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The Role of Carbon Nanotubes in Enhancement of Photocatalysis

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1. Introduction

The chemical, physical and mechanical properties of carbon nanotubes (CNTs) have stimulated extensive investigation since their discovery in the early 1990s (Iijima, 1991). CNTs, which are considered quasi-one dimensional nanostructures, are graphite sheets rolled up into cylinders with diameters of the order of a few nanometers and up to some millimeters in length. Types of nanotubes are the single-walled nanotubes (SWCNTs), double-walled nanotubes (DWCNTs) and the multi-walled nanotubes (MWCNTs). The MWCNTs consist of multiple layers of graphite arranged in concentric cylinders.

During the early stage, the primary research interests include the synthesis or growth of CNTs to prepare enough amounts of CNTs with desired dimension and purity. Several methods like arc discharge, laser ablation of graphite, the more productive chemical vapor deposition (CVD) and plasma enhanced CVD method, have been used to prepare high purity CNTs with controllable wall-thickness and length and acceptable price (Meyyappan, 2004). CNTs attract considerable attention due to their special structure and high mechanical strength which makes them to be good candidates for advanced composites. They can be either semiconducting, semimetallic or metallic, depending on the helicity and the diameter of the tube (Ebbesen et al., 1996; Yang et al., 2003). Based on the structure and shape, CNTs conduct electricity due to delocalization of the pi bond electrons. On the other side, researchers found that CNTs are efficient adsorbents due to their large specific surface area, hollow and layered structures and the presence of pi bond electrons on the surface. Besides that, more active sites can be created on the nanotubes. Thus, CNTs can be used as a promising material in environmental cleaning.

Photocatalytic oxidation using a semiconductor such as TiO_2 , ZnO and WO_3 as photocatalyst is one of the advanced oxidation processes used for degradation of various pollutants in in-

dustrial wastewaters. As the semiconductor is illuminated with photons having energy content equal to or higher than the band gap, the photons excite valence band (VB) electrons across the band gap into the conduction band (CB), leaving holes behind in the valence band. Thus, there must be at least two reactions occurring simultaneously: oxidation from photogenerated holes, and reduction from photogenerated electrons.

The holes react with water molecules or hydroxide ions (OH^-) producing hydroxyl radicals ($\cdot\text{OH}$). The generation of such radicals depends on the pH of the media. Targeted pollutants which are adsorbed on the surface of the catalyst will then be oxidized by $\cdot\text{OH}$. On the other hand, the excited electrons (e^-) to the conduction band (CB) can generate hydroxyl radical ($\cdot\text{OH}$) and can also react with O_2 and trigger the formation of very reactive superoxide radical ion ($\text{O}_2^{\cdot-}$) that can oxidize the target.

The band gap is characteristic for the electronic structure of a semiconductor and is defined as the energy interval (ΔE_g) between the VB and CB (Koci et al., 2011). VB is defined as the highest energy band in which all energy levels are occupied by electrons, whereas CB is the lowest energy band without electrons. The rate of a photocatalytic reaction depends on several parameters. First and most important is the type of the photocatalytic semiconductor. The second factor is the light radiation used or the stream of photons, as over supply of light accelerates electron-hole recombination (Koci et al., 2008). Third factor is pH of the medium with which the semiconductor surface is in contact with the targeted molecules. Fourth factor is the concentration of the substrate influencing the reaction kinetics. Fifth parameter is the temperature of the media where higher temperatures cause frequent collision between the semiconductor and the substrate (Koci et al., 2010).

The degradation rate can be enhanced by reducing the electron-hole recombination rate; preventing the particles agglomeration; and increasing the adsorption capacity, as it is a key process in the photocatalysis. In order to improve the photocatalytic efficiency, several methods have been investigated. This includes:

1. increasing the surface area of the metal oxide by synthesizing nano-size materials;
2. generation of defect structures to induce space-charge separation and thus reduce the recombination;
3. modification of the semiconductors with metal or other semiconductor; and
4. adding a co-sorbent such as silica, alumina, zeolite or clay (Yu et al. 2002; Rusu and Yates, 1997)

CNTs based composites have attracted considerable attentions due to the intrinsic properties that have been created owing to the addition of CNTs into the composite. Functionalization of CNTs, or attachment of individual atoms, molecules or their aggregates to CNTs, further extend the field of application of these nanosystems in different fields like in photocatalysis process (Dresselhaus & Dresselhaus, 2001; Burghard, 2005; Saleh, 2011). CNT/Metal oxide composites have been recently reported to be used for the treatment of contaminated water. In this chapter, therefore, the application of CNTs to enhance the photocatalytic activity of TiO_2 , ZnO and WO_3 will be discussed.

2. Synthesis of carbon nanotube/catalyst composites

There are two main steps for the synthesis of CNT/catalyst nanocomposites. The first step is the grafting of oxygen-containing groups on the surface of the nanotubes and the second step is the attachment of the metal oxides on the active surface of the nanotubes.

2.1. Grafting of oxygen-containing groups on CNTs

Grafting of oxygen-containing groups on the surface of the nanotubes or activation of CNTs can be achieved by oxidation treatment. It can be performed using oxidizing agents such as nitric acid, sulfuric acid, or a mixture of both. For example, oxygen-containing groups can be grafted on the surface of the nanotubes by the following procedure. Initially, CNTs are dispersed by sonication in concentrated acidic media. Then, the mixture is treated by reflux while stirring vigorously at temperature of 100-120°C. After refluxing process, the mixture is allowed to cool at room temperature. The oxidized CNTs are purified by extraction from the residual acids by repeated cycles of dilution with distilled water, centrifugation and decanting the solutions until the pH is approximately 5-6. After the purification process, the oxidized CNTs are dried overnight in an oven at 100°C. After that, the dry oxidized CNTs are pulverized in a ball-mill.

The presence of oxygen containing groups on the surface of the oxidized nanotubes are characterized by the means of Fourier transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD), field emission scanning electron microscopy (FESEM) and the transmission electron microscopy (TEM).

As an example, IR spectra, in the range of 400-4000 cm^{-1} , were recorded in KBr pellets using a Thermo Nicolet FT-IR spectrophotometer at room temperature. Samples were prepared by gently mixing 10 mg of each sample with 300 mg of KBr powder and compressed into discs at a force of 17 kN for 5 min using a manual tablet presser. Figure 1 depicts IR spectrum of oxidized MWCNTs. In the spectrum, a characteristic peak at 1580 cm^{-1} can be assigned to C=C bond in MWCNTs. The band at about 1160 cm^{-1} is assigned to C-C bonds. Also, the spectrum shows the carbonyl characteristic peak at 1650 cm^{-1} , which is assigned to the carbonyl group from quinone or ring structure. More characteristic peak to the carboxylic group is the peak at 1720 cm^{-1} (Ros et al., 2002; Yang et al., 2005; Xia et al., 2007). The observation of IR spectra corresponding to the oxidized MWCNTs suggests the presence of carboxylic and hydroxylic groups on the nanotube surface.

Figure 2 depicts the typical XRD pattern of the oxidized MWCNTs. The strongest diffraction peak at the angle (2θ) of 25.5° can be indexed as the C(002) reflection of the hexagonal graphite structure (Rosca et al., 2005; Saleh et al., 2011; Lu et al., 2008). The sharpness of the peak at the angle (2θ) of 25.5° indicates that the graphite structure of the MWCNTs was acid-oxidized without significant damage since any decrease in the order of crystallinity in

MWCNTs will make the XRD peaks broader and shift the peak diffraction towards lower angles. The other characteristic diffraction peaks of graphite at 2θ of about 43° , 53° and 77° are associated with C(100), C(004) and C(110) diffractions of graphite, respectively.

Energy dispersive X-ray spectroscopy (EDX) measurement is also used as a quantitative analysis for the presence of the oxygen containing groups on the surface of the nanotubes. Figure 4 represents the results of the oxidized MWCNTs. The results shows the presence of oxygen in the sample in addition to carbon element. SEM and TEM are used to characterize the morphology of the nanotube and to ensure that the structure of the nanotube has not been destroyed by the acid treatment. As an example, SEM image and the inset TEM image in Figure 3 confirm that there is no damage effect on the nanotubes using mixtures of nitric acid sulfuric acid for the treatment of the nanotubes.

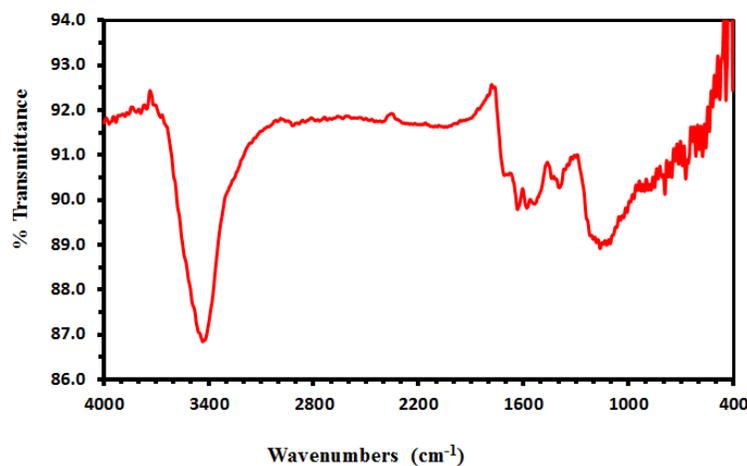


Figure 1. FTIR spectrum of MWCNT oxidized with $\text{H}_2\text{SO}_4/\text{HNO}_3$ mixture for 6h at 100°C .

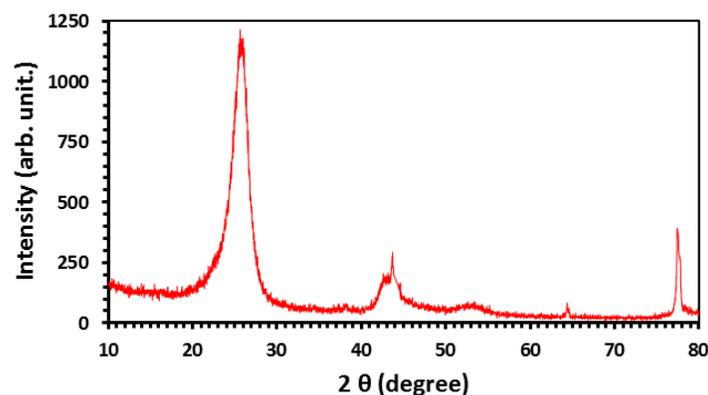


Figure 2. XRD patterns of MWCNT oxidized with $\text{H}_2\text{SO}_4/\text{HNO}_3$ mixture for 6h at 100°C .

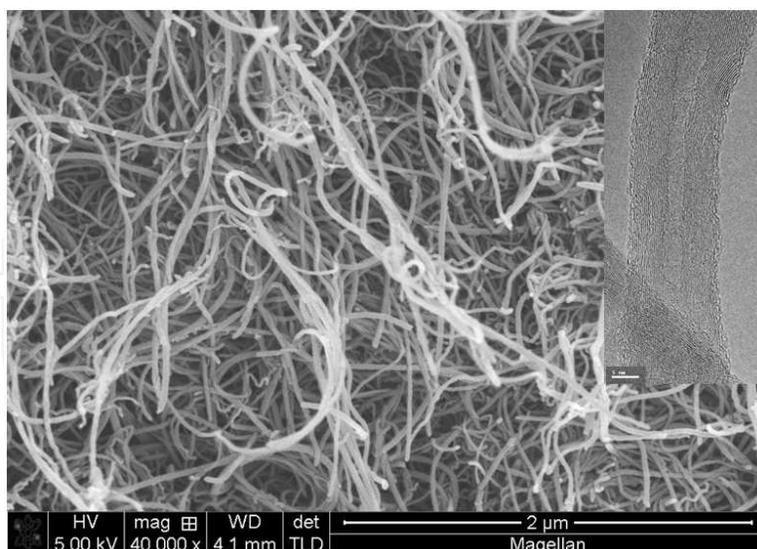


Figure 3. Field emission scanning electron microscopy (FESEM) image of the MWCNTs oxidized with H_2SO_4/HNO_3 mixture for 6h at $100^\circ C$; Inset is the transmission electron microscopy (TEM) image of the same.



Figure 4. EDX spectrum of the MWCNTs oxidized with H_2SO_4/HNO_3 mixture for 6h at $100^\circ C$; inset is the table showing the percentage of each component in the nanotubes.

2.2. Synthesis of CNT/catalysts nanocomposites

CNT/metal oxide nanocomposites can be synthesized by different methods which fall into two basic classes. The first class involves the prior synthesis of nanoparticles that subsequently connected to surface functionalized CNTs by either covalent or noncovalent interactions (Eder, 2010; Peng et al., 2010; Hu et al., 2010). The second class is the one step method which involves direct deposition of nanoparticles onto MWCNT surface, in situ formation of nanoparticles through redox reactions or electrochemical deposition on CNTs (Chen et al., 2006; Gavalas et al., 2001; Yang et al., 2010; Sahoo et al., 2001; Lee et al., 2008). The second class has the advantages where uniform nanomaterials can be prepared due to the presence of active sites on oxidized CNT surfaces.

As an example, CNT/ZnO nanocomposites are prepared by the following procedure (Saleh et al., 2010). Zinc precursor like $Zn(NO_3)_2 \cdot 6H_2O$, is dissolved in doubly deionized water. Then,

ammonia is added drop-wise under continuous stirring into the solution to form a clear solution. The oxidized MWCNTs is added into the solution. The mixture is refluxed at 100°C. The composite are separated and dried at 80°C prior to the calcination in vacuum at 300°C.

Different techniques can be applied for the characterization of the nanocomposite. For example XRD is employed to determine crystalline phases and average crystalline size. FT-IR is used for qualitative analysis of the binding of the metal oxide into the nanotube surface. The morphology of the nanotubes and particle size are examined by the field emission scanning electron microscope (FESEM) and high resolution transmission electron microscopy (HRTEM). EDX measurement is also used as a quantitative analysis for the presence of the oxygen containing groups on the surface of the nanotubes. As an example, Figure 5 depicts the EDX data of the CNT/ZnO nanocomposite. The table shows the percentage of each component in the composite. Figure 6, SEM image and the inset HRSEM image, confirm the presence of zinc oxide particles on the surface of the nanotubes.

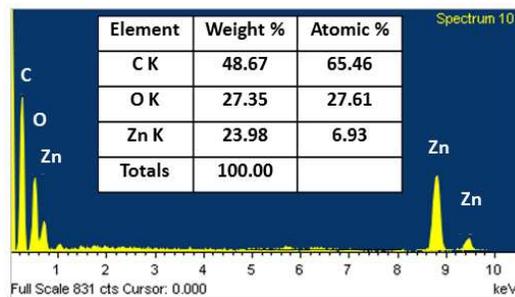


Figure 5. EDX spectrum of the MWCNT/ZnO nanocomposites; inset is the table showing the percentage of each component in the nanotubes.

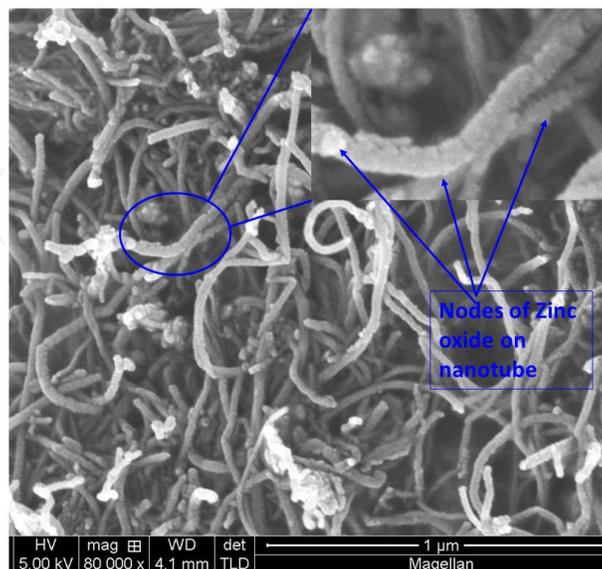


Figure 6. Field emission scanning electron microscopy (FESEM) image of the MWCNT/ZnO; Inset is the HRSEM image.

3. Applications of CNT/Catalyst nanocomposites

CNTs are considered to be good support material for catalysts, because they provide large surface area support and also stabilize charge separation by trapping electrons transferred from metal oxides, thereby hindering charge recombination.

A significant number of papers have been published on the application of CNTs in conjunction with TiO_2 , reflecting the focus of recent research (Jitianu et al., 2004; Huang and Gao, 2003; Woan et al., 2009; Feng et al., 2005). One of the most important applications of such composite is to act as photocatalyst for some chemical reactions, especially for the decontamination of organic pollutants in waste waters. The photocatalytic activity of MWCNT/ TiO_2 composite toward the degradation of acetone under irradiation of UV light was investigated by the detection of the hydroxyl radical ($\cdot\text{OH}$) signals using electron paramagnetic resonance. It has been reported that the agglomerated morphology and the particle size of TiO_2 in the composites change in the presence of CNTs, which provide a large surface area resulting in more hydroxyl group on the surface of the composite with no effect on the mesoporous nature of the TiO_2 . The composite have been reported to be of higher photocatalytic activity than commercial photocatalyst (P25) and TiO_2 /activated carbon (AC) composite (Yu et al., 2005a,b).

The photocatalytic activities of MWCNT/ TiO_2 under visible light have also been reported using the decolorization of dyes like methylene blue, methyl orange, azo dye and other dyes in model aqueous solutions (Cong et al., 2011; Gao et al., 2009; Hu et al., 2007; Saleh and Gupta, 2012; Yu et al., 2005; Kuo, 2009). TiO_2 loading of 12% was found to result in the highest photoactivity in comparison with 6% and 15% loadings. Little TiO_2 or excessive nanotubes addition shielded the TiO_2 and reduced the UV intensity, due to photon scattering by the nanotubes. However, a high TiO_2 content was found to be ineffective in suppressing exciton recombination because of the large distance between the titania and the nanotubes (Li et al., 2012). Optimum ratio of titania and nanotubes provides a large surface area support and stabilize charge separation by trapping electrons transferred from TiO_2 , thereby hindering charge recombination with minimum photon scattering. The composite provides high surface area which is beneficial for photocatalytic activity, as it provides high concentration of target organic substances around sites activated by ultraviolet (UV) radiation.

Also, the activity of MWCNT/ TiO_2 composites has been investigated in photodegradation of phenol and photocatalytic oxidation of methanol under irradiation of visible light (Wang et al., 2005; An et al., 2007; Yao et al., 2008; Dechakiatkrai et al., 2007). The catalysts exhibited enhanced photocatalytic activity for degradation of toluene in gas phase under both visible and simulated solar light irradiation compared with that of commercial Degussa P25 (Wu et al., 2009). It exhibited high activity for the photoreduction of Cr(VI) in water (Xu et al., 2008). Its efficiency was higher compared to a mechanical mixture of TiO_2 and MWCNTs. A probable synergistic effect of TiO_2 and MWCNTs in a composite MWCNT/ TiO_2 on the enhancement of visible light performance, have been proposed where MWCNTs act as support, absorbent, photo-generated transfer station and carbon-doping source to narrow the band gap of TiO_2 .

The composite has been reported for photoinactivation of *E. coli* in visible light irradiation (Akhavan et al., 2009). The efficiency of the nanocomposite was high toward photocatalytic hydrogen generation and for the reduction of CO_2 with H_2O (Dai et al., 2009; Xia et al., 2007).

Zinc oxide, a direct wide band gap (3.37 eV) semiconductor with a large excitation binding energy (60 meV), has been investigated as a potential non-toxic photocatalyst used to successfully degrade organic pollutants. Recently, ZnO nanoparticles have received much attention due to its high photoactivity in several photochemical, UV light response, photoelectron-chemical processes and its low cost production possibility (Wu et al., 2008; Neudeck et al., 2011; Gondal et al., 2010; Drmosh et al., 2010).

Experimental results proved that CNT/ ZnO nanocomposites display relatively higher photocatalytic activity than ZnO nanoparticles for the degradation of some dyes like rhodamine B, azo-dyes, methylene blue, methylene orange (Dai et al., 2012; Zhu et al., 2009). The complete removal of azo-dyes such as acid orange, acid bright red, acid light yellow, after selection of optimum operation parameters such as the illumination intensity, catalyst amount, initial dye concentration and the different structures of the dye on the photocatalytic process, can be achieved in relatively short time by using CNT/ZnO composites.

The MWCNT/ZnO nanocomposites exhibits excellent photocatalytic activity toward other pollutants such as acetaldehyde and cyanide in model solutions (Saleh et al., 2011; Saleh et al., 2010). CNTs act as a photogenerated electron acceptor and retard the recombination of photoinduced electron and hole. The adsorption and photocatalytic activity tests indicate that the CNTs serve as both an adsorbent and a visible light photocatalyst. The experimental results show that the photocatalytic activity of the ZnO/MWCNTs nanocomposites strongly depends on the synthetic route, which is probably due to the difference of surface states resulted from the different preparation processes (Zhang, 2006; Kim and Sigmund, 2002; Jiang and Gao, 2005; Agnihotri et al., 2006).

CNT/ WO_3 nanocomposites have been synthesized via different routes (Pietruszka et al., 2005; Wang et al., 2008; Saleh and Gupta, 2011). The utilization of carbon nanotubes to enhance photocatalytic activity of tungsten trioxide has also been investigated. The photocatalytic activities are greatly improved when CNT/ WO_3 nanocomposite has been used for the degradation of pollutants such as rhodamine B under ultraviolet lamp or under sunlight. The results showed that photocatalytic activity of the MWCNT/ WO_3 composites prepared by chemical process is higher than that prepared by mechanical mixing. The photocatalytic activity is enhanced when WO_3 nanoparticles are loaded on the surface of CNTs. The enhanced photocatalytic activity may be ascribed to the effective electron transfer between the nanotubes and the metal nanoparticles.

A possible synergistic effect between the semiconductor nanoparticles and CNTs on the enhancement of photocatalytic activity is proposed in Figure 7. The mechanism is based on the results of the structure characterizations and the enhancement in photocatalytic activity of the prepared composite.

When the catalyst is irradiated by photons, electrons (e^-) are excited from the valence band (VB) to the conduction band (CB) of catalysts or the metal oxide nanoparticles (NP) creating a

charge vacancy or holes (h^+), in the VB. Some of the charges quickly recombine without creating efficient photodecomposition of the pollutant. In the case where the composite is applied, the strong interaction between the nanotube and the metal oxide results in a close contact to form a barrier junction which offers an effective route of reducing electron-hole recombination by improving the injection of electrons into the nanotube. Therefore, CNTs acts as a photo-generated electron acceptor to promote interfacial electron transfer process since CNTs are relatively good electron acceptor while the semiconductor is an electron donor under irradiation (Saleh and Gupta, 2011; Riggs et al., 2000; Subramanian et al., 2004; Geng et al., 2008). The adsorbed oxygen molecules on the nanotubes react with the electrons forming very reactive superoxide radical ion ($O_2^{\cdot-}$) which oxidize the target. On the other side, the hole (h^+) oxidize hydroxyl groups to form hydroxyl radical ($\cdot OH$) which can decompose the target.

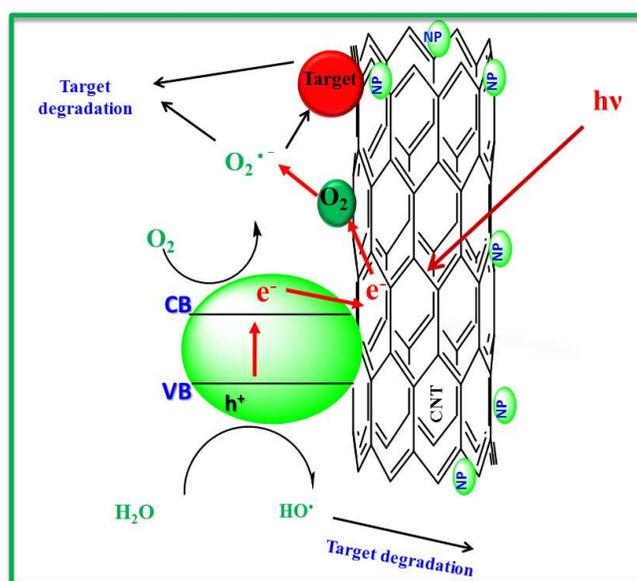


Figure 7. Schematic diagram of the proposed mechanism of photodegradation over CNT/MO composite.

Some important points of such process can be highlighted as:

- Stronger adsorption on photocatalyst for the targeted molecules of pollutant is achieved by the incorporation of the nanotubes, due to their large specific surface area and high quality active sites.
- The nanotubes can act as effective electron transfer unit because of their high electrical conductivity and high electron storage capacity.
- The nanotubes manifest higher capture electron ability and can prompt electron transfer from the conduction band of the metal oxide or semiconductor nanoparticles (NP) towards the nanotube surface due to their lower Fermi level (Cong et al., 2011).
- Schottky barrier forms at the interface between the CNTs and the semiconductor. The photo-generated electrons may move freely towards the CNT surface, thus the left holes can move to the valence band (Woan et al., 2009; Chen et al., 2005).

- The presence of the nanotubes in the composite can inhibit the recombination of photo-generated electrons and holes, thus, improving the photocatalytic activity.
- The transmission stability of promoted electron between the nanotubes and the conduction band is enhanced by the strong interaction and intimate contact between the nanoparticles and the surface of the nanotubes.

4. Conclusion

The chapter discusses the preparation of the nanocomposites consisting of carbon nanotubes and metal oxides like titania, zinc oxide and tungsten trioxide. For the preparation of such composite, the oxygen-containing groups are grafted on the surface of the nanotubes by acid treatment. This is followed by the attachment of the metal oxides nanoparticles on the nanotubes surface. The chapter also highlights the means by which the composite is characterized. These include Fourier transform infrared spectroscopy, X-ray powder diffraction, field emission scanning electron microscope, energy dispersive X-ray spectroscopy and transmission electron microscope.

The UV, visible light and sunlight photocatalytic activity of the CNT-based nanocomposites is higher than that of the metal oxide or mechanical mixture of the metal oxide and CNTs. CNTs are considered to be good support materials for semiconductors like TiO_2 , ZnO and WO_3 because nanotubes provide a large surface area support with high quality active sites. Also they stabilize charge separation by trapping electrons, thereby hindering electron-hole recombination by modification of band-gap and sensitization.

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