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A novel $\text{Ca}_3(\text{PO}_4)_2$ - CaCO_3 support mixture for the CVD synthesis of roughened MWCNT-carbon fibres

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A novel $\text{Ca}_3(\text{PO}_4)_2\text{--CaCO}_3$ support mixture for the CVD synthesis of roughened MWCNT-carbon fibres

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Multiwalled carbon nanotubes (MWCNTs) with unusual rough surfaces (including pits) have been synthesised by the chemical vapour decomposition process of acetylene using a novel $\text{Ca}_3(\text{PO}_4)_2\text{--CaCO}_3$ support mixture. An Fe–Co bimetallic mixture (50:50, w/w) was impregnated (5 wt% loading) onto either $\text{Ca}_3(\text{PO}_4)_2$ to give <1% MWCNTs or CaCO_3 to give high yields of MWCNTs with smooth surfaces. Mixtures of $\text{Ca}_3(\text{PO}_4)_2\text{--CaCO}_3$ (0/100–100/0) yielded tubes with very rough surfaces ($t = 30$ min, 1 h) and the CNT yield increased with respect to the amount of CaCO_3 in the support mixture. The inner walls of the CNTs possessed a regular orientation of crystalline graphite sheets (3–5 nm), while the outer surface of the CNTs had a thick, rough, compact layer (~30 nm) of carbon with a random orientation of graphite sheets. These induced extremely rough surfaces of the CNTs could serve as ‘docking stations’ that can harbour a variety of metal catalyst particles for industrially important applications.

Keywords: carbon nanostructures; chemical vapour deposition; transmission electron microscopy; microstructure

1. Introduction

Carbon nanotubes (CNTs) and fullerenes are classified as one allotropic modification of carbon. Other allotropes include diamond, graphite and amorphous carbon. The CNTs are one of the strongest and stiffest materials known, in terms of their tensile strength and elastic modulus respectively, which is the consequence of the covalent sp^2 bonds formed between the individual carbon atoms [1–5]. The extraordinary properties of CNTs (e.g. electrical conductivity, thermal stability and mechanical properties) have made these materials potentially useful in many applications in nanotechnology, such as electronics, optics, catalysis, biomedicine and fuel cells [2,3,6–13]. Ever since the report of the identification of CNTs by Iijima [14], these materials have attracted much attention from researchers, and the methods to make CNTs have been extensively investigated.

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The synthesis of CNTs can be done using arc discharge [14–16], by laser ablation [17], by thermolysis in a closed environment at high pressure [18–27] or by chemical vapour deposition (CVD) procedures [28]. The latter is generally classified into two categories, namely, the floating catalyst process, which is a gas phase process, and the substrate CVD process. The substrate CVD process involves the use of a thermally stable material to support metal particles that are responsible for the molecular decomposition of carbon to form the CNTs [13]. The CVD process is generally the most widely used method because it is a low-cost process that is industrially scalable, versatile, and allows for the controlled growth of high purity CNTs.

The support in the substrate CVD process plays an important role in influencing the activity of the catalyst used to make the CNTs. Several factors should be considered when choosing a support. These include

- (1) the decomposition temperature of the support and hence its useful reaction range,
- (2) the surface area of the support and
- (3) the metal catalyst–support interaction that controls the size of the catalyst particle and the sintering potential of the catalyst.

High surface area materials, such as SiO_2 , Al_2O_3 , TiO_2 and zeolites provide excellent support for the production of catalytic CNTs. However, their nature does not allow for easy removal and thus the purification of the CNTs produced on these supports remains a challenge, and often requires several acidic/oxidation steps that result in damage to the CNT graphitic structures. Environmental aspects should also be taken into consideration because the solvents used during the purification process must be disposed of. To circumvent these environmental problems, the use of readily removable supports has been studied both by others and by us [29–42]. These supports include MgO , MgCO_3 , CaO , $\text{Ca}(\text{OH})_2$, CaCO_3 , etc.

Calcium carbonate (CaCO_3) has proven to be a support of choice for mono- and bimetallic transition metal particles (typically Fe, Ni and Co) because it satisfies both the catalytic activity and environmental aspects in the synthesis of CNTs. Previous studies have revealed the advantages of using this material as a support for CNT synthesis [29–38]. The disadvantage, however, is that the CaCO_3 loses CO_2 to give low surface area CaO at $T > 800^\circ\text{C}$. The presence of this released CO_2 has however been proposed to favour CNT growth [33,34].

In this article, we report on the use of a novel material, tricalcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, as well as $\text{CaCO}_3/\text{Ca}_3(\text{PO}_4)_2$ mixtures as a support for CNT synthesis. $\text{Ca}_3(\text{PO}_4)_2$ has a high melting point (1670°C), a high surface area of $42\text{ m}^2/\text{g}$ (compared to CaCO_3 , $10\text{ m}^2/\text{g}$), is insoluble in water and alcohols, soluble in mild acids and is not expensive [43]. These properties would render the material highly suitable for the CVD synthesis of CNTs.

The formation of carbon fibres can occur on par with pyrolytic thickening of MWCNTs [44–46]. The presence of CO_2 in the CVD synthesis of CNTs has been reported to play an important role in the yield and quality of CNTs obtained [33,34]. Our previous studies using CaCO_3 as a support for CNT synthesis have proved that the presence of defects on the surface of CVD-CNTs can act as ‘docking stations’ for metal catalyst nanoparticles, and thus assist in avoiding the deactivation of catalysts through sintering in catalytic reactions, such as the Fischer–Tropsch reaction [47].

2. Experimental procedure

The materials $\text{Ca}_3(\text{PO}_4)_2$, $\text{Ca}_3(\text{PO}_4)_2\text{-CaCO}_3$ mixture (prepared by physically mixing the two materials) and CaCO_3 , which supported Fe–Co catalysts (2.5% Fe and 2.5% Co by mass), were prepared using a wet impregnation process [35]. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were purchased from Sigma-Aldrich and were used as sources of Fe and Co, respectively. The values of metal loading concentrations were confirmed by inductively coupled plasma–atomic emission spectroscopy (ICP–AES) measurements and by quantitative thermogravimetric analysis (TGA) using a Perkin Elmer Pyris 1 TGA. For thermal analysis, the CNTs were decomposed under a continuous flow of air or nitrogen (40 ml/min) at a heating rate of $10^\circ\text{C}/\text{min}$.

The CNTs were characterised by transmission electron microscopy (TEM) using either a JEOL 100S Electron Microscope or a Philips CM200 equipped with a Gatan imaging filter for higher magnifications, and energy dispersive X-ray spectroscopy (EDS). BET surface area analysis (Micromeritics TriStar Surface Area and Porosity Analyzer), Raman spectroscopy (Jobin-Yvon T64000 micro-Raman spectrometer), X-ray photoelectron spectroscopy (XPS) (Physical Electronics Quantum 2000) and powder X-ray diffraction (PXRD) (Bruker axs D8 Advance PXRD) techniques were also used in this study.

MWCNTs were grown using a horizontal fixed bed reactor consisting of an electronically controlled furnace and a quartz tube reactor [35]. The calcined catalyst (typically 200 mg) was uniformly spread on a quartz boat (120×15 mm) at room temperature and the boat was placed in the middle of the reactor. The furnace was then heated at $10^\circ\text{C}/\text{min}$ with N_2 flowing over the catalyst at 40 ml/min. Once the temperature reached 700°C , the N_2 flow rate was increased to 240 ml/min and C_2H_2 was introduced at a constant flow rate of 90 ml/min. After 60 min of reaction time, the C_2H_2 flow was stopped and the furnace was left to cool down to room temperature with a continuous flow of N_2 (40 ml/min). The boat was then removed from the reactor, and the carbon deposit along with the catalyst was weighed and analysed using TEM.

From our previous studies [35], it was observed that the activity of Fe–Co catalysts was largely influenced by the reaction temperature and the ratios of nitrogen/acetylene gas mixtures. In this study, the synthesis of CNTs was performed by varying only the temperature ($600\text{--}1000^\circ\text{C}$) using a $\text{C}_2\text{H}_2:\text{N}_2$ flow rate of 1:3. Experiments were also carried out using C_2H_2 without a carrier gas (N_2) in order to determine the activity of the catalyst under this condition. The effect of the synthesis time on the CNT structure and yield was investigated.

Purification of the CNTs was carried out using a single step process that involved the use of mild acid (5%, 10% and 30% HNO_3) to dissolve and remove the support and metal particles from the final product. This was achieved by continuously stirring the mixture of the CNTs and acid (e.g. 3 g in 100 ml) for 30 min to 24 h at room temperature. The product was then washed with distilled water until the washings were neutral.

3. Results and discussion

The Fe–Co catalysts supported on $\text{Ca}_3(\text{PO}_4)_2\text{-CaCO}_3$ mixtures were evaluated for the production of CNT.

3.1. BET surface area analysis

Table 1 presents the details of the catalysts used, the amount of raw product obtained shown as yield (g) and the average diameters of the CNTs produced. The total surface areas of the catalyst materials were seen to decrease as the weight of CaCO_3 added to $\text{Ca}_3(\text{PO}_4)_2$ was increased from 5% to 95%. The decrease in the surface area was expected, since CaCO_3 has a much lower surface area ($10.5 \text{ m}^2/\text{g}$) than $\text{Ca}_3(\text{PO}_4)_2$ ($41.6 \text{ m}^2/\text{g}$).

The $\text{Ca}_3(\text{PO}_4)_2$ catalysts were tested for the synthesis of CNTs under the conditions described in Section 2. As can be observed (Table 1), the reactions over pure $\text{Ca}_3(\text{PO}_4)_2$ gave very little carbon deposit, which consisted of CNTs (<1%) and some amorphous carbon. Reactions over CaCO_3 as expected gave a high yield of CNTs with near 100% selectivity (Table 1). The decomposition of C_2H_2 was then performed using CaCO_3 physically mixed with varying amounts of $\text{Ca}_3(\text{PO}_4)_2$ (5, 50 and 95 wt%) prepared using the same impregnation procedure. With the $\text{Ca}_3(\text{PO}_4)_2$ - CaCO_3 supports, the CNT yield decreased with increasing $\text{Ca}_3(\text{PO}_4)_2$ in the mixture.

3.2. TEM analysis

TEM analysis was performed on the product obtained from the Fe-Co on $\text{Ca}_3(\text{PO}_4)_2$ - CaCO_3 support mixtures. The TEM analysis revealed that CNTs were obtained and that all the CNTs were multiwalled in nature with average outer diameters of about 50 nm (synthesis time = 1 h; Figure 1). The inner diameters of the CNTs were in the range of 5–10 nm. The Fe-Co on the $\text{Ca}_3(\text{PO}_4)_2$ - CaCO_3 produced CNTs with outer diameters twice the size of the CNTs obtained using 100% CaCO_3 . The TEM images showed that the CNTs synthesised in the presence of $\text{Ca}_3(\text{PO}_4)_2$ possess extremely rough (pitted) surfaces, when compared to the CNTs produced from CaCO_3 (Figure 2) under the same synthesis conditions. Further, the purified CNTs synthesised from $\text{Ca}_3(\text{PO}_4)_2$ - CaCO_3 have high surface areas $\sim 132 \text{ m}^2/\text{g}$ compared to the CNTs synthesised over CaCO_3 ($\text{SA} = 94 \text{ m}^2/\text{g}$).

CNTs with a rough outer wall structure have been observed by Escobar et al. [48] when they were synthesised using Fe on a SiO_2 substrate. The amorphous non-crystalline surface of the CNTs was attributed to the concentration of acetylene in the synthesis. At high

Table 1. Chemical composition of the catalysts used (200 mg) for the synthesis of CNTs (synthesis time = 1 h) at 700°C .

Reaction	Catalyst composition				Product analysis		
	$\text{Ca}_3(\text{PO}_4)_2$ (wt%)	CaCO_3 (wt%)	Fe^{3+} (wt%)	Co^{2+} (wt%)	BET SA (m^2/g)	Yield (g)	Outer diameter (nm) ^c
1	100	0	2.5	2.5	41.6	0.29	–
2	95	5	2.5	2.5	39.6	0.40	50
3 ^a	50	50	2.5	2.5	29.2	0.86	50
4	5	95	2.5	2.5	13.8	1.03	50
5 ^b	0	100	2.5	2.5	10.5	1.15	25

^aSee Figure 2(b) for TEM image.

^bSee Figure 2(a) for TEM image.

^c ± 5 nm for all samples.

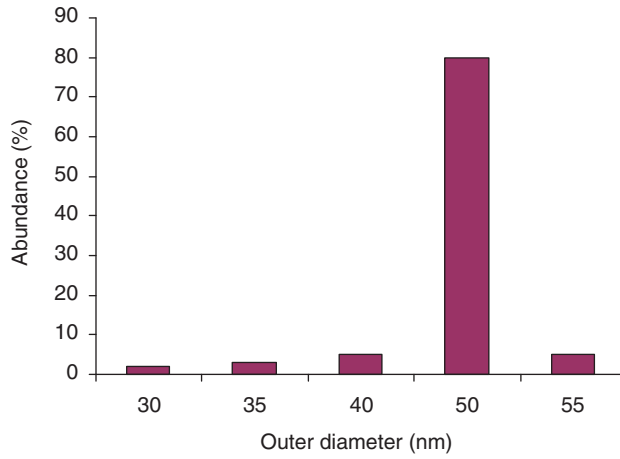


Figure 1. A size distribution graph of the CNTs synthesised using a 50/50, w/w $\text{Ca}_3(\text{PO}_4)_2$ - CaCO_3 support mixture after 1 h synthesis time.

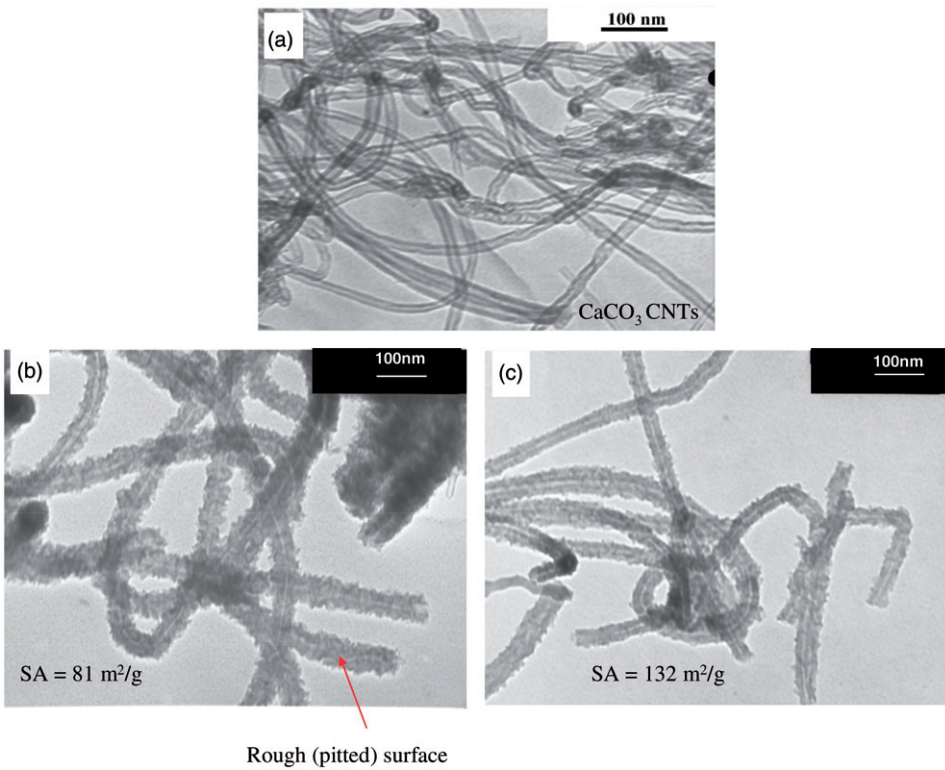


Figure 2. A TEM image of MWCNTs synthesised over CaCO_3 (a) and TEM images of MWCNTs synthesised over 50 wt% CaCO_3 /50 wt% $\text{Ca}_3(\text{PO}_4)_2$ before (b) and after purification (c) with 30% HNO_3 .

acetylene concentrations, carbon nanoparticles grew, covering the surface of CNTs, giving a compact coating [48].

A high-magnification TEM (HMTEM) image of the CNTs synthesised over $\text{Ca}_3(\text{PO}_4)_2/\text{CaCO}_3$ (50:50, w/w) with a rough surface is shown in Figure 3(a) and Figure 4. A closer inspection of the outer surface (Figure 3(b)) revealed that the surface is covered with an amorphous layer of carbon. The amorphous nature of the CNTs has been observed in several other studies: Luo et al. [49] synthesised long amorphous CNTs by a

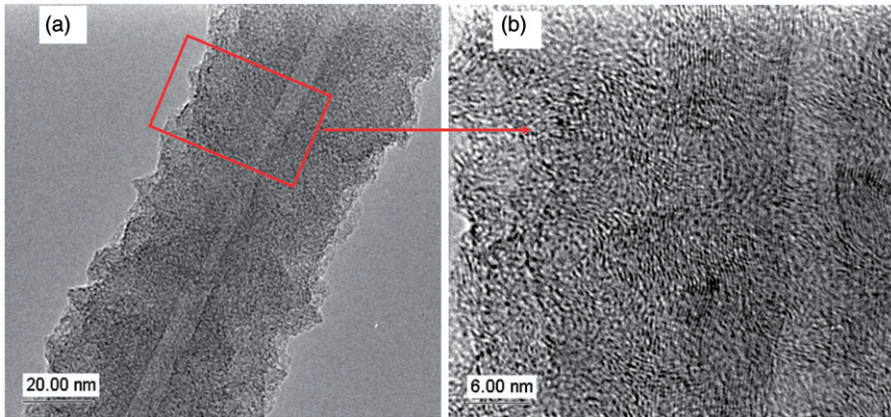


Figure 3. A TEM image of a CNT synthesised over 50 wt% CaCO_3 /50 wt% $\text{Ca}_3(\text{PO}_4)_2$: (a) shows a large CNT with a rough surface and (b) shows the same picture at higher magnification.

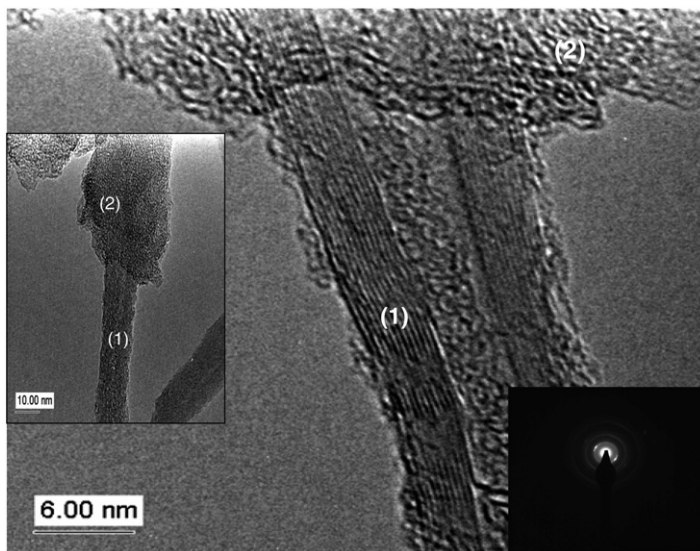


Figure 4. A HMTEM image of CNTs synthesised over 50 wt% CaCO_3 /50 wt% $\text{Ca}_3(\text{PO}_4)_2$ after 1 h showing the perfect orientation of graphite sheets of the inner tubes (region 1) and the amorphous part of the CNTs (region 2). An X-ray diffraction pattern of region 2 is shown in the inset.

solvothermal treatment, in which ferrocene and sulphur powder were the reactants and benzene served as a carbon source. The CNTs were entirely amorphous. This was also reported in a similar study by Xiong et al. [50]. Nishino et al. [51] have also grown amorphous CNTs using poly(tetrafluoroethylene) and ferrous chloride. Amorphous CNTs have also been produced in large scale by temperature-controlled arc discharge in a hydrogen atmosphere with Co/Ni alloy powders [52].

The CNTs produced in this study are not entirely amorphous. The random orientation of carbon is limited to the outer part of the CNT walls as shown by the HMTEM image in Figure 4 (region 2). Clearly, the inner wall is graphitised and the amount of defects in this region is low, as shown Figure 4, region 1. The graphite sheets are arranged in a perfect orientation, contrary to the outer layer shown in region 2. An X-ray diffraction pattern of region 2 revealed the semi-crystalline nature of the nanotubes.

Escobar et al. [48] proposed that during the synthesis of CNTs, amorphous carbon nanoparticles nucleate on the external wall of the CNTs. But the mechanism of this observation has not been explained. However, we believe that the deposition of carbon occurs by a mechanism similar to the nucleation of carbon black soot that takes place during the direct pyrolysis of hydrocarbons (e.g. CH_4 , C_2H_2 and C_2H_4) in the absence of a catalyst at high temperatures [53].

The synthesis of CNTs for different time periods revealed that the roughness of the CNTs is time-dependent. The CNTs were synthesised under the same reaction conditions after 5 min, 30 min, 1 h, 3 h and 6 h, respectively. TEM images of the CNTs synthesised after 5 min show that they do not contain rough surfaces as found in CNTs synthesised after 1 h (Figure 5). Therefore, while it is speculated that the $\text{Ca}_3(\text{PO}_4)_2$ substrate promotes roughness of the CNTs, these reactions occur with time.

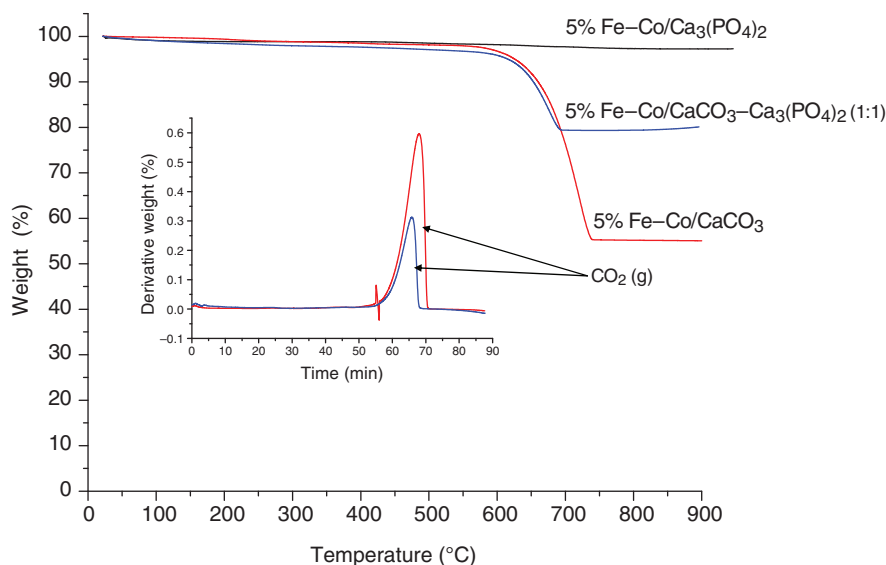


Figure 5. TGA profiles and derivative weight profiles (inset) of the catalyst support mixtures heated in nitrogen.

Our observation is in agreement with studies by others, which have shown that the presence of a small amount of a species that contains oxygen atoms in addition to the carbon source dramatically improves the yield of the reaction in the CVD synthesis of the CNTs [34,54,55]. Indeed Magrez et al. [33] have shown that when CaCO_3 is used as support, CO_2 is generated *in situ* when the CaCO_3 decomposes at the synthesis temperature, 700°C . The CO_2 is assumed to act as an etching agent to prevent the encapsulation of catalyst particles by amorphous carbon.

When $\text{Ca}_3(\text{PO}_4)_2$ is used as a support, no oxygen atoms are generated, and when equal amounts of $\text{Ca}_3(\text{PO}_4)_2$ and CaCO_3 are used, the amount of oxygen in the form of CO_2 is reduced by 50% and the yield and quality of the CNTs produced are also reduced. This was confirmed by performing TGA analysis (Figure 5) of the supports when heated in N_2 .

In addition, it was observed that the outer diameters of the CNTs increase with time and break into shorter tubes (Figure 6(c) and (d)). It can thus be said that the increasing CNT synthesis time using the mixture of supports not only results in good yield and roughening of the CNTs, but also causes fragmentation of the CNTs. The fragmentation of the CNTs can be associated with the deposition of carbon on the already formed CNTs, which results in their fragmentation due to stress. Indeed many of the fragments revealed an amorphous carbon layer deposited on an inner crystalline tube as seen in Figure 6(c) and (d) (see circled regions). If the tube has defects, the defects will provide a point for tube rupture. We suggest that it is the defects on the CNTs that cause the CNTs to fragment after carbon deposition on the tubes. These could be associated with the presence of pentagons and heptagons along the length of the tube [56]. To ensure that the fragmentation of the CNTs was not due to sonication during preparation for TEM analysis, both sonicated and unsonicated portions of the sample were viewed under TEM. It was observed that both the samples looked the same. This was repeated for all the samples synthesised for different times, and it was clear that the sonication process did not have an effect on the CNT lengths.

The rough CNTs were also characterised by Raman spectroscopy (Figure 7). The two peaks occurring at 1348 and 1597 cm^{-1} , corresponding to the D- and G-vibration modes of the graphite sheets, respectively, can be used to indicate the degree of defects/disorder of the graphite sheets. The degree of disorder is given by the ratios of the intensities of the D- and G-bands ($I_{\text{D}}/I_{\text{G}}$). The $I_{\text{D}}/I_{\text{G}}$ ratios of the MWCNTs synthesised after 5 and 60 min were ~ 0.8 and ~ 1.0 , respectively, suggesting that the disorder of the graphite sheets was very high and increased with exposure to C_2H_2 . Raman analysis was also carried out on the purified (24 h, room temperature, 30% HNO_3) CNT samples. The $I_{\text{D}}/I_{\text{G}}$ ratio for the purified MWCNTs (synthesised in 1 h) was ~ 1 , the same as that measured for the impurified CNTs. Thus, the acid treatment process did not affect the graphitic nature of the wall structure of the CNTs.

3.3. Thermogravimetric analysis

Differential thermogravimetric (DTG) profiles of purified CNTs synthesised over CaCO_3 and $\text{CaCO}_3\text{-Ca}_3(\text{PO}_4)_2$ are shown in Figure 8. These profiles indicate that the decomposition of carbon occurs at the same temperature (550°C) for different types of CNTs. Thus, the type of support used or the CNT roughness has little effect on the thermal stability of the CNTs. However, the CNTs synthesised over the support mixture

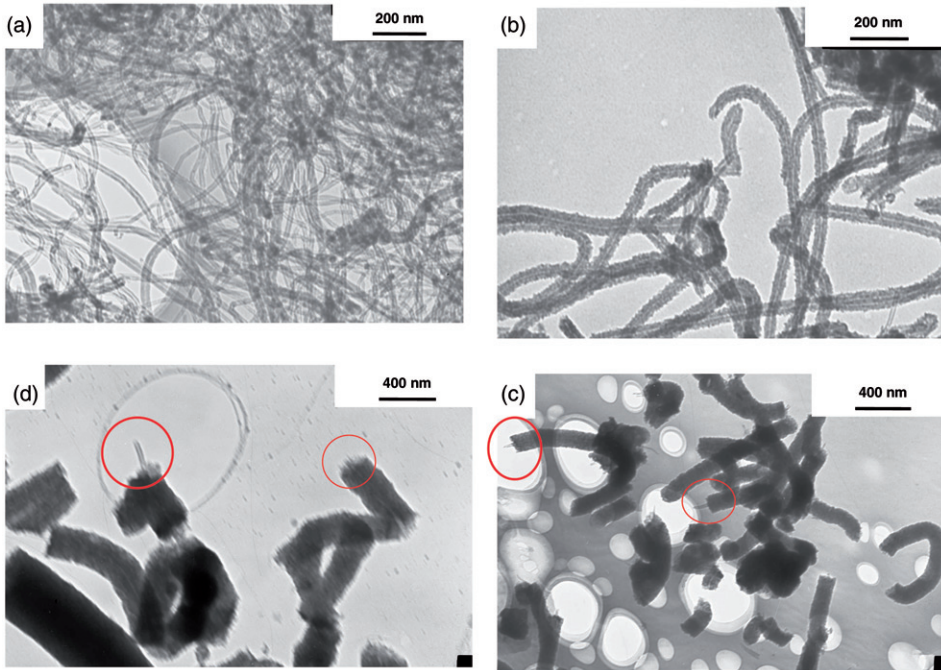


Figure 6. TEM images CNTs synthesised over 50 wt% CaCO_3 /50 wt% $\text{Ca}_3(\text{PO}_4)_2$ for (a) 5 min (b) 60 min (c) 3 h and (d) 6 h synthesis time.

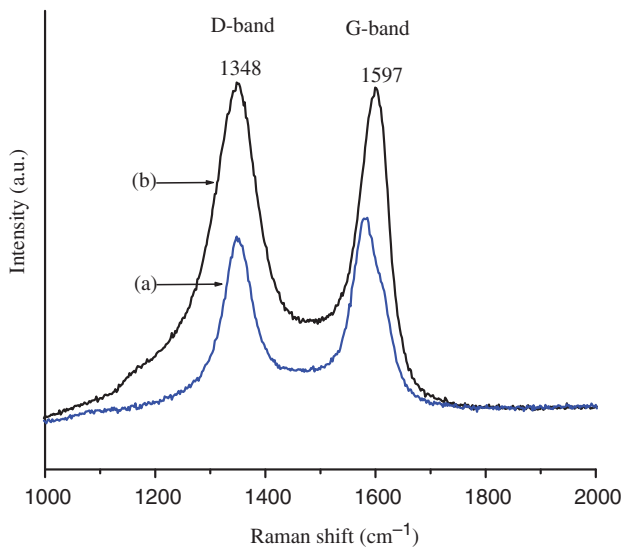


Figure 7. Raman spectra of MWCNTs synthesised over 50 wt% CaCO_3 /50 wt% $\text{Ca}_3(\text{PO}_4)_2$ for (a) 5 min and (b) 60 min.

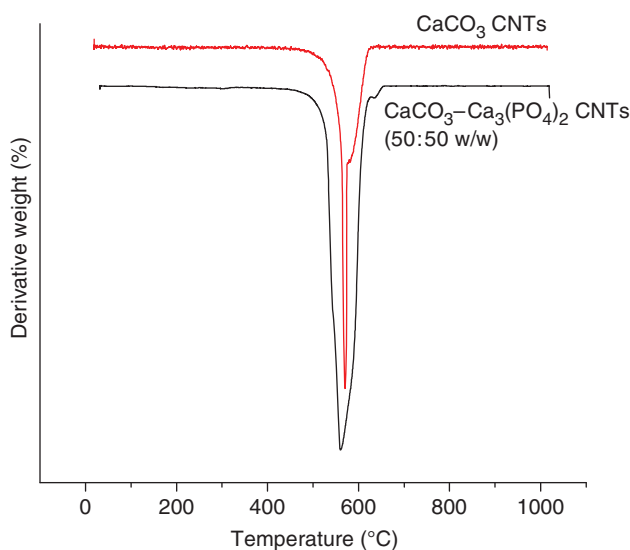


Figure 8. DTG graphs of CNTs synthesised over CaCO_3 and 50 wt% CaCO_3 /50 wt% $\text{Ca}_3(\text{PO}_4)_2$ (under air).

have broader DTG profiles. This suggests that the carbon decomposes over a wide range of temperature, which could be due to the presence of small amounts of phosphorus (P). Phosphorus is known to be a fire retardant and this property could be responsible for the modified decomposition of these CNTs [57]. The presence of P in the CaCO_3 - $\text{Ca}_3(\text{PO}_4)_2$ support is also assumed to ‘kill’ the CNT growth as reflected by the lower yields of CNTs formed as a function of phosphate concentration.

3.4. Elemental composition and purification

The elemental composition of the as-synthesised CNTs was determined using XPS analysis. The CNT wall structure was shown to contain C (96.3%) and O (3.3%) (Figure A1). The spectra of the raw and purified CNTs revealed that the materials are composed mainly of carbon. The elemental composition of the materials was also confirmed by EDS. The elemental analysis revealed that the CNTs are relatively pure and contain undetectable amounts ($<0.5\%$) of Ca or P, implying that large particles of CaO or $\text{Ca}_3(\text{PO}_4)_2$ are not embedded in the CNT walls. It is, however, possible that small particles with size less than 3 nm could be deposited on the walls of the nanotubes [58]. No large crystalline particles of Ca, P or CaO were observed by TEM.

The effectiveness of the purification process was also studied using TGA. The acid was able to remove the impurities, as shown in Figure 9. Very dilute solutions of HNO_3 (5%, 10% and 15%) were found to be effective in removing the support and metal particles (Figure 9), thus the use of concentrated acids and multistep purification can be avoided. As anticipated, higher the concentration (e.g. 15%) of the acid, more effective the purification process was in removing the impurities. The decomposition of the CNTs also occurs over a narrow temperature range suggesting increased purity.

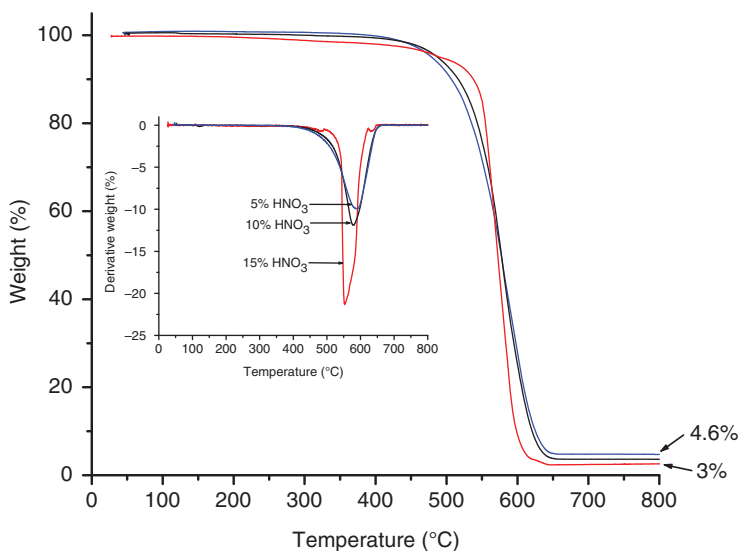


Figure 9. TGA and DTG (inset) profiles of purified MWCNTs synthesised over 50 wt% CaCO_3 /50 wt% $\text{Ca}_3(\text{PO}_4)_2$ supported Fe–Co catalyst with different amounts of acid (5%, 10%, 15% HNO_3 ; $t = 12$ h).

4. Conclusions

This study reports a novel approach for the synthesis of ‘rough’ MWCNTs in high yields. While these CNTs possess a rough surface, the TEM analysis revealed that the inner walls of the CNTs possess a regular array of crystalline graphite sheets (typically 3–5 nm in length). Raman analysis revealed that the rough CNTs synthesised in 1 h contained a high degree of defects on the graphite sheets. The study showed that the growth of CNTs over longer synthesis times ($t > 2$ h) results in thickening and fragmentation of the CNTs due to the deposition of carbon on the CNTs formed. The $\text{Ca}_3(\text{PO}_4)_2$ – CaCO_3 (50 : 50, w/w) mixtures can be readily removed from the CNTs by dissolving them in very dilute acid (5% HNO_3). The purification process does not affect the graphitic structure of the CNTs. The support mixture is thus ideal for the large-scale production of CNTs. The rough surfaces ‘pits’ of the CNTs could serve as ‘docking stations’ for metal particles in catalytic reactions, such as the Fischer–Tropsch synthesis, thus reducing the rate of deactivation of the catalyst through sintering of the metal particles.

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Appendix

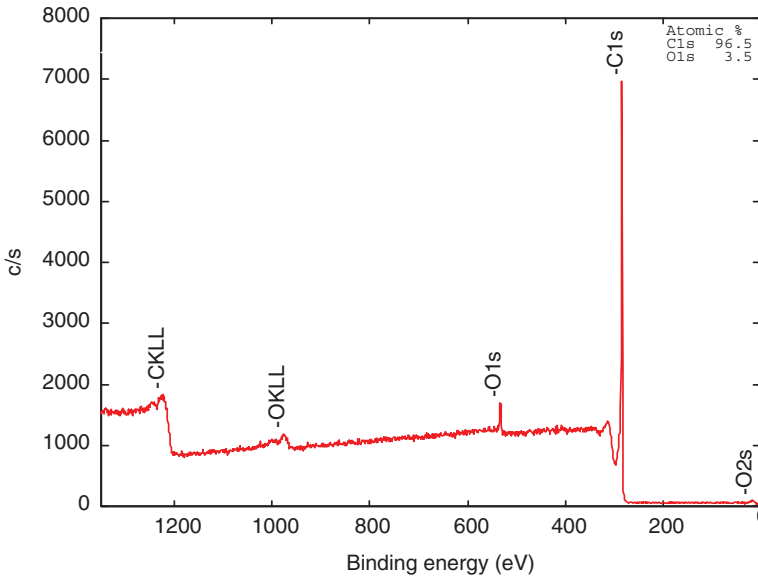


Figure A1. An XPS spectrum of as-synthesised CNTs obtained using 50 wt%CaCO₃/50 wt%Ca₃(PO₄)₂.