

# Electrochemical performance of multi-walled carbon nanotube composite electrodes is enhanced with larger diameters and reduced specific surface area

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**Abstract** Multi-walled carbon nanotubes (MWCNT) have been widely used to fabricate composite electrodes due to their electrochemical properties. MWCNTs can be fabricated by various approaches and a range of MWCNT types and sizes has been developed. This study focuses on understanding the influence MWCNT diameter and specific surface area has on the electrochemical properties of a composite electrode. MWCNTs with fixed length range and diameters ranging from 10–20 to 50–80 nm were examined in this study. The amount of MWCNT utilised to fabricate the electrodes was identical and above the percolation threshold. MWCNT electrodes fabricated with larger diameters showed enhanced thermodynamic and kinetic properties towards common redox species which covered surface-insensitive, surface-sensitive and adsorption-based processes. Overall, these findings indicate that the number of strands of MWCNT alone is not essential for enhanced conductivity in composite materials but other geometric parameters play important roles.

**Keywords** Carbon nanotubes · Nanotube diameter · Voltammetry · Composite electrodes

## Introduction

Multi-walled carbon nanotubes (MWCNTs) have been widely used in electrochemistry owing to their electrical, mechanical and structural properties. MWCNTs can be found in a wide

range of electrochemical systems where their properties greatly affect the functioning of the final device. These include capacitors [1, 2], fuel cells [3, 4], modifying electrode surfaces [5], incorporation into polymer substrates [6], ‘cut’ into carbon nanofibres [7], electromagnetic interference shielding material [8], water purification [9], solar cells [10] and electrochemical sensor/biosensor devices [11–16].

MWCNTs are fabricated in a wide range of different forms which vary in their diameter, length, number of nanotube layers and chemical treatments. This has resulted in a wide range of MWCNTs readily available for use. However, each individual MWCNT type may provide significant variation in the electrochemical performance of the final material. There have been few studies that have investigated the differences in diameters and porosity [17–19]. Studies using varying diameters of MWCNTs showed that discharge capacity was enhanced with increasing diameter [18].

MWCNTs are produced as a fine powder and thus require some form of supporting material to create an electrochemical device. Various approaches have been utilised; however, the most common types are either to incorporate the MWCNTs into a polymer and deposit this on the electrode surface or to fabricate composite electrodes. In both cases, the supporting material is typically non-conductive. Conductivity is achieved through connections formed between individual MWCNT strands and this can be influenced by the amount of MWCNTs utilised in that there are enough connections to provide an electrical path throughout the entire material. This is known as the percolation threshold. However, studies have not investigated how other MWCNT geometric factors can influence the electrochemical performance.

This study examines how variations in the diameter and specific surface area (SSA) of the MWCNT can influence the electrochemical performance of MWCNT-epoxy resin composite electrodes. The diameter of the MWCNTs utilised

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varied from 10–20 to 50–80 nm. Each MWCNT diameter range was fabricated as composite electrodes using a fixed ratio of MWCNT to epoxy resin. These composite electrodes were examined for their kinetic and thermodynamic electrochemical properties towards surface-insensitive, surface-sensitive and adsorption-based redox couples as well as the influence of the MWCNT diameter on the properties of the electrochemical circuit of this system.

## Experimental

### Chemicals and solutions

Potassium chloride, potassium ferricyanide, potassium ferrocyanide, dopamine, ferrocene carboxylic acid (Sigma-Aldrich, USA), epoxy resin and hardener (Robnor Resins Ltd., UK) were used as received. Solutions for potassium ferricyanide, potassium ferrocyanide and ferrocene carboxylic acid were prepared in 1 M KCl whilst dopamine was prepared in 0.1 M phosphate buffered saline. Four different MWCNTs were utilised, where in each case the length was fixed between 10 and 30 nm. The outer diameters of the MWCNT investigated were 10–20 nm (inner diameter of 3–5 nm and SSA of 233 m<sup>2</sup>/g); 20–30 nm (inner diameter of 5–10 nm and SSA of 110 m<sup>2</sup>/g); 30–50 nm (inner diameter of 5–10 nm and SSA of 60 m<sup>2</sup>/g) and 50–80 nm (inner diameter of 5–10 nm and SSA of 60 m<sup>2</sup>/g). For all materials, removal of unwanted materials was accomplished by refluxing in 4 M  $\text{HNO}_3$  for 36 h.

### Fabrication of various-diameter MWCNT-epoxy composite sensors

The MWCNT composites were created using vice compression [20]. Initially, a 15 % MWCNT/85 % epoxy resin (*w/w*) mixture was created. This mixture was then placed into a 5-cm section of PTFE tubing (internal diameter of 3.2 mm). Previously prepared 3.2 mm diameter epoxy discs and rods were used to provide compression of the composite material through the use of a vice. The tubing had a working pressure value of 375 psi and the pressure was kept at ~300 psi to avoid deforming the tubing for a duration of 10 min. The composite mixtures were then left to set for 48 h at ambient room temperature, 20 °C.

The MWCNT-epoxy composite-packed tubing was cut into 2-mm-thick discs using a diamond wafer blade (Buehler saw). Electrical contact was achieved using a wire connected to one side of the composite disc using silver-loaded epoxy resin (Circuit Works, RS Components, Corby, UK). The finished electrode was produced by encasing the electrode in epoxy resin in a cylindrical

mould reminiscent of a commercial electrode casing. This was left to set for 48 h at ambient room temperature in order for the epoxy to set. It was then cut once again at its base, removing 1 mm from the discs' thickness, with the diamond wafering blade, to expose a MWCNT-epoxy composite disc electrode and to ensure that the edges of the composite disc were sealed within the epoxy. The dimensions of the final electrode disc are 1 mm in thickness and 3.2 mm in diameter. The electrode was polished sequentially in 1, 0.3 and 0.05  $\mu\text{m}$  alumina slurry to reduce surface roughness to acceptable levels.

### Electrochemical assessment of composite electrodes

Electrochemical assessment of the different MWCNT-based electrodes were carried out using a three-electrode system, which consisted of a Ag|AgCl (3 M KCl) reference electrode, a platinum wire auxiliary electrode and the various MWCNT composite electrodes as the working electrode.

The electrochemical characteristics of the MWCNT-based composite electrodes were assessed by using the well-understood redox couples of 1 mM potassium ferricyanide, 1 mM ferrocene carboxylic acid and 1 mM dopamine to probe their behaviour at the different MWCNT-based electrodes. Cyclic voltammograms were performed over potential windows of –200 to 600 mV for potassium ferricyanide, –100 to 700 mV for ferrocene carboxylic acid and –200 to 800 mV for dopamine with a scan rate of 10 mV/s. Solutions were degassed with nitrogen gas. AC impedance studies were performed in a mix of 0.5 mM potassium ferricyanide and 0.5 mM potassium ferrocyanide in 1 M KCl with at a potential equal to the  $E_{1/2}$  of the redox couple (250 mV). A high frequency limit of  $1 \times 10^5$  Hz, a low frequency limit of 1 Hz and an amplitude of 15 mV were utilised. Tafel plots were performed in 0.5 mM potassium ferricyanide and 0.5 mM potassium ferrocyanide in 1 M KCl using an initial potential of –200 mV, a final potential of 700 mV and a scan rate of 10 mV/s. All Tafel plots were performed under convection.

### Data analysis

Electrochemical data was recorded and measured using CHI760 software. The oxidation peak potential,  $E_{\text{pa}}$ , oxidation peak current,  $I_{\text{pa}}$ , oxidation and reduction peak potential separation,  $\Delta E$ , and the half-way potential between the oxidation and reduction peak,  $E_{1/2}$ , were extracted from the cyclic voltammograms. Experimental data was compared statistically using one-way ANOVA tests with ad-hoc Tukey tests via GraphPad Prism software.

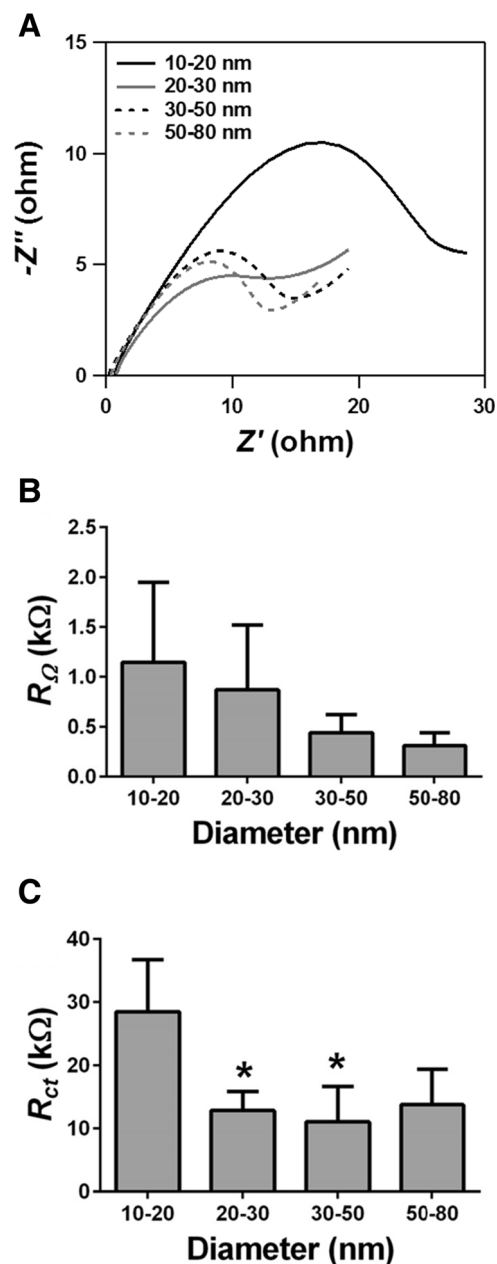
## Results and discussion

### Investigation of electrode properties

To explore the electrochemical properties and surface effects of the MWCNT composite electrodes of different diameters, AC impedance studies were performed with an equal mix of potassium ferricyanide and potassium ferrocyanide (Fig. 1). The resistance to charge transfer ( $R_{ct}$ ) and solution resistance ( $R_{\Omega}$ ) was measured. The  $R_{\Omega}$  for the MWCNT composite electrodes of different diameters varied from 0.5 to 2 k $\Omega$  (Fig. 2b), which is much greater than a commercial glassy carbon electrode, where  $R_{\Omega}$  values are in the range of 0.01 to 0.1 k $\Omega$ . The higher resistance observed on the MWCNT composite electrode is due to increased internal resistance. High variability in the electrodes was observed due to the difficulty in obtaining a homogeneous composite material, which is a limitation of composite-based electrochemical sensors. Figure 1b shows that there is a non-significant decrease in the  $R_{\Omega}$  of these electrodes with increasing MWCNT diameter and decreasing SSA. In order to accurately control the applied potential to the system of interest when using one of these electrodes, lower internal resistance is desirable. Figure 1c shows a significant decrease in the  $R_{ct}$  with composite electrodes made using MWCNT with a diameter >20 nm ( $P < 0.05$ ,  $n = 3$ ). This would indicate that composite electrode made with MWCNT diameters greater than 20 nm are more likely to respond rapidly to changes in the applied potential. A Tafel plot with the same redox couple is shown in Fig. 2. This was utilised to measure the exchange current ( $I_0$ ) which is inversely proportional to  $R_{ct}$ . Figure 2b shows that there was a non-specific increase in the  $I_0$ , which supports that observed in Fig. 1c. This would indicate that composite electrodes made with larger MWCNT are more likely to respond rapidly to the applied potential.

### Behaviour of redox probes at the different electrode surfaces

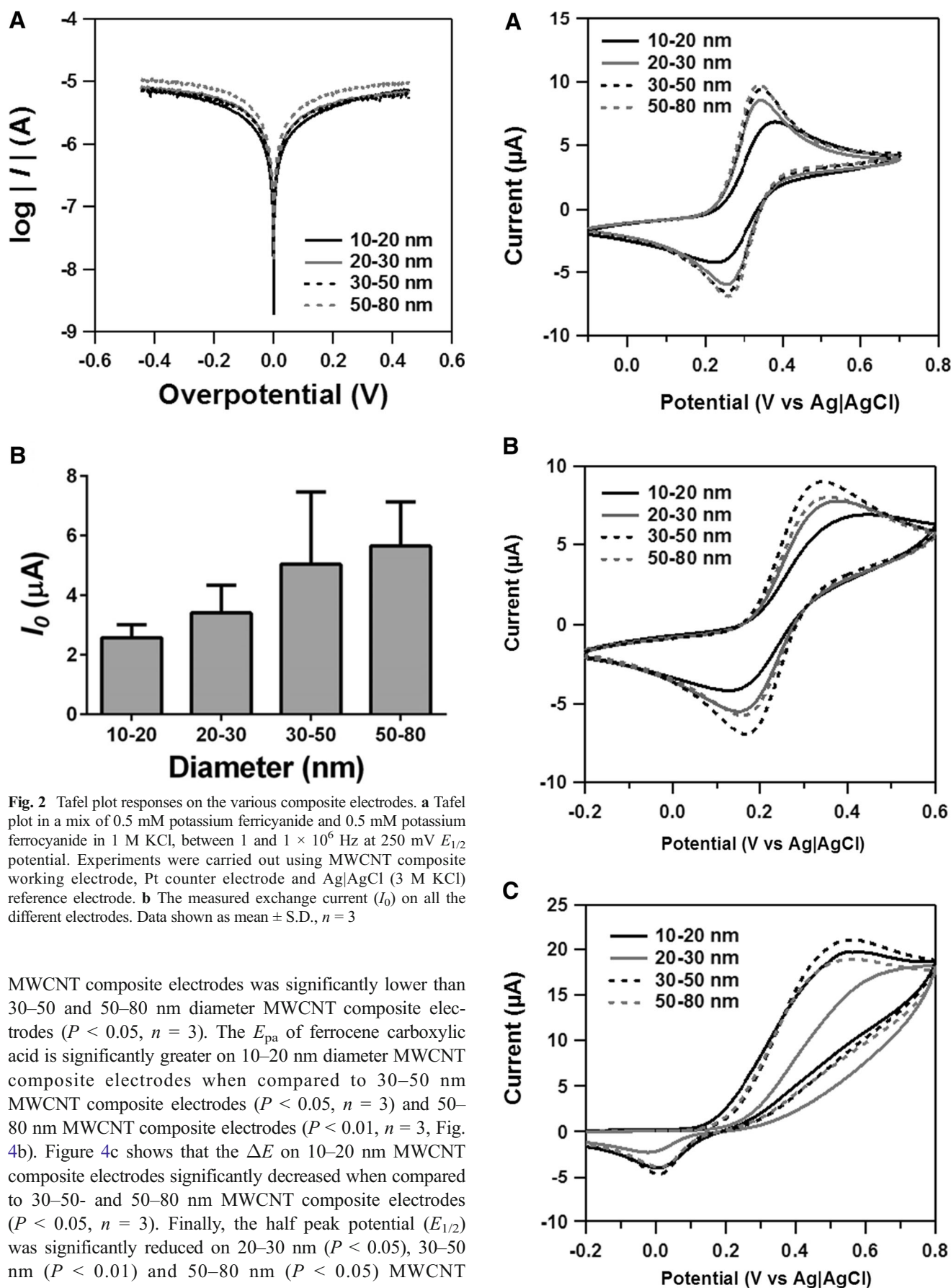
The response of the MWCNT composite electrodes was investigated on a variety of electrochemical processes. Redox couples where the electron transfer processes were either surface-insensitive, surface-sensitive or via adsorption were investigated. Figure 3 shows representative cyclic voltammograms of ferrocene carboxylic acid (surface-insensitive), potassium ferricyanide (surface-sensitive) and dopamine (adsorption-based). These redox couples were chosen based on previous literature [21–24]. Clear variations in the shape and amplitudes of the cyclic voltammograms were observed on composite electrodes of different MWCNT diameters. Key electrochemical parameters from the cyclic voltammograms for each redox species were obtained and comparisons between the composite electrodes of different MWCNT diameters were made (Figs. 4, 5, and 6).



**Fig. 1** Assessment of the electric properties of the composite material. **a** AC impedance voltammetry in a mix of 0.5 mM potassium ferricyanide and 0.5 mM potassium ferrocyanide in 1 M KCl, between 1 and  $1 \times 10^5$  Hz measured using a  $E_{1/2}$  potential of 250 mV and 15 mV amplitude. Experiments were carried out using MWCNT composite working electrode, Pt counter electrode and Ag|AgCl (3 M KCl) reference electrode. **b** Mass transfer resistance ( $R_{\Omega}$ ) response on all electrodes. **c** Charge transfer resistance ( $R_{ct}$ ) on all electrodes. Data shown as mean  $\pm$  S.D.,  $n = 3$ , \* $P < 0.05$  vs 10–20 nm diameter

### Surface-insensitive electron transfer process

Figure 4 shows the electrochemical parameters evaluated for ferrocene carboxylic acid. Figure 4a shows the  $I_{pa}$  significantly increases as the diameter of the MWCNT increases ( $P > 0.001$ ,  $n = 3$ ). The  $I_{pa}$  on 10–20- and 20–30 nm diameter



**Fig. 2** Tafel plot responses on the various composite electrodes. **a** Tafel plot in a mix of 0.5 mM potassium ferricyanide and 0.5 mM potassium ferrocyanide in 1 M KCl, between 1 and  $1 \times 10^6$  Hz at 250 mV  $E_{1/2}$  potential. Experiments were carried out using MWCNT composite working electrode, Pt counter electrode and Ag|AgCl (3 M KCl) reference electrode. **b** The measured exchange current ( $I_0$ ) on all the different electrodes. Data shown as mean  $\pm$  S.D.,  $n = 3$

MWCNT composite electrodes was significantly lower than 30–50 and 50–80 nm diameter MWCNT composite electrodes ( $P < 0.05$ ,  $n = 3$ ). The  $E_{pa}$  of ferrocene carboxylic acid is significantly greater on 10–20 nm diameter MWCNT composite electrodes when compared to 30–50 nm MWCNT composite electrodes ( $P < 0.05$ ,  $n = 3$ ) and 50–80 nm MWCNT composite electrodes ( $P < 0.01$ ,  $n = 3$ , Fig. 4b). Figure 4c shows that the  $\Delta E$  on 10–20 nm MWCNT composite electrodes significantly decreased when compared to 30–50- and 50–80 nm MWCNT composite electrodes ( $P < 0.05$ ,  $n = 3$ ). Finally, the half peak potential ( $E_{1/2}$ ) was significantly reduced on 20–30 nm ( $P < 0.05$ ), 30–50 nm ( $P < 0.01$ ) and 50–80 nm ( $P < 0.05$ ) MWCNT

◀ **Fig. 3** Cyclic voltammograms of the various composite electrodes on surface-insensitive, surface-sensitive and absorption-based redox species. **a** Responses of the electrodes in 1 mM ferrocene carboxylic acid in 1 M KCl. **b** Responses of the electrodes in 1 mM potassium ferricyanide in 1 M KCl and **c** responses of 1 mM dopamine in 0.1 M PBS. All responses are carried out at a scan rate of 100 mV/s

composite electrodes when compared to 10–20 nm diameter MWCNT composite electrodes ( $n = 3$ , Fig. 4d). However, these changes were quite negligible as they only varied by a few millivolts, but were significant due to the reduced variation. Overall, the 30–50- and 50–80 nm diameter composites displayed enhanced electrochemical performance for the determination of a surface-insensitive electron transfer species. These findings clearly suggest that the diameter and/or SSA of the MWCNTs can have an influence on the electrochemical behaviour of the composite electrode.

### Surface-sensitive electron transfer process

Ferricyanide was utilised to see how the composite electrodes of varying MWCNT diameters behaved during a surface-sensitive electron transfer process. There was no significant difference in the  $I_{pa}$ ; however, there was a general trend showing an increase in the  $I_{pa}$  with increased diameter MWCNT composite electrodes (Fig. 5a). In Fig. 5b, the  $E_{pa}$  was significantly lower in 30–50- and 50–80 nm MWCNT composite electrodes when compared to 10–20 nm MWCNT composite electrodes ( $P < 0.05$ ,  $n = 3$ ). This would indicate that a lower over-potential is

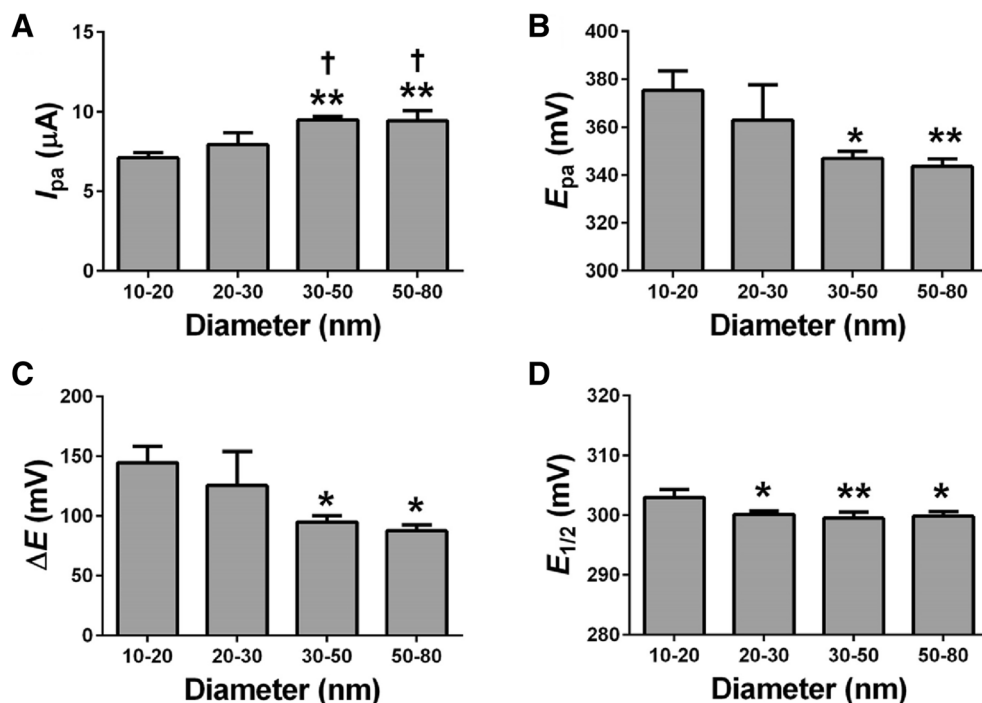
required for oxidation of a species that undergoes a surface-sensitive electron transfer process. There was no significant difference observed for  $\Delta E$  between all the various composite electrodes (Fig. 5c). In Fig. 5d, the  $E_{1/2}$  was significantly different between the 10–20 nm MWCNT composite electrodes when compared to the 50–80 nm MWCNT composite electrodes with the  $E_{1/2}$  shifting from 311 to 262 mV ( $P < 0.05$ ,  $n = 3$ ). Unlike the study with the species that undergoes a surface-insensitive electron transfer process, the absolute values are now more varied.

Whilst the trends on the surface-sensitive electron transfer process are similar to those observed on the surface-insensitive electron transfer process, there are limited significant differences observed. Composite electrodes by nature would have varying electrode surfaces due to difficulties in achieving homogenous composite materials. It is evident that the variation in the responses observed on the species undergoing surface-sensitive electron transfer process is greater than that for the surface-insensitive electron transfer process as the nature of surface is important for electron transfer.

### Adsorption-based electron transfer process

Dopamine mechanism of electron transfer is known to occur following absorption on the electrode surface. Dopamine is known to undergo an electrochemical followed by chemical reaction process, and therefore, as observed in Fig. 3c, there is a small reduction peak observed.

**Fig. 4** Electrochemical performance parameters from 1 mM ferrocene carboxylic acid in 1 M KCl. **a**  $I_{pa}$ , **b**  $E_{pa}$ , **c**  $\Delta E$  and **d**  $E_{1/2}$ . Data shown as mean  $\pm$  S.D.,  $n = 3$ , \* $p < 0.05$ , \*\* $p < 0.01$  vs 10–20 nm diameter, † $p < 0.05$  vs 20–30 nm diameter





**Fig. 5** Electrochemical performance parameters from 1 mM potassium ferricyanide in 1 M KCl. **a**  $I_{pa}$ , **b**  $E_{pa}$ , **c**  $\Delta E$  and **d**  $E_{1/2}$ . Data shown as mean  $\pm$  S.D.,  $n = 3$ , \* $p < 0.05$  vs 10–20 nm diameter

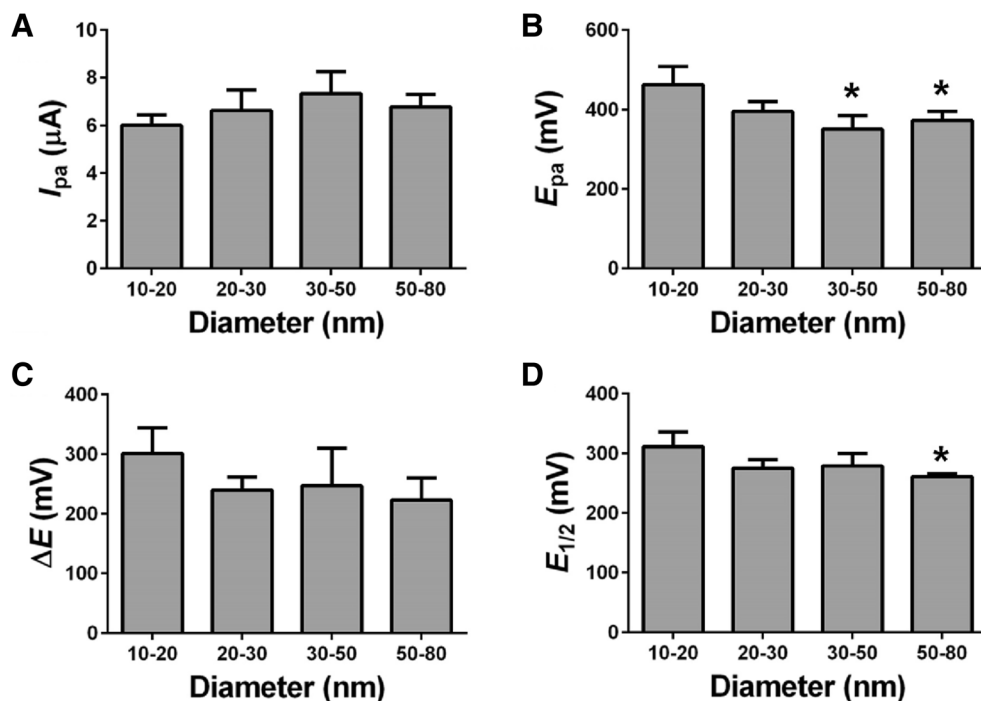
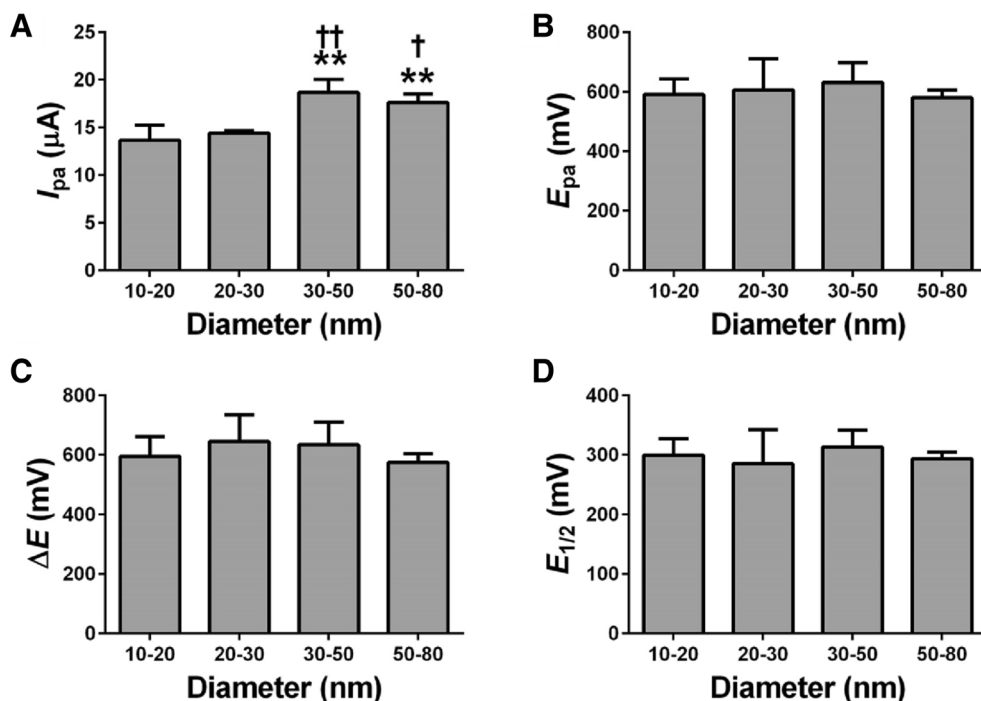


Figure 6a shows that there is a significant difference in the  $I_{pa}$  with increasing MWCNT diameter ( $P < 0.01$ ,  $n = 3$ ). There was a significant increase in the  $I_{pa}$  from 10 to 20 nm MWCNT composite electrodes to 30–50 nm MWCNT composite electrodes and 50–80 nm MWCNT composite electrodes ( $P < 0.01$ ,  $n = 3$ ). There was also a significant increase in the  $I_{pa}$  from 20–30 nm MWCNT

composite electrodes to 30–50 nm MWCNT composite electrodes ( $P < 0.01$ ,  $n = 3$ ) and 50–80 nm MWCNT composite electrodes ( $P < 0.05$ ,  $n = 3$ ). This behaviour indicates that an increase in the number of dopamine oxidation reactions is taking place at these larger diameter MWCNT-based electrodes, but generally indicates that for all process of electron transfer, larger diameter MWCNT

**Fig. 6** Electrochemical performance parameters from 1 mM dopamine in 0.1 M PBS. **a**  $I_{pa}$ , **b**  $E_{pa}$ , **c**  $\Delta E$  and **d**  $E_{1/2}$ . Data shown as mean  $\pm$  S.D.,  $n = 3$ , \*\* $p < 0.01$  vs 10–20 nm diameter; † $p < 0.05$  and †† $p < 0.01$  vs 20–30 nm diameter



composite electrodes with smaller SSA have enhanced performance. There was no significant variation in the  $E_{pa}$ ,  $\Delta E$  and  $E_{1/2}$  (Fig. 6a, c and d).

### Influence of MWCNT diameter and SSA on electrochemical performance of composite electrodes

Composite electrodes fabricated using MWCNT with diameters greater than 30–50 nm and reduced SSA appear to provide an enhanced performance for the detection of a range of different redox species under varying mechanisms of oxidation. The majority of electrochemical performance improvements occur between 20–30- and 30–50 nm diameter MWCNT composite electrodes. There are few improvements in 50–80 nm diameter MWCNT composite electrodes when compared to 30–50 nm diameter MWCNT composite electrodes.

In these composite materials, conductive pathways through the composite are provided by the conductive material, in this case MWCNTs, whilst the material providing the structural support, in this case epoxy, is electrically insulating. A minimum amount of conductive material is required in order for the material to be conductive, which is known as the percolation threshold [25]. In our case, the percolation threshold is achieved by interlinking strands of MWCNT from the electrode surface to electric connection. In this study, each MWCNT composite electrode was composed of the same percentage weight of MWCNT (15 %), which was greater than the percolation threshold; however, only the diameter and the SSA of the MWCNT used varied from 10–20 to 50–80 nm. The number of individual strands and the SSA of the material with smaller MWCNT diameter are far greater than that of a material with a larger MWCNT diameter for the same amount. This would imply that a greater electrochemical performance would be anticipated on the smaller diameter MWCNT materials as conductive pathways through the composite would be aided by the increased number of MWCNT strands as they provide more possible connections through the material. However, our findings clearly show that there is a decrease in the internal resistance and an enhancement of the electrochemical behaviour of the material as the MWCNT diameter is increased, suggesting that the MWCNT diameter plays a more significant role in enhancing the number of conductive pathways formed between the MWCNTs through the composite material than SSA. Our findings indicate that larger MWCNT diameter provides a stronger basis for forming connections than having a greater quantity of MWCNT strands. This would also indicate that electrical conductance is better facilitated through larger diameter MWCNT as it may increase the ability to make more point-to-point connections.

### Conclusion

This study indicates that the diameter of MWCNTs plays more of a significant role in the final electrochemical properties of MWCNT-based composite electrodes than the SSA. Variations in the kinetic and thermodynamic behaviour of surface-insensitive, surface-sensitive and adsorption-based redox processes were observed as the MWCNT diameter was increased from 10–20 to 50–80 nm. In addition, variations in the internal and charge transfer resistance of the MWCNT composite electrodes were observed with increasing MWCNT diameter. This study shows that MWCNT diameter is more significantly important to enhance electrochemical performance of composite electrodes than the number of MWCNT strands and SSA. These findings indicate that the dimensional properties of the MWCNT can have a significant influence on the electrochemical performance.

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