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**Advanced microwave-assisted production of hybrid electrodes for energy applications**

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## Advanced microwave-assisted production of hybrid electrodes for energy applications

### Abstract

Carbon nanotubes are one of the most prominent materials in research for creating electrodes for portable electronics. When coupled with metallic nanoparticles the performance of carbon nanotube electrodes can be dramatically improved. Microwave reduction is an extremely rapid method for producing carbon nanotube-metallic nanoparticle composites, however this technique has so far been limited to carbon nanotube soot. An understanding of the microwave process and the interactions of metallic nanoparticles with carbon nanotubes has allowed us to extend this promising functionalisation route to pre-formed CNT electrode architectures. Nanoparticle reduction onto pre-formed architectures reduces metallic nanoparticle waste as particles are not formed where there is not sufficient porosity for electrochemical processes. A two-fold increase in capacitive response, stable over 500 cycles, was observed for these composites, with a maximum capacitance of 300F/g observed for a carbon Nanoweb electrode.

### Keywords

hybrid, electrodes, microwave, assisted, energy, advanced, applications, production

### Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

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# Advanced microwave-assisted production of hybrid electrodes for energy applications

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Carbon nanotubes are one of the most prominent materials in research for creating electrodes for portable electronics. When coupled with metallic nanoparticles the performance of carbon nanotube electrodes can be dramatically improved. Microwave reduction is an extremely rapid method for producing carbon nanotube-metallic nanoparticle composites, however, this technique has so far been limited to carbon nanotube soot. An understanding of the microwave process and the interactions of metallic nanoparticles with carbon nanotubes have allowed us to extend this promising functionalisation route to pre-formed CNT electrode architectures. Nanoparticle reduction onto pre-formed architectures reduces metallic nanoparticle waste as particles are not formed where there is insufficient porosity for electrochemical processes. A two-fold increase in capacitive response, stable over 500 cycles, was observed for these composites, with a maximum capacitance of 300 F g<sup>-1</sup> observed for a carbon Nanoweb electrode.

Next-generation nanostructured electrochemical devices are anticipated to play a key role in future portable electronics. Components of these devices such as supercapacitors and lithium-ion batteries have attracted intense research effort. Carbon is a widely studied electrode material due to its broad abundance, ease of processing, and variety of allotropes. Of these allotropes, carbon nanotubes (CNTs) have proved theoretically to be one of the most promising electrode materials to date.<sup>1,2</sup> CNTs demonstrate phenomenal physical properties,<sup>3,4</sup> which make them excellent materials for use as high performance electrodes in a variety of applications.<sup>5,6</sup> CNT/amorphous carbon mats or 'buckypapers' are one such example of a CNT electrode structure.<sup>7,8</sup> Recently, the authors have reported on the

generation of a range of high electrochemically active surface area carbon electrodes suitable for use in a variety of electrochemical devices.<sup>9</sup> In spite of the established high porosity and available surface area of these structures, the measured electrochemical capacitance is generally quite low (*ca.* 45–150 F g<sup>-1</sup>).<sup>11</sup>

Decorating CNT materials with metallic nanoparticles (mNPs) is of great interest due to potential increases in electronic conduction, active surface area and therefore electrochemical performance.<sup>12</sup> Many of the methods reported in the literature require long (up to 10 h) reaction times to achieve high nanoparticle loadings.<sup>10,13</sup> Microwave-assisted reduction has been shown to be capable of producing metallic colloids<sup>12–17</sup> and is preferable over conventional heating as the reaction time is shortened significantly.<sup>17</sup> Preparation of CNT–nanoparticle composite materials *via* microwave reduction has been reported on CNT soot.<sup>9,11,16,17,19</sup>

To date, this dependence on CNT soot as the starting material is one of the most significant impediments to the generation of viable microwave-synthesised mNP/CNT electrodes. The problematic processability of CNT soot into a finite number of structures is well documented, and, in addition, a large proportion of the metallic nanoparticles remain unavailable to the electrolyte after processing due to pore filling effects. To the best

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## Broader context

Hybrid carbon nanotube electrodes doped with metallic nanoparticles are powerful materials for a diverse array of applications in the electrochemical industry. Previous reports have focused on the production of carbon nanotube composites from powders; however, these require significant post-processing to form stable structures for practical use. Herein we demonstrate the first case of decorating pre-formed carbon nanotube structures with metallic nanoparticles by a rapid, microwave-assisted reduction technique. This technique has several advantages over conventional power reduction strategies, specifically producing more durable electrodes, and eliminating several post-processing steps. These hybrid electrode materials have a non-faradic capacitance of double that of the raw carbon nanotube architecture with specific capacitances up to 300 F g<sup>-1</sup> and a cyclic stability of 98% over 500 cycles.

of the authors knowledge, at this time, there is no prior reported microwave-assisted metallic reduction on pre-assembled CNT architectures.

The key advantage of decorating mNPs on pre-formed three dimensional (3D) CNT nanostructures is that nanoparticles can only be deposited where there is sufficient porosity for the reducing agent and precursor salt to interact with the CNTs. Thus maximising the metal content utilised throughout the electrochemical device, which is a highly advantageous economic perspective.<sup>18,20</sup>

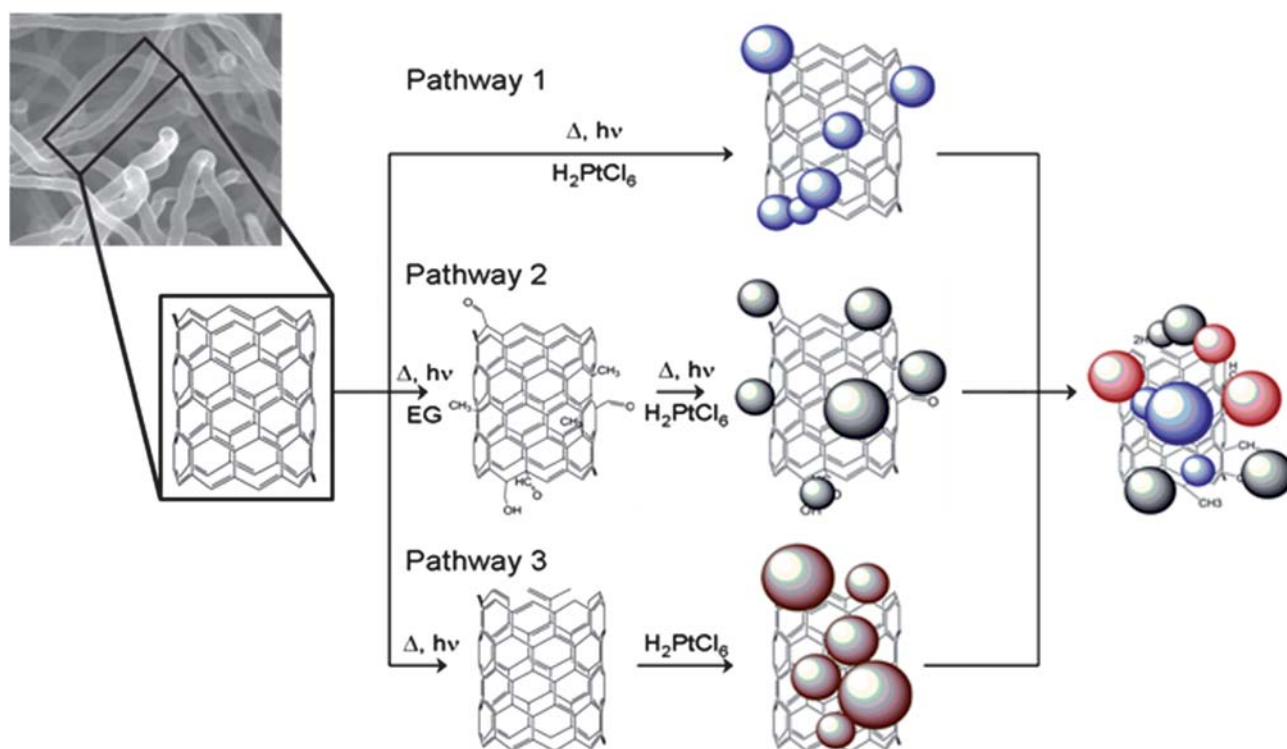
In this paper we report a rapid approach to generate metallic nanoparticles *via* an adapted microwave-assisted reduction method. This method, unlike previous literature reports, is capable of decorating bulk 3-D CNT architectures with mNPs, generating composite electrode architectures for use in electrochemical devices, all in a single step. Additionally, no visible damage to the underlying carbon architecture is apparent. Microwave-assisted reduction was performed on a metallic salt (between 20  $\mu\text{L}$  and 100  $\mu\text{L}$ ) and ethylene glycol (3mL Sigma-Aldrich) mixture. The metallic salt utilized in these experiments was  $\text{H}_2\text{PtCl}_6$  (8% v/v in dilute HCl).

To convert the process into a decoration procedure, CNTs were simply added to the above precursor solution as: multi-wall nanotube (MWNT) soot,<sup>12</sup> single wall nanotube buckypapers,<sup>7</sup> SWNT/hyaluronic acid (HA) fibers<sup>18</sup> or MWNT/conducting carbon 3D Nanowebbs.<sup>19</sup> The mixture was irradiated in

a conventional 1200 W Panasonic Inverter microwave oven, for 20 to 40 seconds until a colour change was observed. The reaction was carried out in 10 second intervals with a 2 second rest period, to reduce overheating and solvent loss from the samples. These 2 second rest periods, are crucial to decorating 3-D pre-formed architectures *via* such a microwave method. Without allowing for these rest periods the high energy environment rapidly results in disintegration of the carbon architecture during decoration. The temperature of the reaction was not explicitly controlled, however, the maximum temperature recorded was 190  $^\circ\text{C}$  just prior to each rest period. Whilst a range of nanoparticles have been deposited using this technique<sup>20</sup> this report focuses on preliminary results of platinum nanoparticle deposition only, as Pt is one of the most common nanoparticles reported in the literature.

Cyclic voltammetry (CV) was performed in a three electrode cell using either acetonitrile with 0.1 M tetrabutylammonium phosphate (TBAP) as a supporting electrolyte (against a  $\text{Ag}/\text{Ag}^+$  reference electrode) or 0.1 M KCl (against  $\text{Ag}/\text{AgCl}$  reference electrode). The auxiliary electrode was a platinum mesh with sufficient surface area to charge compensate the working electrodes and was arranged parallel to the working electrode. CVs were performed at a variety of different scan rates (5–200  $\text{mV s}^{-1}$ ) and the specific capacitance was measured at 0 V.

The addition of chloroplatinic acid to the ethylene glycol resulted in a solution colour change from clear to light orange.

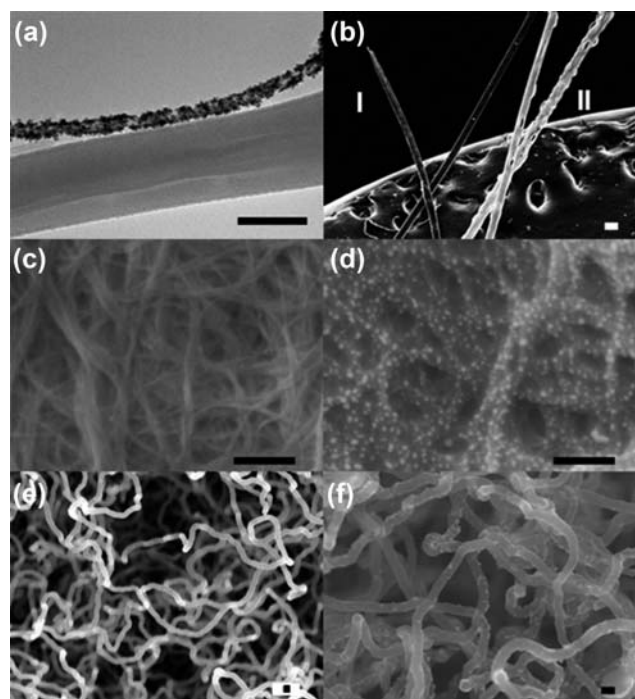


**Scheme 1** Proposed schematic of the potential reactions undergone by a 3-D carbon nanotube (CNT) architecture during microwave irradiation in the presence of chloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ ) and ethylene glycol (EG). Pathway 1 represents solution formation of platinum nanoparticles followed by direct interaction with the CNT. Pathway 2 shows the initial functionalisation of the CNT sidewall with carboxylic, alcohol and carbonyl groups *via* the interaction of the CNT with ethylene glycol, followed by reduction of platinum specifically at these sites. Pathway 3 shows the formation of  $\text{sp}^3$  defects on the CNT sidewalls, which act as sites for platinum to reduce specifically on the backbone. The final composite product is the result of varying proportions of all three of these mechanisms.

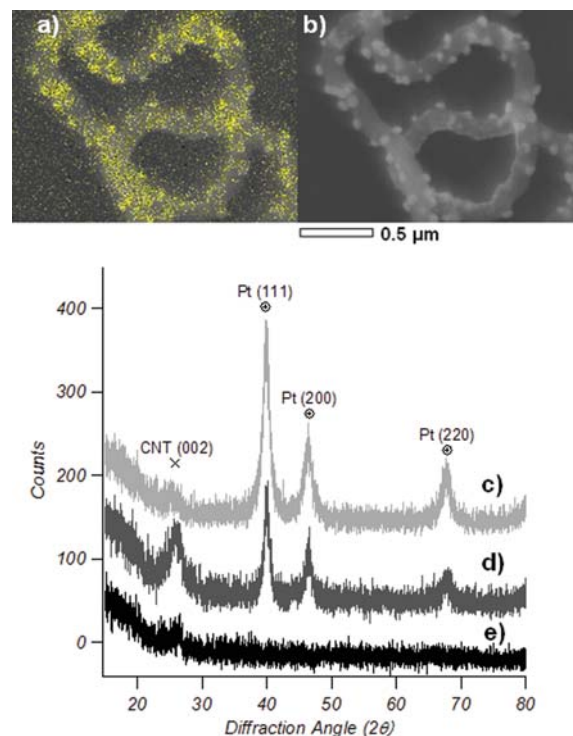
Upon exposure of this solution to microwave radiation, a secondary colour change was observed with the appearance of a brown colouration throughout the solution. This secondary colour change corresponds with the known visual appearance of platinum nanoparticles.<sup>14,15</sup> The generation of nanoparticles, in the solution phase, was confirmed by photon correlation spectroscopy performed using a Malvern Zetasizer ZS (not shown) which revealed a mean particle size of approximately 8 nm at the time of synthesis. Platinum reduction by ethylene glycol is thermodynamically favoured, however, the addition of significant thermal energy is required to activate the reactants kinetically.<sup>21</sup> Exposure of these solutions to microwave radiation in the presence of CNTs provides kinetic activation at two levels, as illustrated in Scheme 1. The microwave radiation thermally excites the ethylene glycol and water in the solution generating significant heat and thermal motion. Secondly, CNTs are known to be excellent microwave absorbing materials<sup>22</sup> and, as such, when exposed to microwave radiation generate quite extreme local temperatures.<sup>14</sup> Furthermore, the absorption of microwaves by CNTs results in the formation of defect sites within the CNT lattice. These radiation-induced defects can then react with the surrounding environment,<sup>16</sup> which in this case can be either the ethylene glycol oxidising the CNTs or the platinum salt decorating the CNT. A second competing mechanism is the combination of these reactions, where the oxidised sections of the CNT react with the platinum salt. In addition to the above mechanism, spontaneous reduction of Pt<sup>4+</sup> in the presence of CNTs can occur, as previously reported.<sup>13,19</sup> The result of which will be CNTs that are mildly oxidised, have an increased defect density

and loaded with Pt particles. Furthermore, as the ethylene glycol is known to decompose under these reaction conditions and binds strongly to the Pt nanoparticles, without annealing (which was not performed in this case) ethylene glycol derivatives will be present in the final composite. It is therefore conceptualised that a combination of these three pathways (Scheme 1), accelerated with a high local temperature at the nanotube/electrolyte interface, generates the high loading levels of Pt observed in the microscopy images (Fig. 1).

Tunneling electron microscopy (TEM), JEOL 1400, on irradiated MWNT soot in the presence of Pt<sup>4+</sup> clearly demonstrated in Fig. 1a that a dense loading of sub-10 nm platinum nanoparticles onto the MWNT was successfully achieved. These particles are comparative in size to those in the literature. To highlight the versatility of the technique and to demonstrate the ability to decorate a range of pre-formed structures, microwave-assisted platinum reduction was performed on a range of CNT electrode architectures (Fig. 1b, c and e). Fig. 1b shows the striking difference between carbon nanotube composite fibers uncoated (I) and coated (II) with the Pt nanoparticles under the Scanning Electron Microscope (SEM). Fig. 1c and d show SEM images of an untreated (c) and treated (d) SWNT/Triton-X100 buckypaper, highlighting the deposition of a large quantity of Pt nanoparticles whilst maintaining overall surface porosity throughout the modified structure. A fourth CNT architecture was also treated in the same manner (Fig. 1e and f). This Nanoweb architecture was previously shown to have a specific



**Fig. 1** (a) TEM of a single MWNT coated with Pt nanoparticles; (b) SEM image containing (I) untreated SWNT/HA fibers and (II) Pt coated SWNT/HA fibers; and SEM images of (c) SWNT/Triton-X100 buckypaper; (d) SWNT/Pt/Triton-X100 composite buckypaper; (e) MWNT Nanoweb; and (f) Pt loaded MWNT Nanoweb (all scale bars except (b) are 100 nm,  $b = 100 \mu\text{m}$ ).



**Fig. 2** Various X-ray spectroscopic analyses of Pt loaded CNT architectures: (a) Energy dispersive X-ray spectroscopy map of the MWNT Nanoweb loaded with Pt (yellow points correspond to Pt signal) and (b) the corresponding secondary electron image to the previous EDX map. X-ray diffraction patterns for (c) Pt-loaded MWNT Nanoweb; (d) MWNT buckypaper loaded with Pt; both showing the Pt 111, 200 and 220 planes, and (e) untreated MWNT Nanoweb.



capacitance as high  $150 \text{ F g}^{-1}$ .<sup>19</sup> All of these CNT electrode architectures were formed prior to microwave reduction of platinum. After irradiation of the architecture in the presence of chloroplatinic acid, platinum peaks were observed in both the Energy Dispersive X-Ray (EDX) spectroscopy and the X-ray Diffraction (XRD) spectra, confirming zero-valent metallic species being present (Fig. 2).

The spatial conformance of the Pt maximum signal from the EDX with the observed secondary electron SEM image (Fig. 2a and b) confirms the deposited metal particle is colloidal or nanoparticulate in nature. According to the 220 peak in the XRD spectra and the Scherrer equation (eqn (1)),<sup>23,24</sup> the particle size of these materials was found to be  $5 \pm 2 \text{ nm}$  and  $4 \pm 1 \text{ nm}$  for the Nanoweb and buckypaper samples respectively.

$$\phi = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

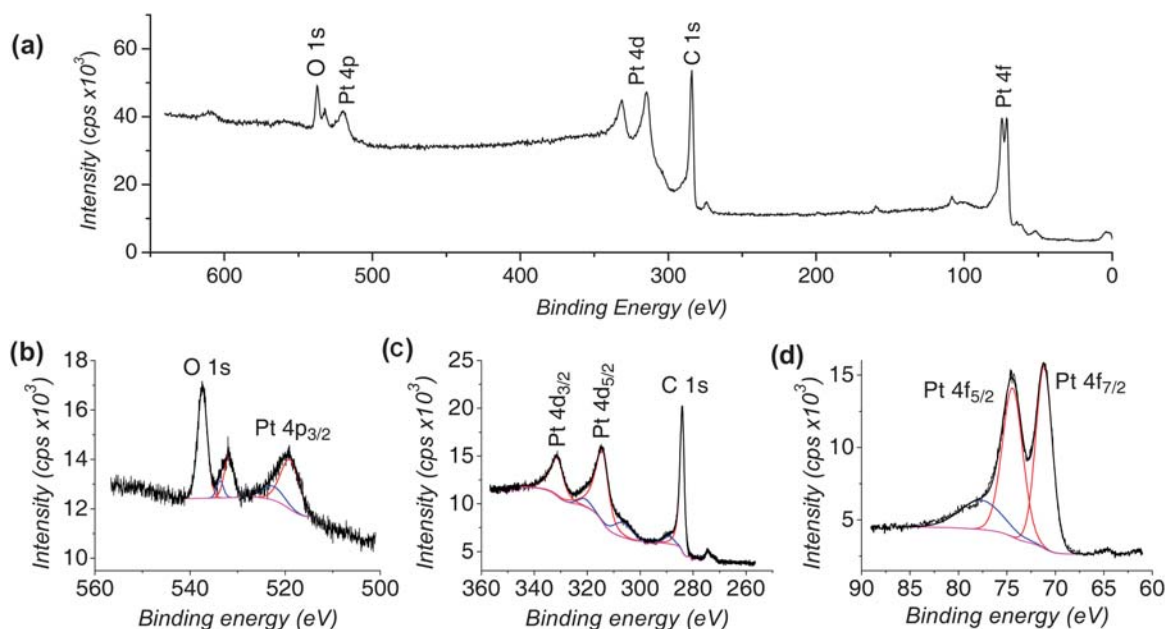
X-Ray photoelectron spectroscopy (XPS) confirmed the presence of Pt, O and C throughout the Nanoweb after irradiation (Fig. 3). The XPS spectra were recorded using the Al  $K\alpha$  radiation at the pass energy of 50 eV for the survey scan (Fig. 3a) and 30 eV for the regions involving the Pt excitations (Fig. 3b and c). The Gaussian–Lorentzian fits of the Pt 4f orbital peaks demonstrated the decoration of Pt(0) species, with a Pt 4f<sub>7/2</sub> present at a binding energy of 71.2 eV,<sup>25</sup> which corresponds to the pure metallic Pt. The minority Pt doublet at BE 78.0 eV corresponds to the presence of small amounts of Pt(IV) within the sample.<sup>26,27</sup> The absence of a Cl 2p peak at approximately 200 eV suggests the complete removal of unreacted chloroplatinic acid from the sample, indicating either complete reduction at the CNT surface or removal of any unbound species after washing.<sup>28</sup> The oxygen peak at a BE of 537.4 eV is thought to arise from either remnant ethylene glycol derivative in solution or more likely, carboxylic groups on the CNT sidewall.

The electrochemical response of the composite electrodes was probed *via* cyclic voltammetry. Fig. 4 shows a noticeable change in the shape of the voltammogram after the samples have been exposed to microwave irradiation. This shape change (towards a classical box-shape CV) indicates a lowering of the overall resistivity of the electrochemical cell due to the irradiation process. Also, the deposition of platinum resulted in a significant increase in the specific current, corresponding to an increased double-layer capacitance of the electrodes. The electrochemical capacitance ( $C$ ) was calculated by dividing the current difference ( $\Delta I$ ) at 0 V by the scan rate ( $v$ ), according to eqn (2).

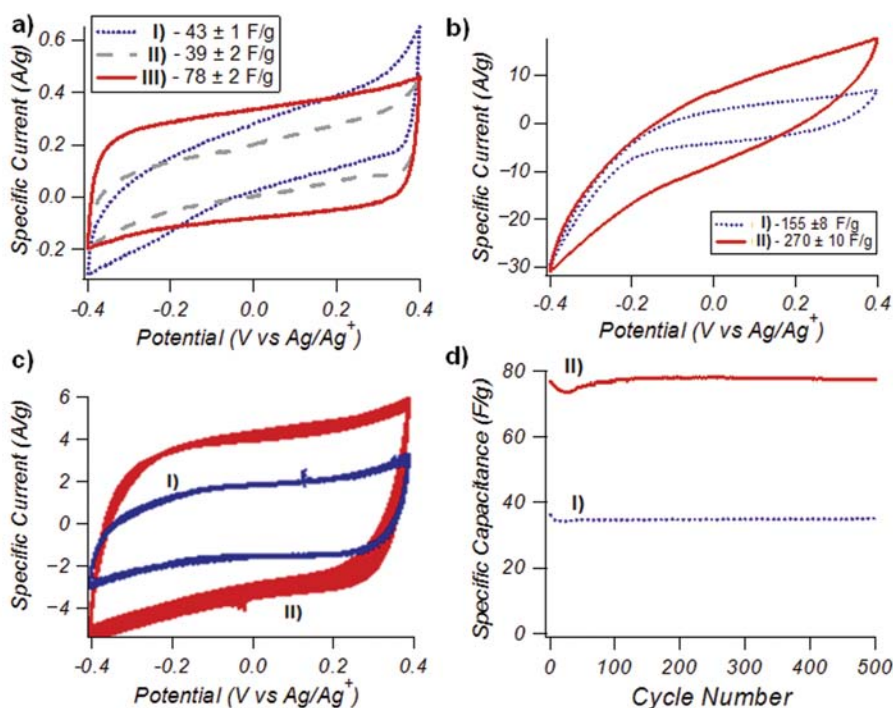
$$C = \frac{1}{2} \times \frac{\Delta I}{v} \quad (2)$$

Using the BP sample as an example, after platinum deposition a two-fold increase in electrochemical capacitance, from  $43 \text{ F g}^{-1}$  to  $78 \text{ F g}^{-1}$ , was observed. To prove that the platinum deposition was the cause of this increase in capacitance, control buckypaper samples were also treated to expose to microwave radiation both in air and in pure ethylene glycol. The electrochemical capacitance of both samples was observed to decrease slightly to  $39 \text{ F g}^{-1}$  (Fig. 4). This slight decrease was consistent over many samples and likely corresponds to the formation of defects in the nanotube lattice during the microwave process. In addition, both samples were tested for capacitive stability through prolonged cyclic voltammetry. Both the untreated and Pt-loaded buckypapers were cycled between +400 mV and –400 mV for 500 cycles. For these samples there is an initial decrease in capacitance between 10 and 20 cycles of around 10%. However, this decrease is recovered and the capacitance is observed to be highly stable. The initial drop in performance is likely to be due to wettability issues at the electrode–electrolyte interface.

The double-layer capacitance for the entangled Nanoweb (Fig. 4b) was found to be  $\sim 270 \text{ F g}^{-1}$  in organic electrolytes and



**Fig. 3** X-Ray photoelectron spectroscopy (XPS) of Pt loaded MWNT Nanoweb architecture: (a) full scan; (b) O 1s, Pt 4p; (c) C 1s, Pt 4d; and (d) Pt 4f focused scans.



**Fig. 4** Comparison of the capacitive behavior of: (a) SWNT buckypapers; (I) a raw SWNT buckypaper; (II) an SWNT buckypaper irradiated with no Pt present; and (III) an SWNT-Pt buckypaper at  $5 \text{ mV s}^{-1}$ , cyclic voltammogram performed in acetonitrile with  $0.1 \text{ M}$  tetrabutylammonium phosphate (TBAP) as a supporting electrolyte. (b) MWNT Nanoweb: (I) raw MWNT Nanoweb and (II) Pt loaded MWNT Nanoweb structure, CV performed in  $0.1 \text{ M}$  KCl. Cyclic stability test for SWNT buckypapers: (c) 500 scan cyclic voltammogram in  $0.1 \text{ M}$  TBAP in acetonitrile (I) untreated SWNT buckypaper and (II) Pt-loaded SWNT buckypaper; and (d) capacitance calculation from (c) showing high stability over 500 cycles.

as high as  $300 \text{ F g}^{-1}$  in aqueous electrolytes, again a two-fold increase in capacitance when compared to the untreated structure. This extremely high capacitance arises from a combination of factors: the balance of micro and nanoporosity available in the structure; the subsequent high electroactive surface area arising from this porosity; and the high conductivity inherent to this structure.

The conductivity of the samples was measured with a Jandl RM2 4-point conductivity probe and a slight increase was observed from  $19 \text{ S cm}^{-1}$  to  $24 \text{ S cm}^{-1}$ . This increased conductivity is unexpected as the microwave irradiation of the CNT architectures generates electron scattering defects within the carbon lattice. It is theorised that the mNPs deposited at the defect sites provide an alternative electron pathway through the CNT network. Consequently, it is proposed that the increase in specific capacitance is due to both an increase in conductivity and electroactive surface area as a result of the deposited mNPs. The effect of concentration of chloroplatinic acid on the capacitance of the buckypaper composite was examined revealing minimal effects over the studied range ( $1:150$  to  $1:6 \text{ H}_2\text{PtCl}_6$ : ethylene glycol v/v). It is noted that there is a significant excess of platinum in solution, even at the lowest concentration used in this study, resulting in the lack of observed change in native capacitance. The capacitance was further enhanced by soaking the buckypaper samples in the chloroplatinic acid/ethylene glycol solutions prior to microwave treatment. This increase of between 10 and 20% is attributed to the time taken for the solution to completely diffuse through the highly porous

CNT architecture, resulting in a more homogenous platinum nanoparticle coating throughout the structure.

In summary, we have presented the first report of an advanced microwave-assisted technique to decorate pre-formed CNT architectures with mNPs. This microwave method is applicable to a wide range of metallic species that can be utilised in the production of a unique variety of electrode materials suitable for a broad range of electrochemical applications. Platinum functionalisation was visualised through TEM and SEM imaging, which demonstrated high levels of nanoparticulate deposits on pre-formed carbon nanotube architectures. These nanoparticles were confirmed to be zero-valent platinum metal particles by XRD and EDX. The electrochemical double layer capacitance of the composite electrodes was found to significantly increase after decoration with the metal nanoparticles. The highest capacitance recorded for these hybrid electrodes was  $\sim 300 \text{ F g}^{-1}$ . The generation of such CNT/metallic nanoparticle composites, *via* microwave-assisted metallic reduction, has numerous potential applications in portable electrochemical devices. XPS and electrochemical cycling show that these composite structures are extremely stable and show particular interest in the area of supercapacitors due to the extremely high capacitive currents being observed.

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