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Surface modification and Pt functionalisation of multi-walled carbon nanotubes in methanol expanded with supercritical CO_2

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ABSTRACT

Microwave acid purification with H_2SO_4 was performed on multi-walled carbon nanotubes (MWNTs) synthesised by fluidised-bed chemical vapour deposition (CVD) to remove Fe catalysts and Al_2O_3 substrates. The surface of these purified MWNTs was then modified with HNO_3 under the influence of an ultrasonic field followed by functionalised with Pt nanoparticles in methanol expanded with supercritical CO_2. The weight loss profile of the purified sample treated at 200 °C under microwave irradiation shows the MWNT purity to be 96.5 wt%. TEM images of Pt functionalised MWNTs show that Pt nanoparticles of approximately 4 nm were deposited on the outer tube walls. SEM/EDX results confirm that the Pt nanoparticles were mono-sized and evenly distributed. Raman spectroscopy suggested that supercritical processing conditions can repair wall defects in MWNTs. XRD analysis confirmed the presence of crystalline Pt particles.

1. Introduction

The deposition of metal nanoparticles onto the external surfaces of carbon nanotubes (MWNTs) is of interest due to the application of metallised MWNTs as cold electron sources in field emission displays [1–3], as catalysts in fuel cells [4–6], as drug carrier [7] and for reversible interconnections in sensors [8]. Recently, MWNT metallisation has been reported using supercritical carbon dioxide (CO_2) [4,9–13], i.e. CO_2, above its critical temperature (31.3 °C) and pressure (73.8 bar) [14], as the reaction medium. The use of supercritical CO_2 is relevant because of its green attributes, i.e. it is non-toxic, non-flammable and inexpensive compared to conventional solvents. Further, it enables the tuning of reaction conditions with changes in the temperature and pressure, while the diffusion coefficient of supercritical fluids is typically two to three orders of magnitude higher than those of gas and liquid states. This increases mass transfer rates, potentially leading to reduced reaction times [11–13,15,16].

In this work, the acid purification (i.e. catalyst and substrate removal) of MWNTs synthesised via fluidised-bed chemical vapour deposition was performed under microwave irradiation [17,18]. The surface of these purified MWNTs was subsequently modified under the influence of an ultrasonic field to ensure that functionalisation of the outer carbon layer was achieved. Pt functionalisation then followed using an inorganic precursor, i.e. platinum chloride ($PtCl_2$) dissolved in methanol expanded with supercritical CO_2. The metallised MWNTs were assessed using thermogravimetric analysis (TGA), transmission electron microscopy (TEM), scanning electron microscopy equipped with energy dispersive X-ray spectrometry (SEM/EDX), Raman spectroscopy and X-ray diffraction (XRD). To the best of our knowledge, this study is the first to report metal deposition onto MWNTs synthesised via fluidised-bed chemical vapour deposition (CVD); this is relevant for the large-scale preparation of metallised MWNTs.

2. Experimental

MWNTs synthesised by fluidised-bed CVD [19] were purified in 4.8 M H_2SO_4 at either 180 °C or 200 °C for 30 min under microwave irradiation (Milestone Microwave Labstation, ETHOS SEL). The resulting MWNT/acid mixtures were filtered through a 0.5 μm hydrophilic PTFE membrane and dried in air at 25 °C for 24 h. Purified MWNTs were then sonicated in 1 M HNO_3 at 25 °C (Branson sonifier 450) at 20 kHz for 10 min. This specific sequence of steps was important and had two objectives: (i) to obtain good dispersion of MWNTs in solution and (ii) to ensure surface modification of the outer layer of the MWNTs with functional groups (i.e. –COOH and –OH) to provide nucleation sites for the deposition of Pt nanoparticles. The surface modification of MWNTs is necessary for metal deposition onto carbon [10,20,21].

For Pt functionalisation in supercritical CO_2, 40 mg treated MWNTs were first sonicated in 10 mL methanol for 10 min. The MWNT-methanol suspension and 20 mg $PtCl_2$ were subsequently loaded into a stainless steel reactor, which was immersed in a

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water bath held at 80 °C [4,9,22–24]. A syringe pump (Model 500D ISCO) was used to feed CO_2 to the reactor to 120 bar. This pressure was maintained for 30 min. The reactor was then gradually depressurised with the exhaust gas passed through a sodium hydroxide (NaOH) scrubber prior to venting to atmosphere. Metallised MWNTs were separated from solution via centrifugation at 7000 rpm, after which the suspension from the centrifuge was dried in air for 12 h to obtain the final products [23]. Metallised MWNTs were examined using thermogravimetric analysis (TGA, TA SDT Q600), TEM (Philips CM120 operated at 120 kV), SEM/EDX (Philips XL 30 CP), Raman spectroscopy (Renishaw Raman using an Ar^+ ion laser at 514.5 nm wavelength) and XRD (Seimens D5000 using nickel-filtered Cu Kα radiation over the range of $10^\circ < 2\theta < 90^\circ$ in 0.02° increments with a 1-s time step).

3. Results and discussion

The as-synthesised reaction products of fluidised-bed chemical vapour deposition typically consist of a mixture of MWNTs, metal catalysts, catalyst supports and reaction by-products [17,18,25]. Acid purification is the most common technique to remove the catalyst, their supports and carbon by-products. Fig. 1 shows weight

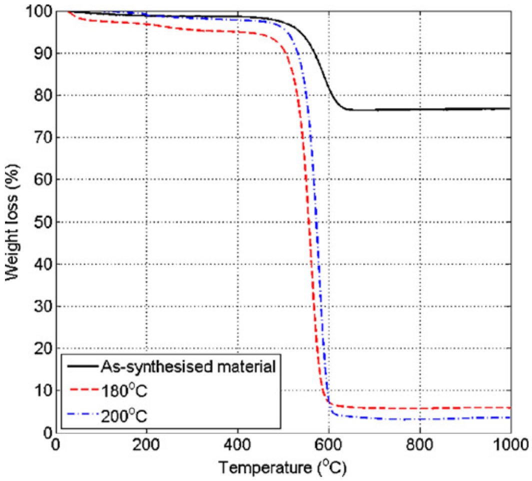

Fig. 1. Thermogravimetric analysis of as-synthesised bed material and acid purified samples (at 180 °C and 200 °C). The purification of CNTs synthesised via fluidised-bed CVD (i.e. as-synthesised material) was performed in 4.8 M H_2SO_4 under microwave irradiation for 30 min. The samples were heated in air between 25 and 1000 °C at a ramp rate of 5 °C/min. The air flow rate was maintained at 100 ml/min.

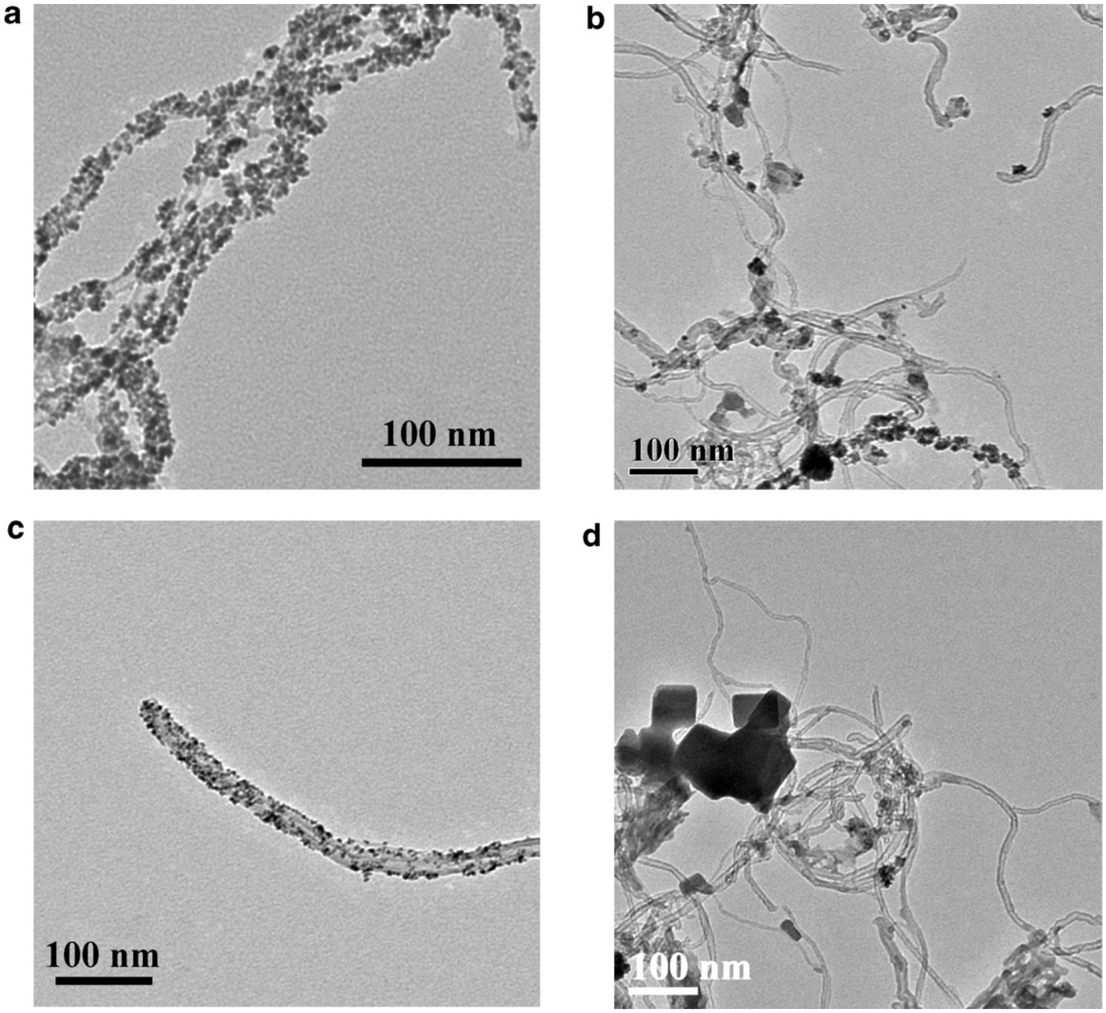

Fig. 2. TEM images of CNTs: (a) purified in 4.8 M H_2SO_4 at 200 °C in a microwave for 30 min, ultrasonicated in 1 M HNO_3 at 25 °C for 15 min and subsequently metallised using $PtCl_2$ as a metal precursor at 80 °C and 120 bar in methanol expanded with supercritical CO_2 for 30 min, (b) purified in 4.8 M H_2SO_4 at 200 °C in a microwave for 30 min, refluxed in 5 M HNO_3 for 24 h (but without ultrasonication) and subsequently metallised using $PtCl_2$ at the temperature of 80 °C and the pressure of 120 bar in methanol expanded with supercritical CO_2 for 30 min, (c) the tube end of a metallised CNT from the product shown in figure a, and (d) purified in 4.8 M H_2SO_4 at 200 °C in a microwave for 30 min, ultrasonicated in 1 M HNO_3 at atmospheric temperature for 15 min and subsequently metallised at 25 °C (below the critical temperature of 31.3 °C) and 50 bar pressure (below the critical pressure of 73.8 bar) for 30 min.

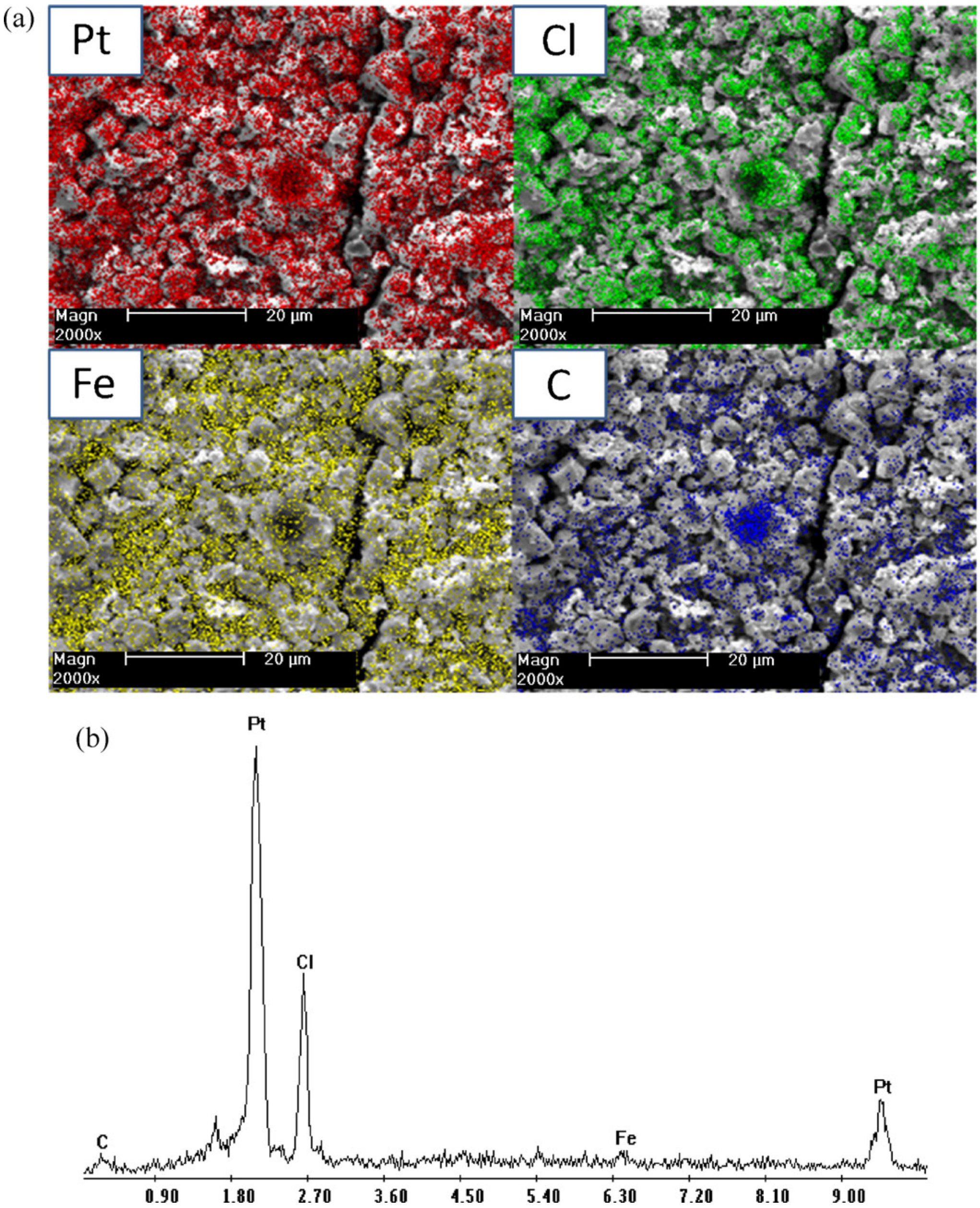

Fig. 3. Elemental mapping and EDS spectra of the CNT products purified in 4.8 M H_2SO_4 at 200 °C in a microwave for 30 min, followed by ultrasonication in 1 M HNO_3 at 25 °C for 15 min and subsequent metallisation $PtCl_2$ in methanol expanded with supercritical CO_2 at 80 °C and 120 bar for 30 min: (a) elemental mapping and (b) EDS spectra.

loss profiles of the as-synthesised bed material and purified samples treated with H_2SO_4 under microwave irradiation at 180 °C and 200 °C. The weight loss of the sample corresponds to the oxidation of carbon in the presence of air at high temperatures, and hence, the greater the weight loss the higher the purity of MWNTs in the samples [17,18,25–27]. Fig. 1 shows that the weight loss increased from 22.4% in the as-synthesised material to 93.9% and 96.5% in the purified samples treated at 180 °C and 200 °C, respectively. MWNTs purified at 200 °C were used in all further experiments.

Fig. 2a shows a TEM image of the MWNT products following purification in 4.8 M H_2SO_4 at 200 °C, followed by ultrasonication in 1 M HNO_3 at 25 °C for 15 min and subsequent reaction with $PtCl_2$ at 80 °C and 120 bar in methanol expanded with supercritical CO_2 for 30 min. The image shows that MWNT surface modification is essential to introduce sufficient active sites for metal functionalisation, confirming the results of Ye et al. [10], Ebbesen et al. [20], Yu et al. [21] and Liu et al. [28]. When appropriate surface modification is not present, the subsequent degree of metallisation is poor. Pt/MWNT bundles synthesised from MWNTs with acid reflux in 5 M HNO_3 for 24 h, but without acid ultrasonication (Fig. 2b) show clusters of Pt nanoparticles in addition to the desired product. The purified MWNT products appear as agglomerates with limited surface area after filtration due to the filtration process used. Thus the use of ultrasonication is also beneficial in obtaining good dispersion, ensuring sufficient mixing of MWNTs with the acid.

Fig. 2a shows that the uniform distribution of Pt nanoparticles occurs on the outer tube walls of the MWNTs, indicating that the surface preparation conditions introduce sufficient functional groups for metal attachment. This treatment is milder and faster than other methods reported in the literature, e.g. conventional acid reflux in oxidising acids for several hours [10,28–30].

Fig. 2c shows evenly distributed and sized Pt nanoparticles covering the end of a MWNT; attributable to the degree of control over the reaction conditions achievable using supercritical CO_2. In con-

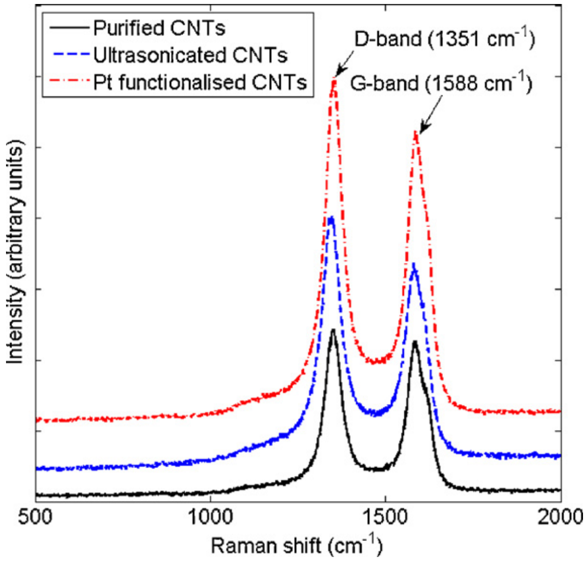

Fig. 4. Raman spectra of CNT products at different steps in the process of surface modification and Pt functionalisation: solid black line—purified CNTs (treatment conditions: as-synthesised CNTs prepared via fluidised-bed CVD were purified in 4.8 M H_2SO_4 at 200 °C in a microwave for 30 min); dashed blue line—ultrasonicated CNTs (treatment conditions: purified CNTs were ultrasonicated in 1 M HNO_3 at 25 °C for 15 min); dash-dot red line—Pt functionalised CNTs (treatment conditions: ultrasonicated CNTs were subsequent metallisation $PtCl_2$ in methanol expanded with supercritical CO_2 at 80 °C and 120 bar for 30 min).

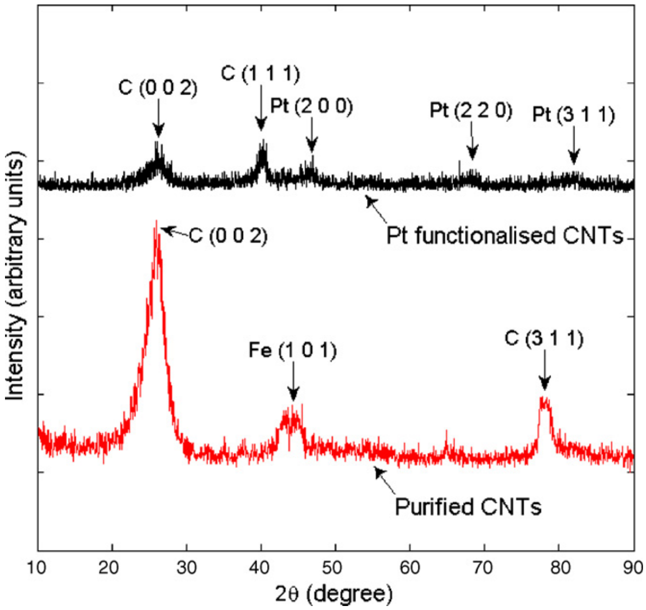

Fig. 5. XRD patterns of purified CNTs (treatment conditions: as-synthesised CNTs prepared via fluidised-bed CVD were purified in 4.8 M H_2SO_4 at 200 °C in a microwave for 30 min) and Pt functionalised CNTs (treatment conditions: purified CNTs were ultrasonicated in 1 M HNO_3 at 25 °C for 15 min and then treated using $PtCl_2$ in methanol expanded with supercritical CO_2 at 80 °C and 120 bar for 30 min).

trast, Fig. 2d shows a TEM image of the MWNT products metallised at 25 °C and 50 bar (below the critical temperature of 31.3 °C and critical pressure of 73.8 bar). The Pt metal forms micron sized, energetically stable crystals. This indicates that elevated temperature and pressure alone is not sufficient to control the Pt reduction and deposition reactions; a supercritical medium is required. This result is consistent with that reported by Sun et al. [9] who found that micron sized Pb particles resulted during metallisation of MWNTs at subcritical conditions.

The product in Fig. 2a was analysed by SEM/EDS to examine the distribution of Pt nanoparticles deposited on the surface of a mat of functionalised MWNTs. Fig. 3a and b shows the elemental mapping and EDS spectra of the as synthesised products purified in 4.8 M H_2SO_4 at 200 °C for 30 min, followed by ultrasonication in 1 M HNO_3 at 25 °C for 15 min and then metallisation with $PtCl_2$ in methanol expanded with supercritical CO_2. Both the elemental mapping and corresponding spectra show an even distribution of Pt, Cl, Fe and C on the surface of the MWNT agglomerates, to the limits of detection of the instrument. The data for Pt are consistent with that measured by An et al. [23]. The peak for Fe indicates there is some residual Fe remaining post purification; this is most likely Fe encapsulated completely by carbon and therefore not able to contact with acid during digestion.

Fig. 4 shows Raman spectra of the MWNT products at different stages of surface modification and Pt functionalisation. The as-synthesised MWNTs of fluidised-bed CVD were purified in a microwave to remove catalysts and substrates (designated 'purified MWNTs' in Fig. 4). The purified MWNTs were ultrasonicated in HNO_3 to perform surface modification (designated 'ultrasonicated MWNTs'). The ultrasonicated MWNTs were then functionalised using $PtCl_2$ in methanol expanded with supercritical CO_2 (designated 'Pt functionalised MWNTs').

Two peaks at approximately 1351 cm^{-1} and 1588 cm^{-1} are clearly observed in Fig. 4. The former is indicative of disordered carbon (D-band), corresponding to amorphous carbon and wall defects of MWNTs; whereas the latter is characteristic peak of graphitic carbon (G-band), corresponding to the crystalline structure of a MWNT [31–34]. The intensity ratio of D-band to G-band (I_D/I_G ratio) is commonly used to investigate the crystallinity and structural properties of MWNTs. The weight loss profile of purified MWNTs (Fig. 1) shows little weight loss below 400 °C, indicating the absence of amorphous carbon. Hence, the D-band peak of purified MWNTs is likely to be due to defects in the outer walls of the MWNTs.

It can be observed that the I_D/I_G ratio increases from 1.10 in the purified MWNTs to 1.28 in the ultrasonicated MWNTs, due to the wall structure damage caused by ultrasonication in acid. This is consistent with the results of Koshio et al. [35] and Chu et al. [36]. However, the I_D/I_G ratio decreases to 1.03 in the Pt functionalised MWNTs treated in supercritical CO_2. This suggests that the wall defects were partially repaired during supercritical CO_2 treatment. The decrease in the D-band of MWNT products treated in methanol expanded with supercritical CO_2 was also reported by Wang et al. [37].

In the XRD pattern of the purified MWNTs (Fig. 5), two diffraction peaks with 2θ value at 26.1° and 78.2°, characteristic of graphitic carbon (0 0 2) and (3 1 1), respectively, were observed. These two peaks correspond to MWNTs with a graphitic structure [38,39]. In addition, a peak of 2θ at 44.7° is attributed to residual Fe (1 0 1) [40,41], which remains post purification. For CNT synthesis, Fe particles were used as the catalyst. Microwave-assisted purification was subsequently performed to remove most of Fe catalyst. However, a small amount of Fe remained in the purified CNTs. The Fe phase shown in the XRD pattern of purified CNTs was caused by this remaining Fe.

The purified product was then ultrasonicated in HNO_3 and metallised using $PtCl_2$ in methanol expanded with supercritical CO_2. The resulting product, i.e. Pt functionalised MWNTs, was also examined by XRD (Fig. 5). The XRD pattern of Pt functionalised MWNTs shows two diffraction peaks for graphitic carbon, namely C (0 0 2) at 26.1° and C (1 1 1) at 38.5°. It can be noted that the crystal plane of graphitic carbon transfers from C (3 1 1) in the purified MWNTs to C (1 1 1) in the Pt functionalised MWNTs; however, the graphitic carbon (0 0 2) remains the same in both products. The crystal plane transformation of graphitic carbon is likely caused by the supercritical CO_2 conditions, which impose both high pressure (120 bar) and high temperature (80 °C) on graphite. In addition, the diffraction peaks at 46.4°, 67.1° and 81.8° corresponded to the crystal planes of Pt (2 0 0), Pt (2 2 0) and Pt (3 1 1), respectively [42–44]. This indicates the presence of Pt nanoparticles, further confirming the results of TEM and SEM/EDX (Figs. 2 and 3).

4. Conclusions

As-synthesised MWNTs prepared by fluidised-bed CVD were purified in acid under microwave irradiation to remove catalysts and substrates. The purified MWNTs were further treated in acid under the influence of an ultrasonic field to induce surface modification. Pt functionalisation was then performed using $PtCl_2$ in methanol expanded with supercritical CO_2. TGA results show that the MWNT purity of purified MWNTs reached 96.5 wt%, confirming that microwave-assisted acid digestion is effective at removing catalysts and substrates. TEM images and SEM/EDX results indicated that the developed process enables Pt nanoparticles of a uniform size to be deposited on the outer tube walls of MWNTs. The SEM/EDX results further confirm that the Pt nanoparticles were evenly distributed on the surface of MWNTs. Raman spectra of the MWNT products suggest that the supercritical condition is able to repair some of the wall defects in the MWNTs caused by the previous acid digestion and ultrasonication. The XRD pattern of Pt functionalised MWNTs indicated the presence of Pt nanoparticles, further confirming the TEM and SEM/EDX results.

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