate oxidant) prior to a chemical reduction treatment with hydrazine to obtain graphene (G-HU). At the same time, a control graphene material was prepared using the Staudenmaier oxidation method,[45] which uses a chlorate oxidant, to produce hydrazine-reduced graphene (G-ST). The

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Table 1: Content of metallic impurities (ppm) in the starting natural graphite and the graphene materials prepared by Hummers method (G-HU) and Staudenmaier method (G-ST) as determined by ICP-MS analysis.

Impurity	Graphite	G-HU	G-ST
Fe	4224	927.6	1685.9
Co	3.3	0.3	7.1
Ni	33.7	18.0	13.8
Mn	24.9	8311.3	17.9

amount of metallic impurities present in the graphite starting material as well as in the graphene products were determined by inductively coupled plasma mass spectrometry (ICP-MS) analysis and summarized in Table 1. All impurities are in the high ppm range with the graphene prepared by the Hummers method, G-HU (using permanganate oxidant), containing a much higher amount of manganese than the graphene prepared by the Staudenmaier method, G-ST (using chlorate oxidant). The higher Mn content in the graphene obtained using the permanganate oxidation method as compared to that obtained from the chlorate oxidation method is consistent with previous findings.[43,44,46]

Even the graphite starting material contains Mn at ppm level, which is likely to be the primary source of contamination in the graphene prepared by the Staudenmaier method (see Table 1). We wish to highlight again here that the previously reported studies on "metal-free" electrocatalysis of the ORR typically applied the Hummers method to prepare the graphene materials,[12–18] and therefore one may expect a similar concentration of manganese in such materials. To better understand the electrocatalytic behavior of the graphene materials, initial investigations on the electrochemistry of metal oxide nanoparticles towards oxygen reduction in KOH electrolyte solution were carried out. We recorded linear sweep voltammograms of glassy carbon electrodes (GCs) modified with Fe_3O_4, NiO, Co_3O_4, and MnO_2 as well as of the bare GC electrode. For a clearer comparison, typical and representative voltammograms have been baseline-corrected and are summarized in Figure 1 (original recordings can be found in Figure S1 of the Supporting Information). The oxygen reduction onset potentials using these metal oxides were practically indistinguishable from that obtained with the bare GC (−267 mV vs. Ag/AgCl; all potentials in this work are stated vs. Ag/AgCl electrode), with the striking exception of MnO_2 (−94 mV). Manganese(IV) oxide-modified GC electrodes showed, in fact, a significant onset potential shift of 173 mV, which indicated a clear catalytic behavior of MnO_2 for the oxygen reduction reaction. Consequently, we investigated the behavior of the graphene materials, G-HU and G-ST.

The graphene materials showed significantly different onset potentials for the reduction of oxygen (Figure 2). G-HU rich in Mn-based impurities (> 8000 ppm) showed an onset potential at −134 mV, which has the largest potential shift of about 133 mV as compared to bare GC. The graphene prepared by the Staudenmaier method, consisting of a very low content of Mn-based impurities (about 18 ppm), gave an onset potential at −183 mV, which was about 50 mV more negative than that recorded for G-HU. It is clear that the Mn-based impurities exhibit a strong influence on the oxygen reduction reaction.

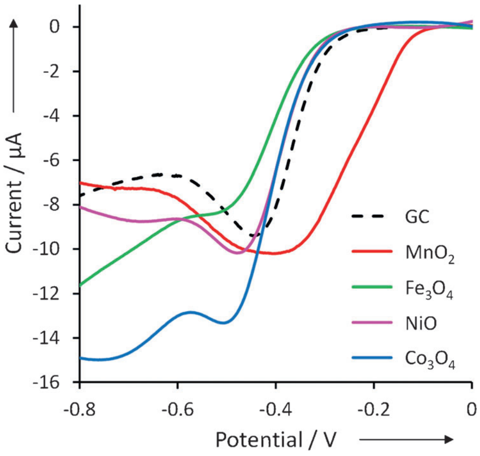

Figure 1. Linear sweep voltammograms recorded in air-saturated 0.1 м KOH solution using a bare glassy carbon electrode (black-dashed line) and a GC electrode modified with Co_3O_4 (blue line), NiO (pink line), Fe_3O_4 (green line), and MnO_2 (red line) nanoparticles. Scan rate: 0.1 Vs^{-1}.

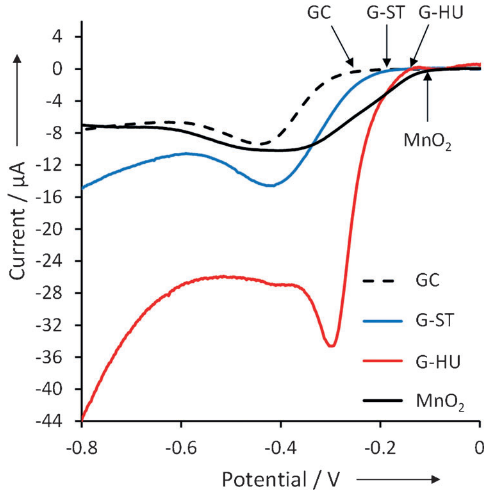

Figure 2. Linear sweep voltammograms recorded in air-saturated 0.1 м KOH solution using a bare glassy carbon electrode (black-dashed line) and a GC electrode modified with G-HU (red line), and G-ST (blue line) graphene materials. Scan rate: 0.1 Vs^{-1}.

A graphical comparison of the onset potentials recorded for all the materials is summarized in Figure 3. It is indicative that the presence of Mn-based impurities in graphene causes a catalytic effect towards the ORR. According to these results a catalytic effect is evident even for the G-ST which despite a Mn content as low as 18 ppm (0.0018 wt %) showed a potential shift of about 80 mV in comparison to the bare GC electrode. This is a clear indication that even a slight trace of Mn metallic impurities in graphene materials is sufficient to alter or dominate their electrocatalytic properties towards oxygen reduction reaction. This result is also consistent with other reports where manganese oxide nanoparticles are used

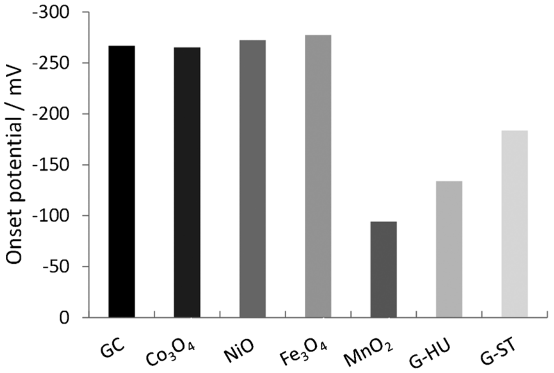

Figure 3. Onset potentials for ORR measured for all materials.

in conjunction with graphene-supported materials to promote the catalytic oxygen reduction at more positive potentials, functioning as electrocatalyst of the ORR.[4–6]

In conclusion, we have demonstrated that trace (ppm) levels of metallic impurities, in our case manganese oxide, found in graphene have profound influences on the observed oxygen reduction reaction potentials. In light of these findings, it is highly recommended to perform precise and complete characterizations of all materials employed for the catalysis of oxygen reduction reactions.

We also wish to draw a more general conclusion from our findings in view of previous reports on electrocatalysis of ORR on graphene surfaces. Impurities in the order of parts per million are inherently present in graphite and very likely increase during subsequent chemical treatments applied to fabricate graphene.[43,44,46] Moreover, reported "metal-free" studies on the catalytic effects of heteroatom-doped graphene materials for the ORR typically employed Hummers (permanganate) method to prepare graphene[12–18] and should therefore likely suffer from a significant contamination of Mn besides other impurities.[43,44,46] It is very probable that trace levels of manganese oxide in these graphene materials were responsible for the reported "metal-free" electrocatalysis.[12–18] As such, we strongly advocate that for all "metal-free" graphene catalytic reactions, elemental analysis of metal contents in graphene should be provided to support the "metal-free" claims.

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