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Residual Metallic Impurities within Carbon Nanotubes Play Dominant Role in Supposedly “Metal-Free” Oxygen Reduction Reaction

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Oxygen reduction reaction (ORR) is of key importance in the area of electrochemical energy production. The replacement of Pt industrial standard with heteroatom doped metal-free carbon nanotubes was previously suggested for ORR. Here we will show that the ORR electrocatalysis on these supposed metal-free materials is likely in fact caused in by the presence of residual metallic impurities within the carbon nanotubes and that these impurities play dominant role.

Oxygen reduction reaction (ORR) is of key importance for fuel cells as well as for zinc-air batteries. Efficient, low potential cathodic reduction of oxygen is typically catalyzed by Pt supported on carbon surfaces.[1] However, due to the high cost of Pt there is a huge interest in replacing Pt with other electrocatalytic systems.1 There is a significant amount of works being published on the utilization of non-noble metal oxide decorated carbon surfaces, including carbon nanotubes for ORR. It has been shown that Fe, Co and Mn-based oxides supported on CNTs act as efficient catalyst for ORR.[2-7] There have also been reports on *metal-free* catalysis of ORR on nitrogen,[8-11] boron,[12] or B/N[13] doped carbon nanotubes. These claims of metal-free electrocatalysis of ORR on CNTs are remarkable as no metal is supposedly involved in the electrocatalysis of ORR8[-13]; if these claims were correct they would indeed have very significant impact on the practical industrial applications of such metal-free materials in energy production and storage devices.

There are two main drawbacks of the claims “metal-free” ORR catalytic reactions on doped carbon nanotubes in the above mentioned works8[-13]. Firstly, the vast majority of carbon nanotubes used have been prepared using metal containing catalyst, i.e. ferrocene,[12,13] iron(II) phthalocyanine,8,9 or other metallic catalysts;[10,11] and this is known to introduce significant amount of residual metallic impurities within the carbon nanotubes.[14] Supposedly "metal-free" synthesis of CNTs leads to the contamination of the CNTs during the processing by metal.[15] Secondly, when claiming the “metal-free” electrocatalysis of ORR on nitrogen-doped CNTs, the authors did not in fact perform any *sensitive* characterization of the CNT materials which would prove that the samples are indeed *metal-free*. Techniques such as ICP-MS/OES, neutron activation analysis or X-Ray fluorescence would have been able to provide an accurate insight to the amount of metal impurities in carbon nanotubes; however, these analyses are not typically performed to prove such metal-free claims. Note that X-ray photoelectron spectroscopy (XPS) which is used in some cases8[,10,12] is not sensitive enough, having a general limit of detection of 0.1% wt. (1000 ppm).[16] In addition, XPS being a surface sensitive technique, it is unable to detect even several wt% of residual catalyst metallic impurities within CNTs.[17]

It is well-known from literature that carbon nanotubes which are grown from metallic catalyst precursors contain residual metallic content[14]. Such residual metallic impurities are practically impossible to remove from the produced carbon nanotubes and will remain within them even after several attempted acid washing procedures, at levels as high as several wt.%.[14,18-22] It should also be noted that methods capable of detecting ppm amounts of metallic impurities include X-ray fluorescence analysis (XRF), electron microscopy/energy dispersive X-ray spectroscopy, ICP-MS/OES (down to ppb levels) or neutron activation analysis (NAA); whereas, as mentioned above, surface analysis methods such as XPS are unable to detect even several wt% of metallic impurities within the CNTs.[17] It has been demonstrated by Compton and co-workers that residual catalyst metallic impurities within the carbon nanotubes are actually responsible for the supposed unique electrocatalytic properties of CNTs towards hydrazine,[19] hydrogen peroxide,[23] glucose,[24] and halothane.[25] We have demonstrated that the residual metallic catalysts within CNTs are responsible for the electrocatalytic oxidation of glutathione[26] and the reduction of a whole group of organic peroxides[27]. Moreover, it has been shown that even 100 ppm (that is 0.01 wt%) of metallic impurities can dominate the electrochemistry of carbon nanotubes.[28] Additionally, it has been demonstrated that residual metallic impurities present in CNTs (i.e. Co/Mo) contain trace levels of impurities (i.e. Fe) within themselves and these “impurities within impurities”, present at the levels of tens of atoms per metallic impurity nanoparticle, can dominate the electrochemistry of the system as well.[29]

Recently there have been reports showing that trace metal residues promote the activity of a supposedly metal-free nitrogen-doped amorphous carbon catalyst for the ORR,[30] and that metallic impurities within graphene are the catalytic sites for ORR in supposedly metal-free graphenes.[31] Here we wish to re-visit the case of carbon nanotubes and ORR, since there were many strong claims that were made on metal-free ORR at nitrogen and/or boron doped carbon nanotubes where these carbon nanotubes were prepared using metal containing catalysts.8[-13] We will show that metallic impurities within carbon nanotubes in fact responsible for the ORR on carbon nanotubes surface.

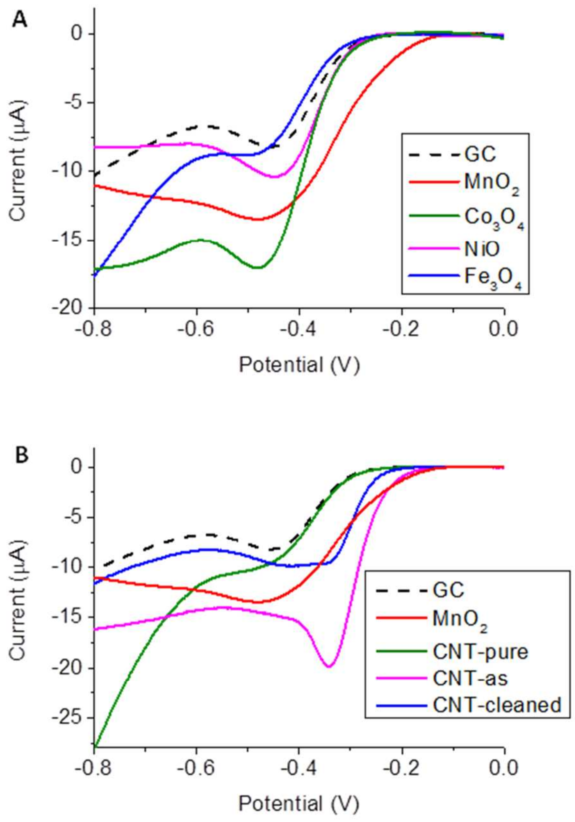

Figure 1. Linear sweep voltammograms recorded in air-saturated 0.1 M KOH solution using a bare glassy carbon electrode (black-dashed line) and (A) GC electrode modified with Co_3O_4 (green line), NiO (magenta line), Fe_3O_4 (blue line), and MnO_2 (red line) materials. (B) GC electrode modified with MnO_2 (red line), CNT-as (magenta line), CNT-cleaned (blue line), CNT-pure (green line). Scan rate: 100 mV s^{-1}.

We chose to investigate the ORR at three different carbon nanotubes- pure CNTs, as received carbon nanotubes and “cleaned” carbon nanotubes. We labeled them CNT-pure, CNT-as and CNT-cleaned, respectively, in the following text. The cleaned carbon nanotubes were prepared from CNT-as by means of extensive purification using chlorine gas at 1000 °C for 10 min.[32] The metal content was determined in the carbon nanotubes by in-house X-ray fluorescence analysis.[32] CNT-as contained 5960 ppm of Mn, 150 ppm of Ni, 30 ppm of Fe and 6160 ppm of Co. CNT-cleaned contained residual catalyst metallic impurities even after an extensive cleaning procedure at levels of 140 ppm of Mn and 200 ppm of Co with no traces of Ni or Fe detected by XRF. This is consistent with previous reports showing that it is highly challenging to decrease the amount of impurities content even by extensive purification.[19-22] CNT-pure were not found to contain detectable amounts of metallic impurities by XRF or ICP-MS. Note that the conductivity of different carbon nanotubes samples used here may differ. However, all of them exhibit metallic conductivity, as they are of multilayer structure. Electrocatalytic properties of CNTs are not related to conductivity (provided they are of metallic conductivity) but to the catalytic sites (either N-doped sites as suggested by many or metals) which are “just” wired by CNTs to the current collector.[33]Therefore the difference in the conductivity of CNTs does not play role in the present study of electrocatalytic effect. Prior to the investigation of ORR on these three CNTs samples we modified glassy carbon (GC) electrode with oxides of metals found in CNTs, such as MnO_2, Fe_3O_4, Co_3O_4 and NiO in an attempt to better understand the potential catalytic effect that metallic impurities found in CNTs can have on the system. The linear sweep voltammograms were recorded at these metal oxide surfaces in air saturated 0.1 M KOH solution. For a clearer comparison, typical and representative voltammograms have been baseline-corrected and are summarized in Figure 1, A (original recordings can be found in Supplementary Information as Figure S1,A). The onset potential for ORR at Fe_3O_4, Co_3O_4 and NiO is -312, -310 and -298 mV, which is close to -298 mV (vs. AgCl) of the underlying GC exhibits (see Figure 2 for graphical representation of onset potentials obtained). This clearly shows that above mentioned iron, cobalt and nickel oxides do not exhibit electrocatalytic effect for the ORR under these conditions. Onset potential for the ORR at MnO_2 is -200 mV, exhibiting catalytic lowering of the overpotential needed for ORR by ∼100 mV. Consequently, we turned our attention to the investigation of ORR on the carbon nanotubes samples in question. Figure 1, B shows the baseline corrected linear scan voltammograms in air saturated KOH (0.1 M) at the as-received, cleaned and pure CNTs (original recordings can be found in Supplementary Information as Figure S1,B). The onset potential for O_2 reduction is -295 mV for pure CNTs, which is practically similar to the onset potential of ORR at GC electrode. This clearly demonstrates that pure CNT do not exhibit any electrocatalytic effect on the ORR. The onset potential for O_2 reduction at the cleaned CNT is lower at -247 mV, while the as-received carbon nanotubes exhibit an onset potential of ORR -219 mV, which is rather close to the onset potential value of MnO_2 (-200 mV). In addition, we performed the control experiments using Fe, FeO, Fe_2O_3, Co and FeOOH and there was no any electrocatalytic effect observed. We show these results as Figure S-2 and S-3 in the ESI. It is thus obvious that with the increasing amount of manganese-based impurities within the CNTs, the onset potential of ORR shifts towards a more positive potential resulting in such CNTs to exhibit an electrocatalytic reduction towards O_2. Therefore, from the comparison of the metal content in the CNTs, it is clear from the metal content and the supposed catalytic properties of CNTs towards ORR, the metallic impurities are the ones truly responsible for the electrocatalytic reduction of O_2, and not inherent CNT materials themselves.

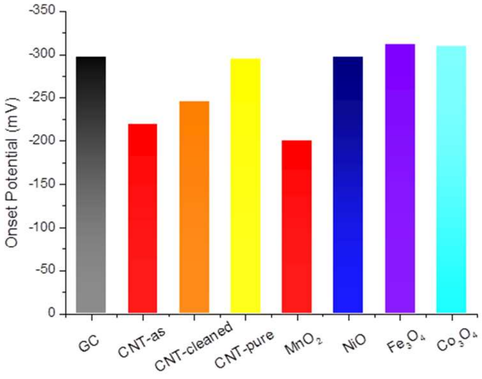

Figure 2. Onset potentials for ORR measured for all studied materials.

In summary, we have demonstrated that pure carbon nanotubes do not exhibit any electrocatalytic effect towards the ORR. We also showed carbon nanotubes that contain residual catalyst metallic impurities, either before or after extensive purification procedures are very much capable of exhibiting strong electrocatalytic properties towards ORR. The catalytic activity is directly correlated to the amount of impurities in the CNTs. In light of these conclusions, it is very likely that the claimed “metal-free” ORR on heteroatom doped carbon nanotubes is in fact a result of residual metallic impurities present within the CNTs. This is supported by the fact that in most of these supposedly “metal-free” ORR catalysis on doped CNTs, the characterization of metal content in the CNT materials have not attempted at all[12,13] or even if it is, the insensitive techniques such as XPS were used8[-10]. We strongly urge the scientists in the community of “metal-free” catalysis on CNTs to use highly sensitive techniques, such as XRF, ICP-MS or nuclear activation analysis to support their *metal-free* claims.

Notes and references

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