Multi-Walled Carbon Nanotube Modified Basal Plane Pyrolytic Graphite Electrodes: Exploring Heterogeneity, Electro-catalysis and Highlighting Batch to Batch Variation

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We highlight the heterogeneity and electro-catalysis of multi-walled carbon nanotubes which is shown to be dependant on batch to batch variation *via* the use of cyclic voltammetry, X-ray photoelectron spectroscopy and transmission electron microscopy. Batch to batch variation is often an overlooked parameter which may limit their use in electrochemistry, and in particular, in the development and realisation of commercial electroanalytical sensors and therefore needs to be considered.

INTRODUCTION

The field of electro-analysis and electro-catalysis has been revolutionised since the introduction of carbon nanotubes [1-8]. Britto [9] and later Wang [10] introduced the concept of carbon nanotubes to promote electron transfer in electroanalytical sensing where electro-catalytic effects were reported. The use of carbon nanotubes, in the two generic forms, multi-walled carbon nanotubes and single-walled carbon nanotubes, continue to be used to enhance electrochemical sensing. Improvements in the electrochemical response include increments in the size of voltammetric signal, enhanced sensitivities, lower detection limits and little or no surface fouling have been reported.

Wang's group showed that the electrocatalytic activity, background current and electroanalytical performance of carbon nanotubes are strongly dependant on their preparation and on the dispersing agent used. They attributed observed

differences in electrochemical reactivity as being due to different surface chemistries [11]. Compton's group have extensively explored the origins of these reported electro-catalytic responses of carbon nanotubes which have been attributed to edge plane like-sites/defects [12,13] occurring at the ends of the open tubes and along the tube axis. That is, carbon nanotubes have been found to be no more reactive than edge plane pyrolytic graphite.

However, there are some instances where deviation from the electro-catalytic origins is observed [14,15]. In these cases, in addition to edge plane sites, the metallic impurities which remain from the catalyst used to fabricate the carbon nanotubes are the origin of the electro-catalytic activity. Again, Compton's group have elegantly explored the role of metallic impurities in MWCNTs upon their electrochemical response demonstrating that iron oxide impurities, which are used in chemical vapor deposition (CVD) fabrication process to fabricate the MWCNTs, can dominate the electrochemical response of the MWCNTs [14,15]. In CVD, carbonaceous metal precursors containing Fe, Co, Ni decompose at high

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temperatures under a reducing environment which form metallic nanoparticles acting as catalytic sites to promote carbon nanotube growth [16]. After fabrication, the carbon nanotubes are purified *via* an acid wash, increasing the purity up to 95%, but it is the composition of the remaining 5% which needs to be addressed. The effect of further acid washing MWCNTs, a common approach in the CNT field has also been explored. It was observed that this has no effect on removing the metallic impurities which suggests that the majority of the impurities are partially trapped within a few graphite layers [14,15].

More recently Pumera [17] has revisited the problem of metallic impurities in multi-walled carbon nanotubes and has considered MWCNTs from NTP Nanotech Port (China) and both MWCNTS and SWCNTs from Sigma-Aldrich. Pumera has demonstrated that after washing MWCNTS and SWCNTS with concentrated nitric acid at 80 ºC, metal catalyst particulates still electrochemically reduce hydrogen peroxide [17]. Through the use of TEM images, it is concluded that the metal impurities are 'sheathed' by graphene sheets, [17] similar to that as inferred by Compton [14,15].

It is important to note that a remarkably small coverage of metallic nanoparticles is adequate to ensure that the electrochemical response behaves similar to that of a corresponding macroelectrode [18]. That means, a few percent of iron is enough to ensure that the electrochemical response is dominated by metal catalyst impurities rather than edge plane-sites/defects. Recently Dai *et al*. have shown that copper impurities in MWCNTs can be used beneficially for the electroanalytical sensing of halothane [19]. However, an often overlooked problem when utilising MWCNTS is the batch to batch variation and workers only ever consider intra reproducibility rather than inter reproducibility. Consequently, in this paper, we highlight the inherent heterogeneity problems of MWCNTS produced *via* CVD which can give rise to varying electrochemical performance of MWCNTs taken from different batches.

EXPERIMENTAL

All chemicals were purchased from Aldrich obtainable at the highest grade available and used directly without further purification. All the solutions were vigorously degassed with oxygen-free nitrogen (BOC Gases, Guildford, Surrey, UK) until oxygen was not electrochemically detectable. All experiments were carried out at a temperature of 295 ± 3 K.

Electrochemical experiments were performed using a μ-Autolab type III potentiostat (Eco-Chemie, Utrecht, Netherlands) controlled by General Purpose Electrochemical Systems v.4.7 software. For all electrochemical experiments carried out in the electrolyte, the working electrode used was a basal plane pyrolytic graphite electrode (4.9 mm diameter BPPG, Le Carbone, Ltd., Sussex, UK). The counter electrode was a bright platinum wire with a large surface area, with a saturated calomel reference electrode completing the circuit.

The BPPG electrode was prepared by first polishing the BPPG electrode surface on carborundum paper and then pressing cellotape on the cleaned BBPG surface before removing along with general attached graphite layers. Before use, the electrode was cleaned in acetone to remove any adhesive. On to this freshly prepared surface, the MWCNTs were cast onto the desired electrode surface by first dispersing 2 mg of MWCNTs into 2 ml ethanol. The suspension is then placed into an ultrasonic bath for 1 min after which 20 µl is pippetted onto the electrode surface. This is allowed to volatize at room temperature producing a presumed random distribution of carbon nanotubes on the electrode surface.

The bamboo multi-walled carbon nanotubes (MWCNTs) were purchased from NanoLab (Brighton, MA) which are 30 ($\pm$15) nm in diameter and 5-20 microns in length. These are grown *via* CVD on a silica wafer which supports the iron metal catalyst. After fabrication, the purity of the MWCNTs are increased from 85% to 95% *via* an acid wash in HF and HCl at 25 ºC for 8 h under convection.

XPS was performed in an ion pumped UHV chamber equipped with a VG nine channel CLAM4 electron energy analyser (base pressure 5×10^{-10} torr) 250 Watt Mg X-ray (1253.6 eV) excitation was used. The analyser was operated at constant pass energy of 100 eV Data was obtained using VGX900-W operating system.

TEM micrographs have been taken on a JEOL 3000FEG (TEM) instrument, which is equipped with an Oxford Instruments energy dispersive X-ray spectrometer (EDS) with a super atmospheric thin window (SATW).

RESULTS AND DISCUSSION

The electrochemical response of bamboo MWCNTs (termed 'batch B') immobilised onto a basal plane pyrolytic graphite (BPPG) electrode was first explored in a solution of 1 mM hydrazine in phosphate buffer of pH 7.1. This electrochemical probe is ideal to study metal impurities since the electrode kinetics of the edge plane like-sites/defects are such that the electrochemical oxidation of hydrazine is not seen within the aqueous accessible potential window. Since the corresponding electrochemical oxidation of hydrazine can only be seen at catalytic metallic surfaces such as iron [14], palladium [20], platinum [21], gold, rhodium [22], nickel [23], cobalt [24], this electrochemical probe is excellent for studying the metal catalyst impurities of carbon nanotubes. It is worth mentioning that the surface oxides are likely to be a key in the electrocatalysis mechanism and, while the exact electrochemical mechanism is unknown, it most likely involves the chemically irreversible oxidation of hydrazine to nitrogen. Figure 1 shows the voltammetric response from the MWCNTs (batch B) but, as observed, no electrochemical signals corresponding to the electrochemical oxidation of hydrazine are seen. In fact, numerous electrochemical interrogations of the MWCNTs were undertaken but still did not produce any electrochemical signals corresponding to the electrochemical oxidation of hydrazine.

Next, the X-ray photoelectron spectroscopy (XPS) was conducted on the MWCNTs (batch B). Analysis of the XPS data, as shown in Fig. 2, indicate that the sample is 98 atomic % carbon and 2 atomic % oxygen with no evidence of iron or other metal catalyst observed. For comparative purposes, the data are depicted in Table 1. Given that the MWCNTs are 30 ($\pm$15) nm in diameter, and the walls of the MWCNTs are only a few nanometers thick and the centre of the tube is hollow, any residual metal particles (if sufficient in number) should be well within the reach of probing using XPS. Even in tubular bundles the uppermost CNTs to the X-ray beam will still be able to be probed all the way through whilst tubes in the centre of the bundle will not. In addition to providing information on possible metallic impurities, XPS can provide information on the amount of oxygen on the nanotubes, which is, in this case, found to be 2 atomic % oxygen. Based on previous work [25], we can relate the amount of atomic % oxygen to give an estimate of the fraction of edge plane like-sites/defects covered by oxygenated species [25], which in this case is
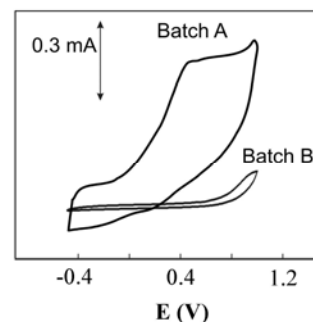
Fig. 1. Cyclic voltammograms of bamboo MWCNTs (batch B) compared directly with previously studied bamboo MWCNTs (batch A). Experimental conditions: 1 mM hydrazine in 0.1 M phosphate buffer of pH 7.1. The MWCNT were immobilised onto a basal plane pyrolytic graphite electrode (see experimental section). Scan rate 100 mV s^{-1}. Date recorded *vs*. SCE.
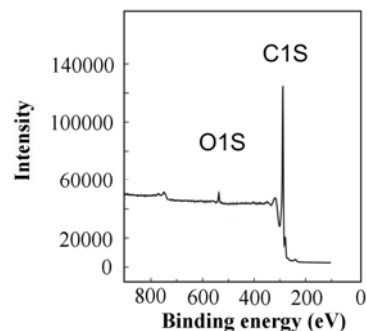
Fig. 2. XPS spectra of batch B bamboo multi-walled carbon nanotubes.

found to be a significant fraction ~0.4. Note that these oxygenated species promote a means for binding adsorbing materials, such as NADH [26].

We next compare this current batch (batch B) of MWCNTs directly with a different batch of MWCNT (known as 'batch A') previously characterized [14,15]. Figure 1 depicts the response of the MWCNTs from this study (batch B) with MWCNTs from a previous batch (batch A). It is evident that the MWCNTs from batch A exhibit a well defined voltammetric signal corresponding to the electrochemical

Table 1. Comparison of XPS Data Obtained from Different Batches of MWCNTs[a]

	Atomic % oxygen	Atomic % carbon	Atomic % iron
Batch A	1.0	98.9	0.1
Batch B	2.0	98.0	0.0

[a]Batch A data has been characterized previously [14,15] and batch B has been characterized in this study.

oxidation of hydrazine. Again, note that this is only observed when metallic impurities are present and if tried using an electrode mimicking carbon nanotubes, *viz*, an edge plane pyrolytic graphite electrode, no voltammetric waves would be observed. In the case of the MWCNTs explored here (batch B), it is clear that no appreciable electrochemical oxidation signals are observed. The XPS data of the MWCNTs from batch A reveal that the sample is 98.9 atomic % carbon, 1.0 atomic % oxygen and 0.1 atomic % iron [14]. For comparative purposes, the data are also depicted in Table 1. In addition to the cyclic voltammetry presented above, the XPS data also clearly highlight the presence of metallic impurities.

The voltammetric and XPS probing of the MWCNTs from different batches clearly indicate that the more recently produced batch (batch B) has very little metallic impurities, if none at all, while batch A has a large amount of metallic impurities. We turn to exploring the MWCNTs with Transmission Electron Microscopy (TEM).

Figure 3A and B show typical TEM images of the bamboo MWCNTs (batch B) where the unique bamboo structure of the MWCNTs can be seen. Exploring the MWCNTs further with TEM, we find evidence of metal impurities. Figure 3C shows a metal impurity within a wall of a bamboo MWCNT while Figs. 3D-E display metal impurities contained within the core of the bamboo MWCNTs. Figure 3F shows two interesting features. In the top left of the picture, a metallic impurity contained within the core of the MWCNT can be observed but in addition a single nanoparticle, which is approximately 20 nm in diameter appears to be trapped in a bundle of MWCNTs. Note that the MWCNT were extensively explored with TEM and it was found that only a few images showed single catalyst nanoparticles but with the majority of the images showing trapped impurities. In contrast, microscopy of the MWCNTs from batch A revealed iron as identified with WDX-SEM in the range of 50 nm and less [14].

Overall, comparison of batch A and batch B reveals that the heterogeneity of the MWCNTs is significantly different. Thus, when assessing the use of carbon nanotubes as electrochemical sensors, one must not only consider the origin of the electrochemical response but also batch to batch variation since, for example, if relying on the heterogeneity *viz*, metallic impurities to catalyse an analyte, this will vary from batch to batch likely producing variable sensors.

The above experiments highlight that the use of cyclic voltammetry and a suitable electrochemical probe can be conveniently used to determine the electrochemical origin of carbon nanotube modified electrodes. Using the electrochemical oxidation of hydrazine or another suitable electrochemical probe, it should be possible to quantify the active catalyst. Note that only a few percent of catalyst nanoparticles need to be present for the electrochemical response to be dominated by the nanoparticles. Given that the carbon nanotubes containing metallic impurities act similar to a nanoparticle array, it may be possible to fit the voltammetric response to theory such as using the diffusion domain approximation [18], or another suitable theory which considers the diffusional profile of the nanoparticles as individual nanoelectrodes [18], to try to quantify the active catalyst. However, the exact relationship between the catalyst accessibility and the electrochemical oxidation of hydrazine is at present unknown.

The observed voltammetry, that is, the absence of any electrochemical response using batch B compared to that of batch A, with complementary XPS and TEM data allows an insight into the location of the catalyst nanoparticle. There are two cases to consider, partially trapped or completely trapped metallic impurities (see Fig. 4). In the latter case, the metallic impurities are completely trapped within the core of the nanotube, as evidenced by TEM and there is an absence of a three-phase boundary meaning that the electrochemical response is due to edge plane like-sites/defects. In the former case, the catalyst nanoparticles dominate the electrochemistry since the partially trapped catalyst nanoparticle is in contact with the solution; thus, the presence of the three phase boundary [27] results in the catalyst nanoparticle dominating
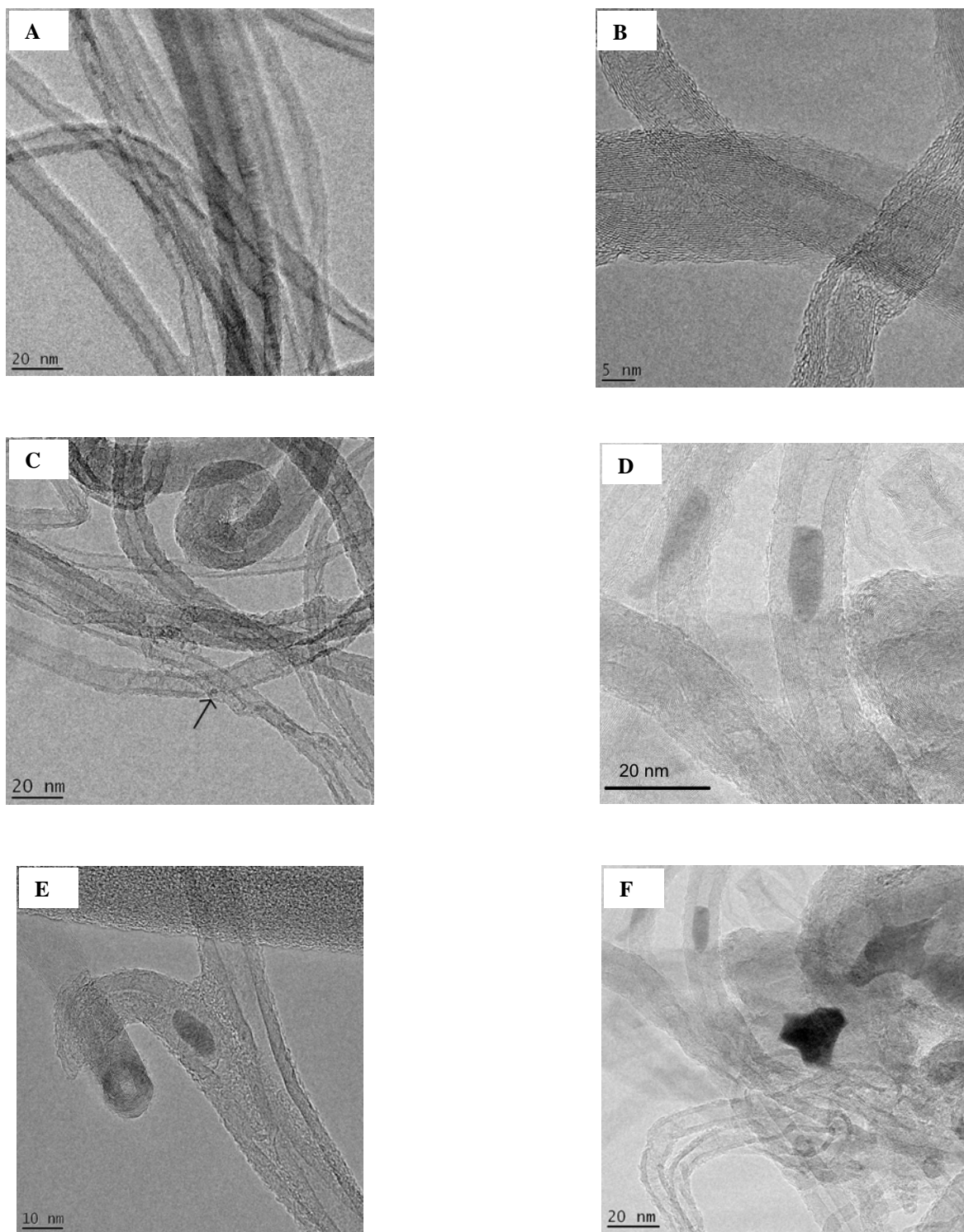
**Fig. 3.** TEM images of batch B bamboo multi-walled carbon nanotubes.

the electrochemical response/activity. Again note that only a few percent of catalyst nanoparticles need to be present for the electrochemical response to be dominated by the nanoparticles, where the carbon nanotubes act akin to a 3D nanoparticle array.

In surveying the MWCNTs (batch B) with TEM, we have found evidence of completely trapped catalyst nanoparticles, as shown in Figs. 3D and 3E, but little, if no evidence of partially trapped catalyst nanoparticles. Note that out of the extensive number of TEM images taken, only one shows a single nanoparticle (Fig. 3C) and its location, whether partially trapped within the tube wall or wrapped within the bundles of the nanotubes, is obviously unclear. The large number of images which show completely trapped catalyst nanoparticles confirm our result above with XPS and voltammetry. That is, the metallic impurities, likely to be iron in this case, are not in contact with the solution, *viz* the absence of a three-phase boundary and hence do not contribute to the electrochemical response. In the case of batch A, the large amount of heterogeneity, as evidenced *via* voltammetry and XPS, dominates the electrochemical response, that is, the iron metallic impurities dominate the electrochemical activity.

It is clear from this study that there are differences in the MWCNTs from batch A and batch B in terms of heterogeneity and observed electrochemical activity. We wish to highlight this fact, which is not addressed in the literature, can limit the electrochemical applications of MWCNTs.

Returning to the question of where the nanoparticles are located with respect to the carbon nanotubes, Pumera [17] has tried to answer this question with careful characterization of MWCNTs from NTP Nanotech Port (China) and both MWCNTS and SWCNTs from Sigma-Aldrich. Through the use of TEM images and voltammetry it was concluded that the metal impurities are 'sheathed' by graphene sheets [17].

However, we believe that the determination of the exact location of the catalyst nanoparticle will likely never be unambiguously confirmed. To do so, one would have to image all the carbon nanotubes used. For example, typically one would study the carbon nanotubes immobilised onto an electrode surface. If we consider the size of the images that are required to gain information about the structure of the nanotubes and try and identify any catalyst impurities, the area of the image is approximately 160 nm by 160 nm, an area of
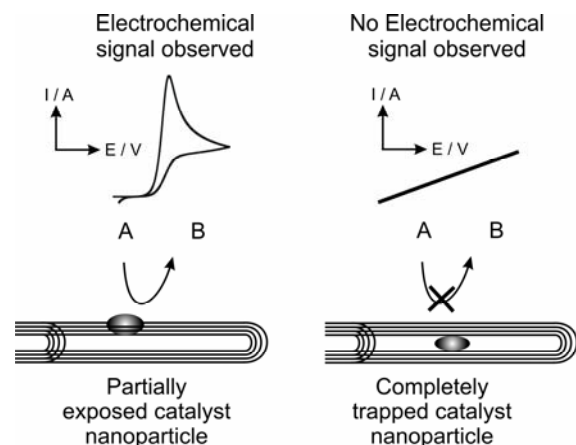
Fig. 4. Schematic representation (not to scale) of a bamboo multi-walled carbon nanotube with a partially trapped catalyst nanoparticle where an electrochemical response is observed due to the presence of a triple-phase boundary and also the case of a completely trapped catalyst nanoparticle where no electrochemical signal is seen due to the absence of a triple-phase boundary. Note that the catalyst nanoparticle may also be partially trapped at the end of the tubes.

2.5×10^{-14} m^2. Usually the carbon nanotubes are placed onto a surface, such as a fully covered electrode which has an area of 7.1×10^{-4} m^2. If we divide one by the other, 2.8×10^{10} images are needed to fully characterize (image) the carbon nanotubes on the electrode surface. Thus it is evident that the progress of an electrochemical project would be severely delayed if one wants to determine the location of metallic impurities or try to quantify the amount of catalyst impurity with microscopy. Note that one can easily miss catalyst nanoparticles since they may be covered or hidden by other carbon nanotubes due to aggregation/bundles etc. Thus one can never unambiguously determine the location of catalyst nanoparticles with respect to carbon nanotubes.

CONCLUSIONS

We have compared two batches of commercial MWCNTs produced *via* CVD with voltammetry, XPS and TEM and have found that the heterogeneity and electrochemical response

greatly vary. To evaluate the MWCNTs in terms of determining whether metallic impurities are the sole origin of the observed electrochemical performance, we suggest that MWCNT should be immobilized onto a suitable electrode surface such as a basal plane pyrolytic graphite electrode with their voltammetric response explored with a suitable electrochemical probe that is catalysed on metal surfaces, such as the electrochemical oxidation of hydrazine [8]. In terms of determining whether edge plane or basal plane like sites/defects are the origin of the electrochemical activity, then the use of edge plane and basal plane pyrolytic graphite electrodes is also encouraged [12,13].

We wish to highlight the batch to batch variation of commercial MWCNTs fabricated *via* CVD and suggest that this is addressed when consider using MWCNTs in electrochemistry, in particular, in commercial electroanalytical sensors. We note that an improved approach to try and ensure that the metallic impurities do not greatly vary may involve dissolution and/or passivation of the impurities *via* electrochemical or other means and then decorate the carbon nanotubes with the desired electrocatalyst [29,30]. Other alternatives based on chemical treatments exist [31] but ultimately damage the structure of the MWCNTs.

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