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# Microwave-Assisted Preparation of Carbon Nanotubes with Versatile Functionality

Yong-Chien Ling and Archana Deokar
*Department of Chemistry, National Tsing Hua University*
*Taiwan*

## 1. Introduction

Since the accidental discovery of carbon nanotubes (CNTs) during the synthesis of fullerene by Iijima (Iijima 1991), tremendous research has been done on CNTs. CNTs are under intense investigation owing to their spectacular mechanical and electrical properties (Vazquez, Georgakilas, and Prato 2002). Many ways are currently available for the production of CNTs, which include arc-discharge (Journet et al. 1997), pulsed laser vaporization (Kokai et al. 2000), chemical vapor deposition (Campos-Delgado et al. 2010). However, commercial applications of CNTs have been inhibited by the lack of large-scale production of purified CNTs. Moreover, the intrinsic Vander Waals attraction of CNTs towards each other leads easily to entangle agglomerates, which results in their insolubility in most of organic and aqueous solvents.

One of the most powerful approaches to improve CNT solubility is the covalent functionalization of their side walls and tips (Tasis et al. 2006). A wide variety of reactions have been described, most of them employing the conventional chemical techniques, such as refluxing and/or sonication in organic solvents or mineral acids, often making use of high temperature and/or pressure (Hu et al. 2003), long reaction time (Holzinger et al. 2003), or highly reactive species (Brunetti et al. 2007). With the aim of optimizing a multiple funcitonalization approach, many research groups have developed new synthetic strategies to produce multifunctional CNTs avoiding the use of long reaction time, toxic solvent, and extreme condition. Vazquez and coworkers described that 1,3-dipolar cycloaddition of azomethineylides can readily occur on CNTs (Brunetti et al. 2007). However, a severe limitation of this process is the great amount of the DMF and the lengthy time (five days) needed to complete this reaction.

Recently, a microwave-assisted synthesis is enabling technology that has been extensively used in organic synthesis (Dallinger and Kappe 2007; Brunetti et al. 2007; Nuchter et al. 2004). Microwave-assisted modification of CNTs is non-invasive, simple, fast, environmentally friendly, and clean method as compared to traditional methods. Usually, the use of the microwave facilitates and accelerates reactions, often improving relative yields. In case of microwave-assisted functionalization of CNTs, microwave irradiation of CNT reduces the reaction time and gives rise to products with higher degrees of functionalization than those obtained by the conventional thermal methods (Vazquez and Prato 2009). Interestingly, Liu and coworkers (Liu, Zubiri et al. 2007) suggest a competitive effect of microwave irradiation that both promotes functionalization and removes some

functional groups that are initially present. On the other hand, Vazquez and coworkers show that a solvent-free technique combined with microwave irradiation produces functionalized nanotubes in just 1 h of reaction, paving the way to large scale production of functionalization (Brunetti et al. 2007).

## 2. Carbon nanotube and microwave interaction

CNT exhibit impressive potentials in many applications such as electrical interconnects, (Kreupl et al. 2004; Li et al. 2003) thermal interface materials, (Biercuk et al. 2002; Liu et al. 2004) high-performance fibers, (Koziol et al. 2007; Vigolo et al. 2000), environmental monitoring (Lee, Sun, and Ling 2009; Lee et al. 2010), and health & biotechnology (Ghule et al. 2007) so on. Although the theoretical intrinsic electrical, thermal, and mechanical properties of an individual CNT are extraordinary, synthesized CNTs in reality are far from being defect-free. Lin and coworkers developed an ultrafast microwave annealing process to reduce the defect density in vertically aligned CNTs. The as-annealed CNTs showed dramatic improvement in thermal stability, mechanical properties, and electrical conductivity (Lin et al. 2010). Thus, microwave opens the door for the defect-free modification or functionalization of CNTs for various possible applications mentioned above.

### 2.1 Mechanism of the carbon nanotube-microwave interaction

Commercially available CNTs contains different impurities such as amorphous carbon and metallic nanoparticles; which are factors to be considered in order to explain the strong microwave absorptions observed. Microwave irradiation may cause heating by two main factors: (1) dipolar polarization and (2) conduction (joule heating) (MacKenzie, Dunens, and Harris 2009). The presence of impurities that are electrically conductive, such as metal or carbon, could support the mechanism based on conduction heating. According to this mechanism, microwaves do not heat the material immediately; rather motion of the electrons is induced by electric field, causing sample heating. In this way, Joule heating induced by the metal catalyst particles should generate localized superheating (Wadhawan, Garrett, and Perez 2003). The behavior of amorphous carbon and graphite impurities under the microwave irradiation is less controversial; extended π-system permits conductivity (and thus joule heating) to enable localized heating. However, another potential source of localized superheating should be considered, namely, the generation of gas plasma from absorbed gases (particularly $H_2$) in CNTs, under the microwave irradiation, which has been reported in some cases (Imholt et al. 2003). A simple model was proposed by Ye and coworkers (Ye et al. 2006), to explain microwave-induced heating of CNTs, through transformation of electromagnetic energy into mechanical vibrations. Within this model, CNTs subjected to microwave irradiation undergoes ultraheating due to a transverse parametric resonance, which arises from the polarization of CNTs in the microwave field. For impure CNTs, Joule heating occurs because imperfections and impurities damp the transverse vibration mode. The same authors claim that, in a dense and viscous local environment, CNTs will not vibrate. Therefore, there is neither transverse resonance not Joule effect thus no heating, which would explain the different results of absorption, in the presence of solvents or under dry conditions, observed by other groups (Vazquez and Prato 2009). Fig. 1 represents schematic of CNTs interaction with microwaves (Lobach et al. 2002; Liu, Gao et al. 2007; Lee et al. 2010; Chajara et al. 2010).

Various methods for purifying CNTs have been reported, including chemical oxidation, thermal oxidation, filtration (Bandow et al. 1997), and chromatography. These methods can be divided into two groups, namely destructive and non-destructive; both are time-consuming and have high thermal budgets. Microwave-assisted heating has been proven to be an efficient method for the purification of CNTs in every aspect.

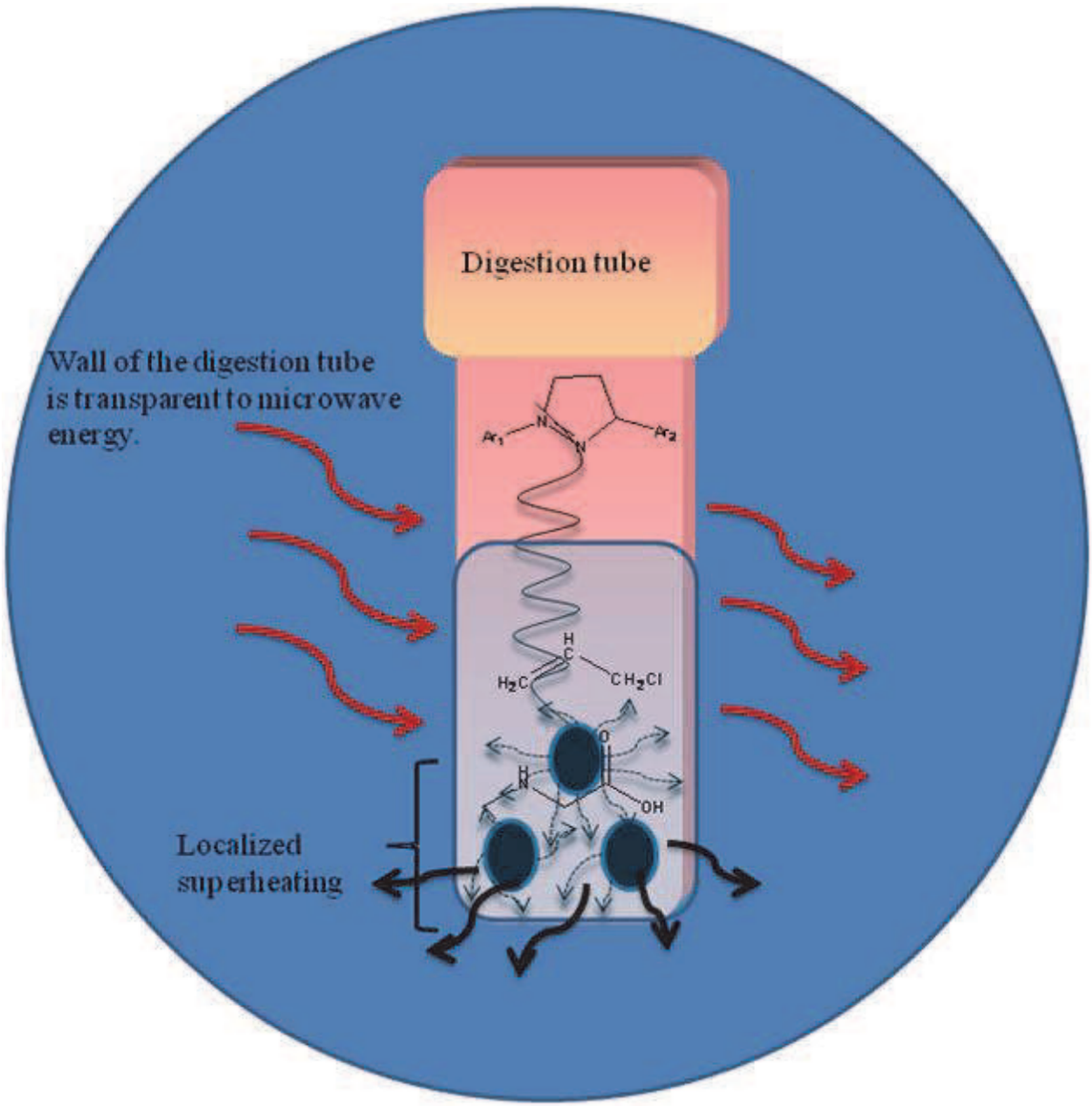


Fig. 1. Schematic of sample heating by microwave

### 2.2 Microwave-assisted purification of carbon nanotubes

Microwave-assisted purification demonstrates significant efficiency improvements over traditional acid reflux with minimal carbon nanotube damage under optimized conditions (MacKenzie, Dunens, and Harris 2009). Table 1 represents the comparison of solution based traditional purification processes with microwave based purification method.

| Method | Reagents used (Vol.) | Temp. | Time period | References |
|---|---|---|---|---|
| **Chemical method (Refluxing)** | 3 M $HNO_3$ (60 ml) | 120°C | 16 hr | (Lobach et al. 2002) |
| **Thermal oxidation** | $O_2$ or Air | 500-800°C | 40-60 min | (Liu, Gao et al. 2007) |
| **Microwave-assisted purification (With solvent)** | 15.8 M $HNO_3$ (5 ml) | 120-180°C | 30 min | (Lee et al. 2010) |
| **Solvent free microwave-assisted purification** | null | 100-150°C | 5 min | (Chajara et al. 2010) |

Table 1. Comparison of the traditional purification methods and the microwave-assisted purification method.

Microwave based method consumes less time, with high sample throughput, small reagent volume, reliable control over amenable temperature and pressure than traditional purification methods. The dispersion of CNTs is the most important issue for CNTs applications. Fig. 2 demonstrates the effect of microwave temperature on the dispersion of the CNTs, we can clearly observe pristine and 100°C heated CNTs appears to settle at the bottom (Fig. 2a and 2b); Whereas, 10 and 30 min, 140°C microwave heated CNTs are well dispersed in the water (Fig. 2c and 2d).

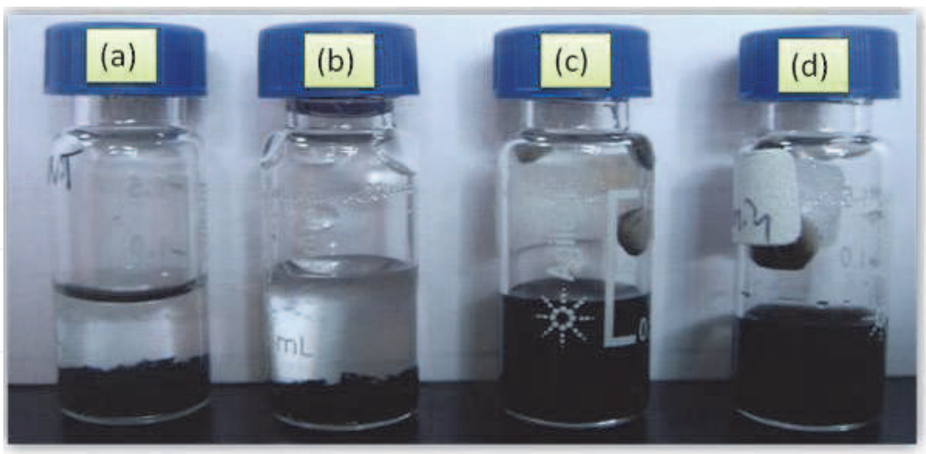


Fig. 2. Microwave-assisted acidification of CNTs: effect of temperature on dispersion of CNTs (a) pristine CNTs, (b) microwave treated CNTs at 100°C for 30 min, (c) at 140°C for 10 min, (d) for 30 min.

Ko.et.al.(Ko et al. 2004) carried out the microwave-assisted purification of multiwall carbon nanotubes (MWNTs) in a closed vessel at 180°C for 30 min in the presence of 20 % hydrogen peroxide and compared efficiency with nitric acid (Fig. 3). This figure indicates that the oxidation power of the reagent is the influencing parameter for microwave-assisted

purification, especially at higher temperatures. Fig. 3 demonstrates that hydrogen peroxide is a more favourable purification agent than the nitric acid. This observation implies that the oxidizing power of hydrogen peroxide toward the decomposition of such defects as amorphous carbon and metal particles is higher than that of nitric acid over a range of temperatures. The gravimetric results demonstrate that the former exhibits better efficiency for removing defects than the latter one. Fig. 4 displays the effect of the purification temperature on the weight loss and plots of derivative thermogravimetric analysis curves as a function of temperature. We can observe that prior to purification the samples undergo two significant weight losses at 195 and 550°C; whereas the samples after purification with hydrogen peroxide exhibit only one significant weight loss temperature. The derivative thermogravimetry curves after purification at 140 and 180°C each display a sharp peak near 520°C. In contrast, after purification at 200°C a broad peak appears in the range 525–575°C. Fig. 4(a) illustrates the first weight loss arises from the combustion of carbonaceous defects in air at ca. 195°C. As the temperature of the thermogravimetric analysis system exceeds 400°C, the nanotube samples begin to decompose in the air and do not fully evaporate until the temperature reaches 650°C. Obviously, the broad peak in the derivative thermogravimetry plot in Fig. 4(d) originates from partial and unsymmetrical decomposition of the nanotubes in the presence of hydrogen peroxide when microwave heating at 200°C.

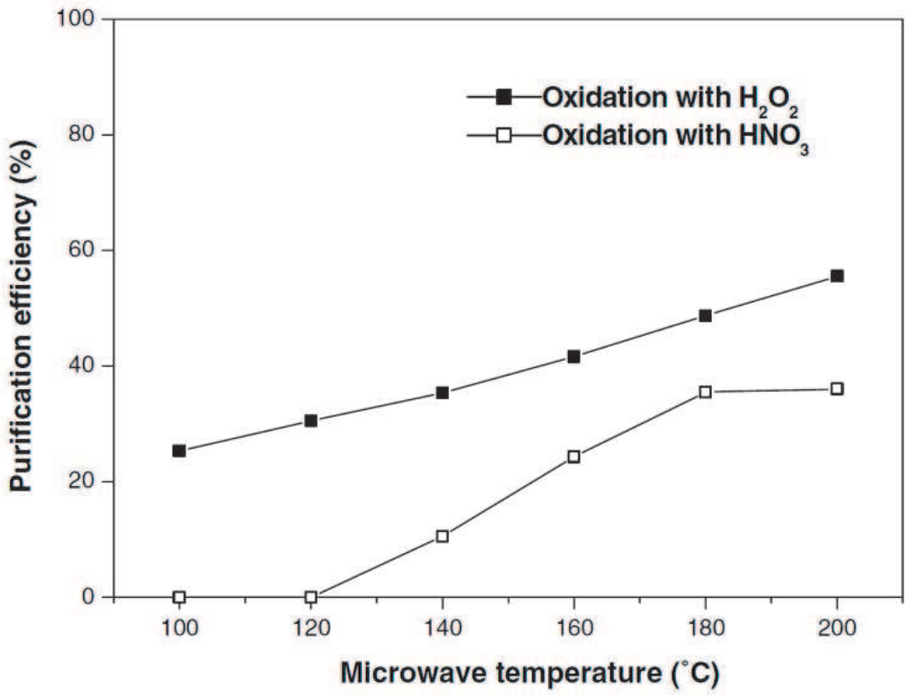


Fig. 3. Effects of temperature and reagent (hydrogen peroxide or nitric acid) on the efficiency of the microwave-assisted purification of nanotubes, as measured by the gravimetric method. Reproduced with permission from ref (Ko et al. 2004) Copyright 2004 Elsevier.

On the other hand, Grennberg (Chajara et al. 2010) and coworkers recently reported reagent -free microwave based method which concurs "green" for the purification of MWNTs as it is extremely faster, with significantly less damage to CNTs, and with less waste compared to previously reported processes.

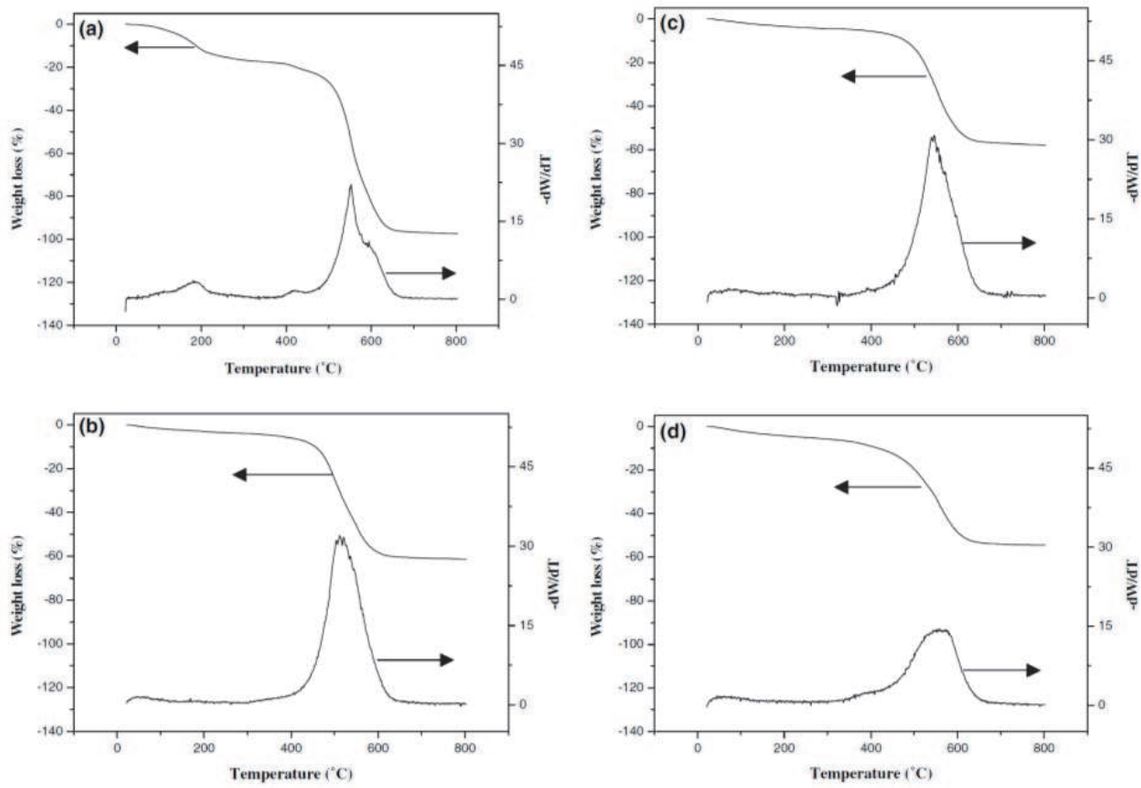


Fig. 4. Thermogravimetric analyses of samples of nanotube purified with hydrogen peroxide at different microwave temperatures. (a) Before purification. After heating at: (b) 140, (c) 180, and (d) 200°C. Reproduced with permission from ref (Ko et al. 2004) Copyright 2004 Elsevier.

Reagent-free microwave-assisted purification yields very pure CNTs within a few min of heating and a simple filtration without the involvement of acidic/oxidative reagents. According to thermogravimetric analysis, Raman and IR spectroscopy, as well as scanning and transmission electron microscopy, the process yields pure nanotubes with a low degree of defects.

The purification is efficient for as-produced and post-synthesis treated CNTs. Morphological observations (Fig. 5) suggests that thermal delaminating of treated non-CNT carbon from CNT is the key step, which attenuated by solubilization of amorphous carbon, preventing re-aggregation. Non-CNT matrix that surrounds the as-received CNTs (Fig. 5a) is transformed into irregularly-shaped amorphous carbon recovered from the filtrate (Fig. 5c and 5d), and the individual MWNTs become more individualized (Fig. 5b). In order to explore the scope of the method, purification protocol has been applied to MWNTs. The left panel in Fig. 6 shows the Raman spectra of the as-received MWNTs, microwave-purified MWNTs (one cycle), and of the filtrate containing the impurities. The D-band was found at 1352 $cm^{-1}$, the G-band at 1578 $cm^{-1}$ and the G′-band at 2708 $cm^{-1}$. The only significant difference between the untreated MWNTs sample and the microwave-purified sample was a decrease in the intensity of the D-band. The D/G ratio was ~0.8 for the as-received sample and ~0.7 for the sample treated once. This is as expected with a decrease in the amount of amorphous carbon in the purified sample. The purification protocol could be repeated several times with fresh solvent, resulting in an increasing purity of the CNT material, However repeating the purification protocol more than twice resulted in some damage to

the MWNTs, as was evident by the small relative increase of the D band intensity (Fig. 6, right panel), but to a very low degree compared to conventional oxidative processes.

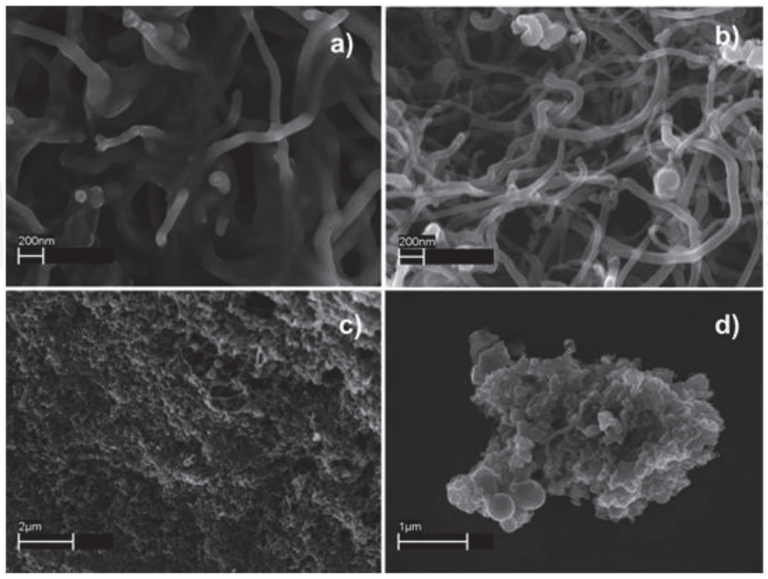


Fig. 5. SEM images of (a) as-received MWNTs (the MWNTs are covered with amorphous carbon), (b) purified MWNTs (two cycles) (the MWNTs are no longer covered with amorphous carbon and appear as individual tubes), (c) filtrate (the image shows amorphous carbon and a few MWNTs) and (d) filtrate with aggregates of amorphous carbon. Reproduced with permission from ref (Chajara et al. 2010) Copyright 2010 Royal Society of Chemistry.

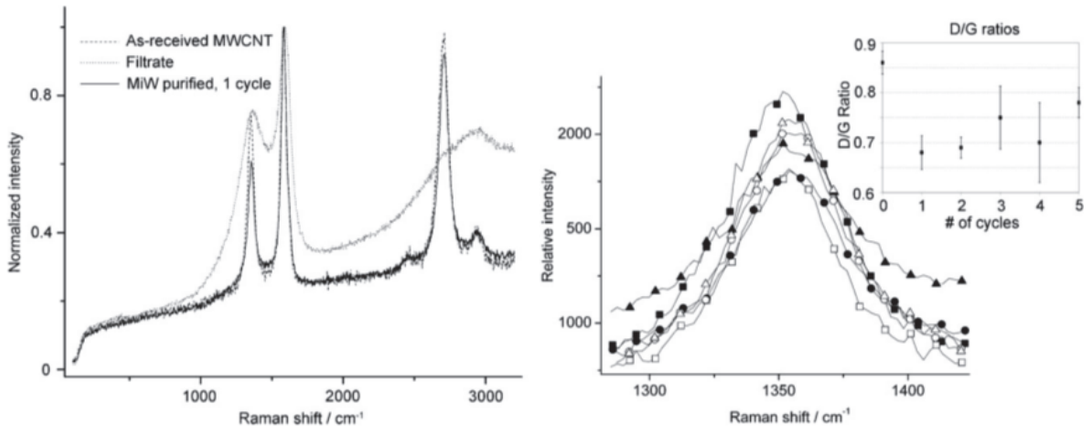


Fig. 6. Raman spectra of the MWNTs (normalized to the G-band). Left panel: as-received MWNTs (dashed line), microwave-purified (MiW) MWNTs (one cycle in $CH_2Cl_2$) (-), filtrate (--). Right panel: expansion of the D-band region of MWNTs treated for 1–5 cycles in $CH_2Cl_2$: ■ As-received MWNTs, □ MiW purified (one cycle), ● MiW purified (two cycles), ○ MiW purified (three cycles), ▲ MiW purified (four cycles), and △ MiW purified (five cycles) (spectra are normalized to the G-band). The inset shows the D/G ratio for the material treated 1–5 times (based on three measurements per sample). Error bars indicate standard deviations. Reproduced with permission from ref (Chajara et al. 2010) Copyright 2010 Royal Society of Chemistry.

## 3. Covalent functionalization of carbon nanotube sidewall

Microwave-assisted synthesis has become an important tool for chemists for rapid organic and inorganic synthesis. A huge number of research papers have appeared over the last decades on the application of microwave technology in organic synthesis (Delgado et al. 2004; Wang, Iqbal, and Mitra 2005; Brunetti et al. 2008). Some major advantages over classical thermal methods are spectacular decrease in reaction time, improved conversion, clean product formation, and wide scope for the development of new reaction conditions.

### 3.1 Microwave-assisted synthesis of CNTs/organic based nanocomopsites by microwave method

For instance, Brunetti and coworkers (Brunetti et al. 2007) have described a solvent-free technique combined with microwave irradiation, which provides a fundamentally different approach when considering the chemistry of CNTs. In the absence of solvents, CNTs absorb the radiation directly and it is possible to take full advantage of the strong microwave absorption typical of pristine nanotubes. Moreover, solvent-free conditions pave the way to green protocols and large-scale functionalization. The method has been applied to produce multifunctionalized CNTs using a combination of two different addition reactions: the 1,3-dipolar cycloaddition of azomethine ylides and the addition of diazonium salts, both *via* a simple, fast, and environmentally friendly method (Fig. 7). The reaction can be followed by Raman spectroscopy, which shows the increase of the D-band (~1300 $cm^{-1}$, $sp^3$ carbons) at the expense of the G-band (~1600 $cm^{-1}$, $sp^2$ carbons).The extremely high temperature observed in the absence of solvent might permit the functionalization of CNTs using new types of reaction that do not work under classical reflux heating (Vazquez and Prato 2009).

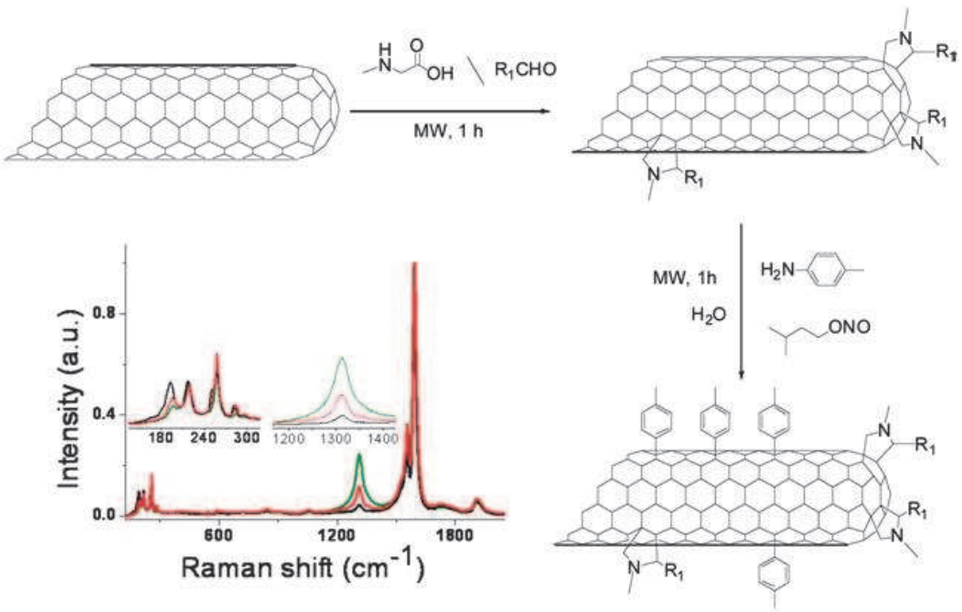


Fig. 7. Microwave-assisted double functionalization of SWNTs: Raman spectra (Exc: 633 nm) of pristine SWNTs (black line), SWNTs functionalized by 1,3-dipolar cycloaddition (red line), and doubly functionalized SWNTs (green line). Reproduced with permission from ref (Vazquez and Prato 2009) Copyright 2009 American Chemical Society.

Using similar approach, a solvent-free microwave-assisted method has also been employed for the covalent functionalization of carbon nanohorns based on the Bingel reaction (Economopoulos et al. 2009) and 1,3-dipolar cycloaddition of azomethineylides (Brunetti et al. 2008).

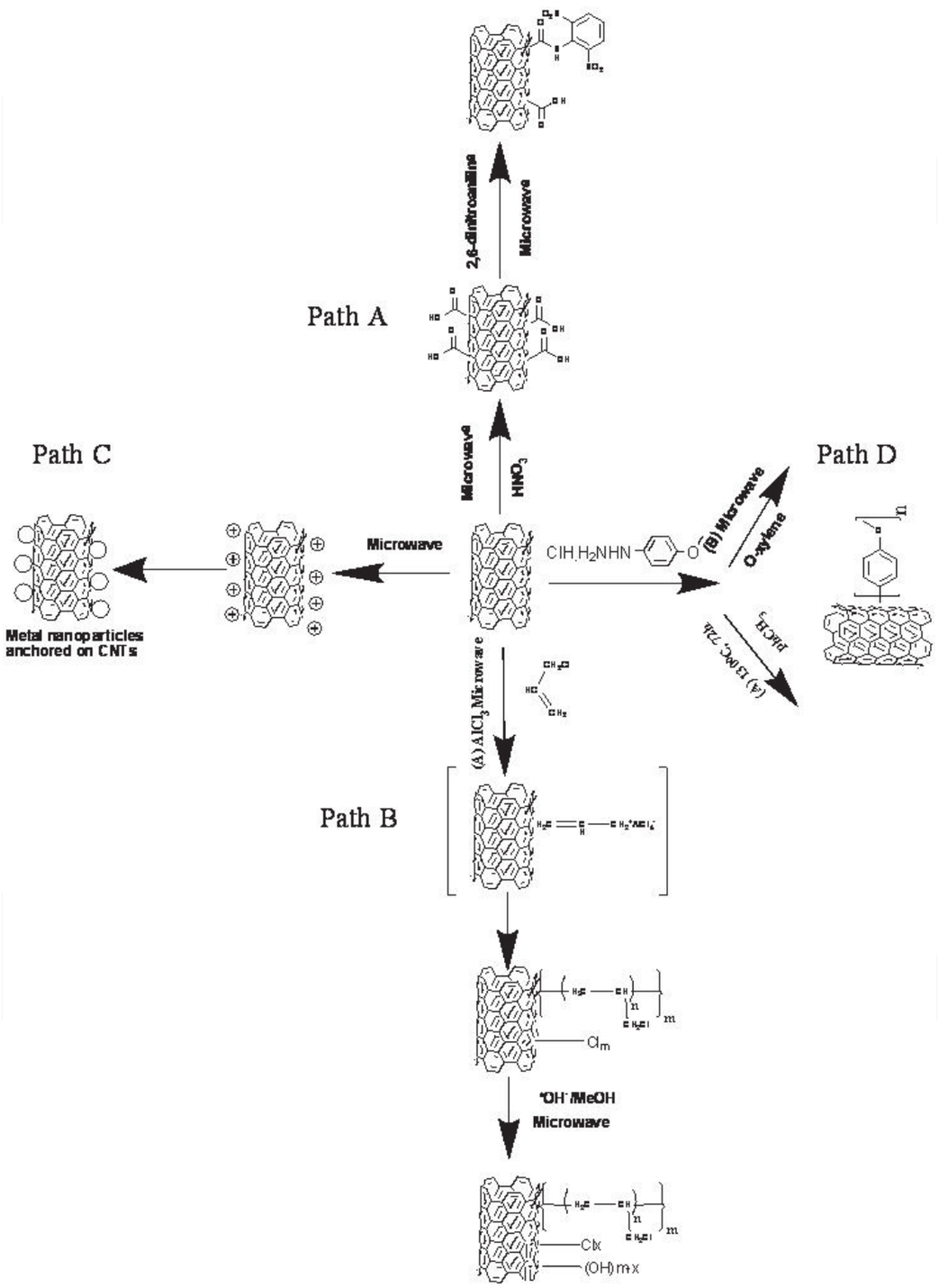


Fig. 8. Schematic representation of various covalent functionlization reactions of carbon nanotube sidewall.

### 3.1.1 Microwave-assisted radical functionalization of single-wall carbon nanotubes

Liu and coworkers compared the efficiencies of two methods for functionalizing single wall carbon nanotubes (SWNTs) through a radical addition of 4-methoxyphenylhydrazine hydrochloride by a classical thermally activated procedure and via a microwave-assisted method. (Path D in Fig. 8) represents the reaction scheme by either classical (a) or microwave method (b) to yield the same product. The experimental signatures of sample functionalized by the classical and microwave methods are quite comparable. With a similar yield of functionalization, the microwave-assisted reaction is far more rapid with an optimal time of around 5 min. This represents a vast reduction in reaction time which for the classical method is often measured in days (Liu, Zubiri et al. 2007).

On the other hand, Tian (Tian et al. 2009) and coworkers have demonstrated a highly efficient approach to prepare the polymer-grafted SWNTs by electrophilic addition with 3-chloropropane based on microwave technique (path B in Fig. 8). In the presence of $AlCl_3$, 3-choloropropene initially was turned into cation $CH_2$=$CH_2$-$CH^+$, which underwent an electrophilic addition to form oligomers. Thus, 3-cholropropene would be attached to the surface of SWNTs in the form of the polymer chains and –Cl groups, and the $Cl^-$ atoms could be substituted by $OH^-$ groups after the hydrolysis with alkaline methanol. The attachment of the hydroxyl groups opens the way to further derivatize SWNTs, and the polymer chains enhance the interaction between modified SWNTs and more polymer molecule chains.

With the combination of different characterization techniques Wang and coworkers (Wang, Iqbal, and Mitra 2005) proved that pristine SWNTs can be covalently functionalized, where the reaction time is reduced to the order of minute.

Two model reactions, namely amidation and 1,3-cycloaddition of SWNTs were carried out successfully in relatively short times using a microwave reactor. The 1-3 dipolar cycloaddition of SWNTs was carried out in 15 min under microwave irradiation. (Please insert Fig. 3 after the above mentioned description)

### 3.2 Microwave-assisted synthesis of CNTs-based hybrid materials

Modifying the CNT surface with desired functional groups is an important step for creating CNT-based hybrid structures and has been used to assemble CNTs and separate CNTs with different structures (Raghuveer et al. 2006). Raghuveer and coworkers describe an eco-friendly approach of using microwaves to rapidly functionalize MWNTs with carboxyl, carbonyl, hydroxyl, and allyl termini, without the use of aggressive oxidants (e.g., $HNO_3$) or ultrasonication. We also adapt this method to derivatize CNTs with nanoparticles synthesized in situ by metal-ion reduction during functionalization, all in a single processing step. This approach offers a new way for efficiently creating hybrid nanostructures. Using similar kind of approach we have synthesized gold nanoparticles coated MWNTs for the adsorption of sulfur compounds as shown in Fig. 8 (path C). Morphological observations illustrates the gold nanoparticles are uniformly anchored onto MWNTs and after the modification still preserved the structure of CNTs (Fig. 9).

Another interesting application of microwave-assisted fabrication is CNT AFM (atomic force microscopy) tips (Druzhinina, Hoeppener, and Schubert 2010). A new, fast, alternative approach for the fabrication of CNT AFM tips is reported. Thereby, the tube material is grown on the apex of an AFM tip by utilizing microwave irradiation and selective heating of the catalyst. The deposition of the catalyst material could be further improved by utilizing particle picking approaches, e.g., by force vs. distance curve recording, to further increase

the controllability of the presented approach. Reaction time as short as three min allowed the fabrication of CNT AFM tips in a highly efficient process. This method demonstrates a promising approach toward a cheaper, faster, and straightforward synthesis of CNT AFM tips as shown in Fig. 10.

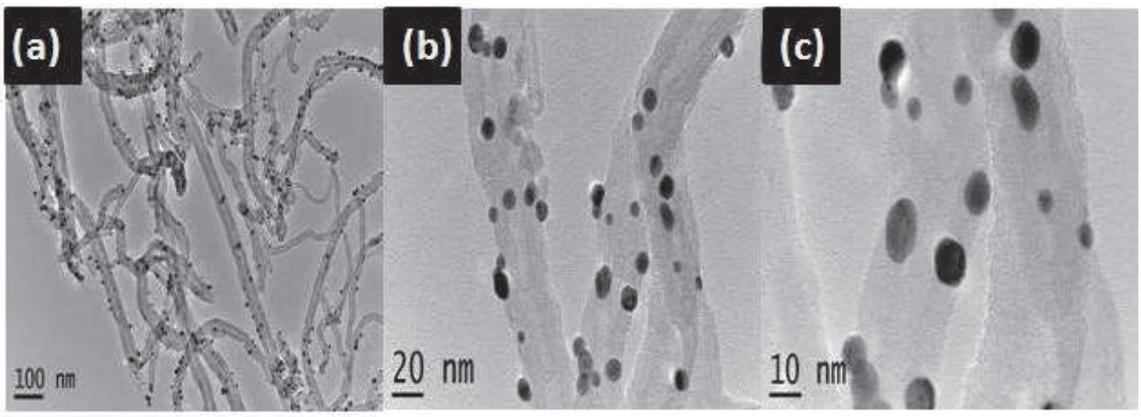


Fig. 9. (a) Low- and (b, c) high magnification micrographs illustrating the decoration of MWNTs with 3-10 nm diameter Au nanoparticles. Note that hollow of the tubes remain intact, indicating that the overall structure of the CNTs are preserved.

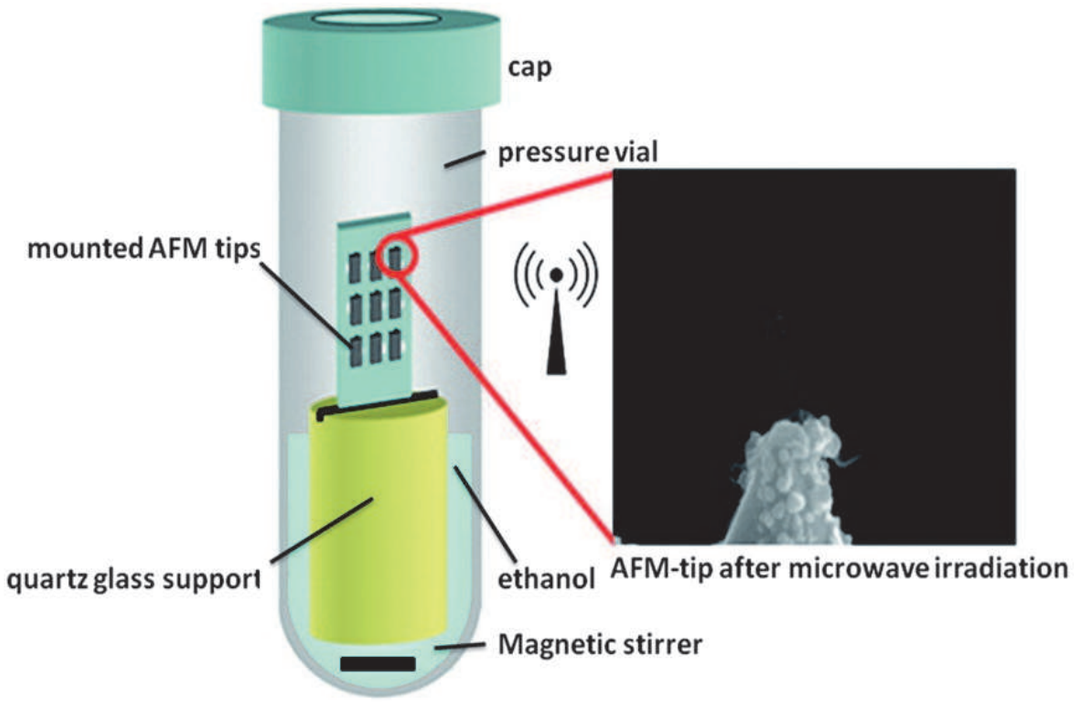


Fig. 10. Quartz glass pressure vial with mounted AFM cantilevers, support, and liquid ethanol reservoir. Morphology of AFM tip after microwave irradiation. Reproduced with permission from ref (Druzhinina, Hoeppener, and Schubert 2010) Copyright 2010 American Chemical Society.

We have carried out microwave-assisted acidification of CNTs, as the first step towards the synthesis of CNTs-based hybrid materials. Various experimental parameters for microwave acidification (e.g. heating temperature and time period of microwave, various types and amounts of oxidative reagent) were investigated. The synthesized hybrid material was used as a gas adsorbent, consisting of magnetic iron-oxide nanoparticles (MINPs) and CNTs (Lee et al. 2010). These hybrid materials were resulted from the electrostatic interaction between MINPs and the surface of microwave-assisted acidified MWNTs as shown in Fig. 11. As compared to traditional Tenax GR adsorbent, our hybrid material shows promising lower detection limit and larger breakthrough volume (Fig. 12 and Table 2).
On the other hand, Chen (Chen et al. 2009) and coworkers have reported microwave-assisted solid state grafting of MWNTs in polyurethane composite, exhibiting excellent optical limiting properties. Wallace (Zhang et al. 2010) research team has synthesized Pt/CNTs based nanocomposite electrocatalyst for proton-exchange membrane fuel cells by using microwave-assisted heating of functionalized SWNTs. Catalytic performance was found to be superior to Pt NPs supported by raw CNTs or by carbon black prepared under the identical condition.


Fig. 11. Synthesis of MWNTs based gas adsorbent.

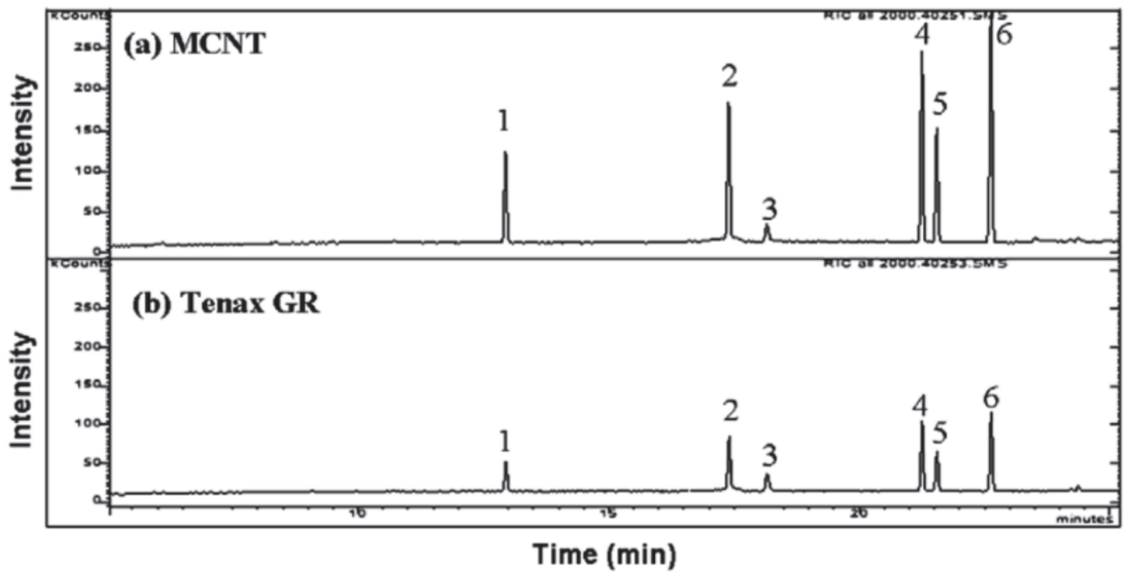


Fig. 12. The total ion chromatogram of BTEXS obtained using (a) 50-mg MWNTs, and (b) 200-mg Tenax GR adsorbent at a sampling rate of 80 mL $min^{-1}$. Peak identity: (1) benzene, (2) toluene, (3) impurity from thermal desorption device, (4) ethyl benzene, (5) xylene, and (6) styrene. Reproduced with permission from ref (Lee et al. 2010) Copyright 2010 Elsevier.

| Compound | Break through volume (BTV) | | Detection limit (DL) | |
|---|---|---|---|---|
| | MWNTs | Tenax GR | MWNTs | Tenax GR |
| Benzene | 100 | 20 | 0.7 | 7.7 |
| Toluene | >100 | 40 | 0.9 | 9.1 |
| Ethyl benzene | >100 | 40 | 0.8 | 8.0 |
| Xylene | >100 | 40 | 0.7 | 7.9 |
| Styrene | >100 | 40 | 0.8 | 8.5 |

a. BTV: $Lg^{-1}$
b. DL: ppbv
c. 50-mg amount

Table 2. Adsorption efficiency of MWNTs nanocomposites over commercially available Tenax GR. Reproduced with permission from ref (Lee et al. 2010) Copyright 2010 Elsevier.

## 4. Summary and future perspectives

For the past decade, despite of the tremendous growth on microwave-driven synthesis, still there are plenty of rooms at the bottom. Microwave is non-invasive, simple, fast, environmentally friendly, and clean processing method as compared to traditional thermal methods. Microwave-assisted method offers excellent reproducibility and avoids all tedious process involved with synthesis of CNTs based nanocomposites by traditional synthesis methods. By controlling the preferential microwave absorption of different types of tubes, it is possible to obtain samples consisting primarily of semiconducting nanotubes, which is critical for many applications. In addition, the extremely high temperature observed, in the absence of solvent, might activate the reactivity of CNTs, permitting their modification in new kinds of reactions that do not work under classical reflux heating. The awareness of the particular microwave absorbing properties of CNTs and their different behavior with respect to typical organic compounds should open the door to the preparation of a wide range of new materials useful in assorted fields, including telecommunications, biomedical applications, and illumination technologies. From the examples discussed here, it is clear that the potential of microwave is worthwhile for the growth of 21st century, however to setup the large-scale microwave for industrial production commands further research and engineering work.

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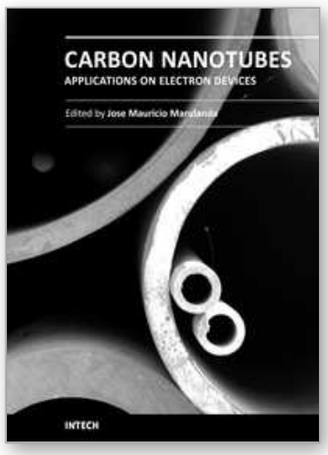


**Carbon Nanotubes Applications on Electron Devices**

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Carbon nanotubes (CNTs), discovered in 1991, have been a subject of intensive research for a wide range of applications. In the past decades, although carbon nanotubes have undergone massive research, considering the success of silicon, it has, nonetheless, been difficult to appreciate the potential influence of carbon nanotubes in current technology. The main objective of this book is therefore to give a wide variety of possible applications of carbon nanotubes in many industries related to electron device technology. This should allow the user to better appreciate the potential of these innovating nanometer sized materials. Readers of this book should have a good background on electron devices and semiconductor device physics as this book presents excellent results on possible device applications of carbon nanotubes. This book begins with an analysis on fabrication techniques, followed by a study on current models, and it presents a significant amount of work on different devices and applications available to current technology.



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**InTech Europe**
University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

**InTech China**
Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

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