

# Demonstration of the importance of oxygenated species at the ends of carbon nanotubes for their favourable electrochemical properties†

Alison Chou, Till Böcking, Nagindar K. Singh and J. Justin Gooding\*

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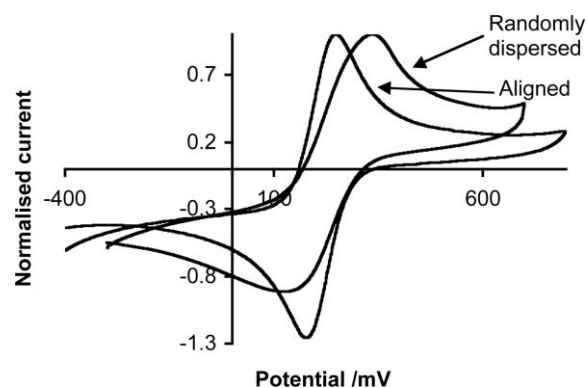
Definitive evidence is presented for the favourable electrochemical properties of carbon nanotube modified electrodes arising from the ends of SWNTs due to oxygenated carbon species in general, and carboxylic acid moieties in particular, produced during acid purification.

Carbon nanotubes have attracted enormous interest because of their unique structural, mechanical and electronic properties. Their small size and conductivity means they can be regarded as the smallest possible electrodes with diameters of less than one nanometer.<sup>1,2</sup> The first application of carbon nanotubes in electrochemistry was by Britto *et al.*<sup>3</sup> where a paste of multiwalled carbon nanotubes (MWNTs) in bromoform was used to study the oxidation of dopamine. The electrochemistry of dopamine at the MWNT electrode was surprisingly good with reversible electrochemistry occurring at low potentials with rates of electron transfer much faster than those observed for graphite electrodes. More recently favourable electrochemistry for many other molecules such as hydrogen peroxide<sup>4</sup> and nicotinamide adenine dinucleotide<sup>5</sup> have been reported at carbon nanotube electrodes which has led to the proposition that carbon nanotubes are electrocatalytic. This supposition that carbon nanotubes have electrocatalytic properties has been questioned by Compton and co-workers<sup>6–8</sup> who showed that carbon nanotubes were no more electrocatalytic than the edge planes of pyrolytic graphite. Their finding appears to be consistent with a previous suggestion that the side walls of carbon nanotubes could be compared with the basal plane of pyrolytic graphite and the open ends with the edge planes of pyrolytic graphite.<sup>9,10</sup> The question that arises is: is the electrochemistry of carbon nanotubes dominated by the ends of carbon nanotubes? If so, what functional groups are responsible for the good electrochemical properties? The work of both Compton and co-workers<sup>6,8</sup> and our group<sup>11,12</sup> has recently provided strong evidence that the end group functionalities are indeed responsible for their electrochemistry. In this communication we present direct evidence that the electrochemistry of carbon nanotube modified electrodes and the rate of electron transfer are dominated by oxygenated species at the ends of the carbon nanotubes.

Recently we have shown that HiPCO single walled carbon nanotubes (SWNTs), shortened by sonication in a 3 : 1 v/v solution of concentrated sulfuric acid (98%) and concentrated nitric acid (70%) could be aligned normal to the surface of a cysteamine

modified gold electrode by self-assembly.<sup>11,12</sup> The resultant log normal length distribution of the nanotubes was shown by transmission electron microscopy to be a function of the cutting time.<sup>11</sup> In the present work, cysteamine modified gold electrodes are further modified with shortened carbon nanotubes in two ways. In the first method, droplets of nanotubes dispersed in ethanol were applied to the cysteamine modified electrode to give a bed of randomly orientated nanotubes whilst in the second, the nanotubes were vertically aligned normal to the surface by self-assembly as confirmed *via* atomic force microscopy (AFM)† images described previously.<sup>11</sup> Cyclic voltammograms in the presence of 1 mM  $K_3Fe(CN)_6$  in a background of 0.05 M  $KH_2PO_4$  and 0.05 M KCl at pH 7.0 at an electrode modified with randomly dispersed nanotubes cut for 2 hours and aligned carbon nanotubes cut for 2 hours are shown in Fig. 1 with the current scale normalised relative to the anodic peak current to account for the different current magnitudes due to different active electrode areas. A comparison between the CVs shows that the difference in potential between the anodic and cathodic peaks for ferricyanide ( $\Delta E_p$ ), is 105 mV for the randomly dispersed SWNTs and 72 mV for the aligned SWNTs. At a bare gold electrode,  $\Delta E_p$  is 93 mV. As  $\Delta E_p$  is a function of the rate of electron transfer, the results suggest that vertical alignment of the cut nanotubes improves the electrochemical properties of the modified electrode.

The heterogeneous rate constant for electron transfer,  $k_{ET}$ , has been proposed to be significantly more rapid from the ends of the nanotubes than the walls,<sup>2,9,11</sup> consistent with the edge planes and basal planes of graphite.<sup>13</sup> With electrodes modified with randomly



**Fig. 1** Cyclic voltammograms of SWNT modified electrodes where the tubes were cut for 2 hours and either randomly dispersed or vertically aligned. CVs are recorded relative to an Ag/AgCl reference electrode in 1 mM  $K_3Fe(CN)_6$  in a background of 0.05 M  $KH_2PO_4$  and 0.05 M KCl at pH 7.0 at 100 mV s<sup>-1</sup>. The y-axis shows the current normalised scale relative to the anodic peak current.

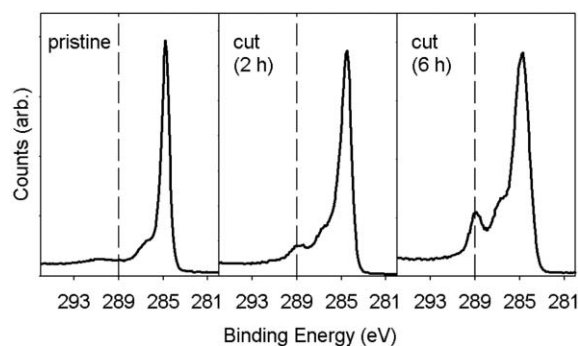
† Electronic supplementary information (ESI) available: TEM images of cut SWNTs, AFM images of aligned carbon nanotubes, infrared spectra, and experimental procedures. See <http://www.rsc.org/suppdata/cc/b4/b415051a/>

\*justin.gooding@unsw.edu.au

dispersed SWNTs, Compton and co-workers have shown that the electrochemistry is dominated by the ends of the tubes.<sup>6</sup> Therefore we propose that with the aligned SWNTs there is a greater presentation of the ends per unit electrode area to the ferricyanide in solution compared with the randomly dispersed SWNTs where it is mostly walls that are presented. Hence in the former case,  $\Delta E_p$  is expected to be smaller, as observed in Fig. 1. If this hypothesis is correct for electrodes modified with randomly dispersed nanotubes, the shorter the nanotubes, the greater the contribution of the ends to the ferricyanide electrochemistry and the lower the  $\Delta E_p$ . Furthermore,  $\Delta E_p$  should be insensitive to cutting time for the aligned SWNT modified electrode which should display the lowest  $\Delta E_p$  of all the nanotube modified electrodes. Table 1 summarises the  $\Delta E_p$  values as a function of the cutting time, and hence length of the SWNTs, for both the randomly dispersed and aligned SWNT modified electrodes. The expected trends of the decrease in  $\Delta E_p$  as the tube length decreases for the randomly dispersed tubes whilst the independence of  $\Delta E_p$  on cutting time for the aligned tubes are clear. The exception to the trend are the SWNTs cut for 8 hours which show an increase in  $\Delta E_p$  for the randomly dispersed SWNTs. In the TEM images,<sup>†</sup> the tubes cut for 8 hours showed a significant amount of aggregated amorphous material which may be adversely affecting the electrochemistry.

The data in Table 1 unambiguously show that the end groups of the carbon nanotubes are responsible for the rapid rates of electron transfer and the good electrochemical performance of carbon nanotube modified electrodes. The question still exists though as to what are the chemical moieties on the SWNTs which provide this good electrochemical performance? The chemistry of the carbon nanotubes was investigated using both infrared spectroscopy and X-ray photoelectron spectroscopy (XPS). Cutting the carbon nanotubes resulted in the appearance of carbonyl stretches in the infrared spectra which were absent in the spectra of the pristine SWNTs.<sup>†</sup> However, with the IR spectra it was very difficult to quantify the extent of carbonyl species with increased cutting times. As a consequence, XPS was used to further characterise the oxygenated species. The relative ratio of the peak areas of the O1s peak to the C1s peak (Table 1) increased with the cutting time indicating that the shorter the SWNTs the greater the proportion of the oxygenated species.

The correlation between cutting time, SWNT length,  $\Delta E_p$  of the randomly dispersed SWNT modified electrode and the XPS results clearly identifies the oxygenated species at the ends of the SWNTs as being responsible for the favourable electrochemical properties, which is consistent with previous observations for other carbon electrodes.<sup>13</sup> The C 1s spectra shed some light on the identity of the



**Fig. 2** C 1s and O 1s spectra of pristine, and acid treated SWNTs after 2 and 6 hours. The C 1s shows the increase in the peak intensity at 289 eV due to the carboxylic acid group after acid shortening.

oxygenated species which are produced at the ends of the SWNTs after oxidative cutting. Fig. 2 shows C 1s spectra of pristine tubes and after cutting for two and six hours. All spectra show the main graphitic peak at 285 eV. The most dramatic change is the appearance of a peak at 289 eV, which has previously been attributed to carboxylic acids.<sup>14</sup> There is also an increase in the peak at 286 eV attributed to quinones. Hence the XPS data provides definitive evidence that oxygenated species, and particularly carboxylate moieties, are responsible for the favourable electrochemical properties of carbon nanotube electrodes. This is consistent with *ab initio* density functional theory calculations and molecular dynamic simulations by Britto *et al.*<sup>15</sup> which have predicted that electron transfer occurs predominantly at sites where oxygenated species exist.

In summary, this communication unambiguously correlates favourable electrochemical properties with the oxygenated species formed at the ends of tubes during cutting by comparing the electrochemistry of randomly dispersed *versus* aligned SWNT modified electrodes, using TEM to quantify the lengths, and XPS and IR to identify the oxygenated species present at the ends of the tubes. The chemical functionalities identified in the XPS of the cut SWNTs are similar to those observed for other carbon electrodes.<sup>13</sup> Therefore our results are entirely consistent with the electrochemical studies of carbon nanotube modified basal plane pyrolytic graphite electrodes by Compton and co-workers<sup>6,8</sup> showing that the electrochemistry of nanotubes is no more electrocatalytic than the edge planes of pyrolytic graphite. The distinct advantage of nanotubes over other electrode materials is that their small size allows them to penetrate places a pyrolytic graphite electrode could never be placed such as inside proteins.<sup>11,12,16</sup>

**Alison Chou, Till Böcking, Nagindar K. Singh and J. Justin Gooding\***  
School of Chemistry, The University of New South Wales, Sydney, NSW, Australia. E-mail: justin.gooding@unsw.edu.au;  
Fax: +61-2 9385 6141; Tel: +61-2 9385 5384

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**Table 1** Summary of the change in length, electrochemical properties and proportion of oxygen–carbon in the XPS spectra with cutting time

Cutting time/hr	Length/nm	$\Delta E_p$ /mV (dispersed)	$\Delta E_p$ /mV (aligned)	O 1s–C 1s area ratio
Pristine	NA	NA	NA	4
2	1400–150	204	76	20
3	900–400	168	75	
4	300–140	105	72	28
5	240–120	97	73	
6	150–70	94	81	36
8	140–70	146	80	33
Bare	NA	93	93	

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