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Synthesis of Carbon Nanotube-Metal Oxides Composites; Adsorption and Photo-degradation

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1. Introduction

The unique chemical, physical and mechanical properties of carbon nanotubes (CNTs) have stimulated extensive investigation since their discovery in the early 1990s (Iijima, 1991). The primary research interests focus on the development of simple and cost effective methods for the synthesis of CNTs. To synthesize single wall carbon nanotubes (SWCNT) and multi wall carbon nanotubes (MWCNT), various techniques have been developed. Examples are laser ablation, arc discharge, and chemical vapor deposition (CVD). However, CVD is considered to be more productive method to produce CNTs with acceptable price. Therefore, the extraordinary properties of CNTs and the continuous decrease in their price make them potentially useful in a wide range of applications like in catalysis, photocatalysis and adsorption. The adsorption properties of CNTs depend on different factors such as their large specific surface area, highly porous and hollow structure, light mass density and strong physical interaction ability.

Recently, the applicability of CNTs as adsorbent has been extensively investigated. The applications of CNTs for the removal of pollutants from aqueous solutions have been studied. Numerous experimental studies have already been carried out on the adsorption of heavy metals and hazardous organic materials (Li, et al., 2002; Li, et al., 2003; Chen, et al., 2006; Hyung and Kim, 2008; Goering, et al., 2008).

For further enhancement the adsorption ability of CNTs, purification and activation or functionalization of CNTs is essential and can be performed via oxidation treatment (Cho, et al., 2010; Shao, et al., 2010). Purification is necessary to remove the impurities, like catalyst particles, soot, amorphous carbon and other forms, which are often found, mixed with CNTs. Impurities can reduce the adsorption by their coating on the surfaces of CNTs, and as a result influencing the adsorption on the external surface of the nanotubes (Agnihotri et al., 2006). The enhancement in the adsorption ability of CNTs via oxidation treatment with oxidizing agent, such as nitric acid, hydrogen peroxide, potassium permanganate, or a mixture of nitric acid and sulfuric acid, is most probably ascribed due to an increase in hydrophilicity of CNTs. Oxidation treatment of CNTs results in creating new functional groups on the surface of nanotubes.

In recent years, metal oxides nanoparticles supported on carbon nanotubes have been extensively studied and found to be effective adsorbent for the removal of heavy metal ions and hazardous organic chemicals from water; and also as catalysts. The synthesis methodology of such materials will be discussed in the followed section. The discussion will highlight the synthesis process starting with activation or functionalization of CNTs as a preliminary step for the synthesis of such materials.

2. Synthesis strategy

The formation of carbon nanotubes/metal oxide (CNT/MO) composites is both of fundamental and technological interest since the composite combines the unique properties of CNTs and metal oxide nanoparticles, and in addition exhibit some new extraordinary properties caused by the interaction between them (Eder, D. , 2010); Chu, et al., 2010). Thus, a new class of nanocomposites can be made with extraordinary properties meeting a wide range of applications in different disciplines. For example, alumina is one of the most widely used ceramic materials because of its high hardness, good oxidation resistance and chemical stability. However, its applications are limited because of its low fracture toughness. CNTs have been widely used to reinforce and increase the fracture toughness of alumina owing to their unique one dimensional structure with robust mechanical and thermal properties (Chan, et al., 2005).

Various approaches are used to synthesize CNT/MOs composites. This includes hot pressing of composite powder, pressureless sintering technique, direct in-situ growth, in situ CVD synthesis route, high-intensity ultrasonic radiation method, assembling pre-synthesized metal oxide nanoparticels as building blocks on CNTs, spontaneous formation of metal oxide nanoparticels on CNTs, thermal decomposition of metal oxides precursor directly onto the surface of carbon nanotube, hydrothermal crystallization, sol-gel followed by spark plasma sintering process, surfactant wrapping sol-gel method, chemical precipitation and controlled heteroaggregation method (Liu et al., 2009; Zhang et al., 2010; Keshri et al., 2010; Datye et al., 2010; Zhen et al., 2007; Flahaut et al., 2000; Lupo et al., 2004; Gupta et al., 2011; Zhang et al., 2006; Gao et al., 2008; Chan et al., 2005; Yang et al., 2009; Estili and Kawasaki, 2008).

Over all, the methods based on what is called wet chemistry are perhaps the most widely utilized methods in everyday chemistry. One of the most important reasons of their popularity is simplicity and cost comparing to others. However, in these methods, activation or functionalization of CNTs is a primary step that should be conducted before the synthesis and preparation of CNT/MO nanocomposite materials. Functionalization of CNTs plays an important role in facilitating the binding, embedding or loading nanoparticels on the surface of nanotubes since it introduces chemical functional groups to the surface of nanotubes. The successful in functionalization of the nanotubes is the first step to properly prepare the nanocomposite.

2.1 Functionalization of CNTs

Activation or functionalization of CNTs by oxidation treatment introduces chemical functional groups. It can be performed using oxidizing agents such as nitric acid, sulfuric acid, a mixture of sulfuric acid and nitric acid, potassium permanganate, sulfuric acid in presence of potassium permanganate, hydrogen peroxide in presence of nitric acid, hydrogen peroxide, ozone, an oxygen-based atmosphere by an inductively coupled plasma

or microwave energy and water (Cuentas-Gallegos et al., 2006; Wang et al., 2009; Smith et al., 2009; Lu et al., 2008; Otvos et al., 2006; Aviles et al., 2009; Haydar et al., 2000; Peng et al., 2011; Ionescu et al., 2006; Hojati-Talemi & Simon, 2009).

Treatment with different oxidizing agents might introduce different functional groups on the CNTs surface including alcoholic, carboxylic, aldehydic, ketonic, and esteric oxygenated functional groups, see Fig.1. Hydroxyl groups (b) on the edge of nanotube could be of phenolic character. Oxygen could be substituted for edge carbon atoms in xanthene- or ether-type (d). Carboxyl groups (a) might give carboxylic anhydrides (e) if they are close together. Also, carbonyl groups might condense to lactone groups (f) or form lactols (g) if they are in close to hydroxyl groups or carboxyl groups. The existence of carbonyl groups could be isolated (c) or arranged in quinone-like structure (h). The groups (a, b, e f, and g) have weak acidic character. The acidity of o-CNTs can be determined by acid-base titration method or Boehm titration (Boehm, 1994).

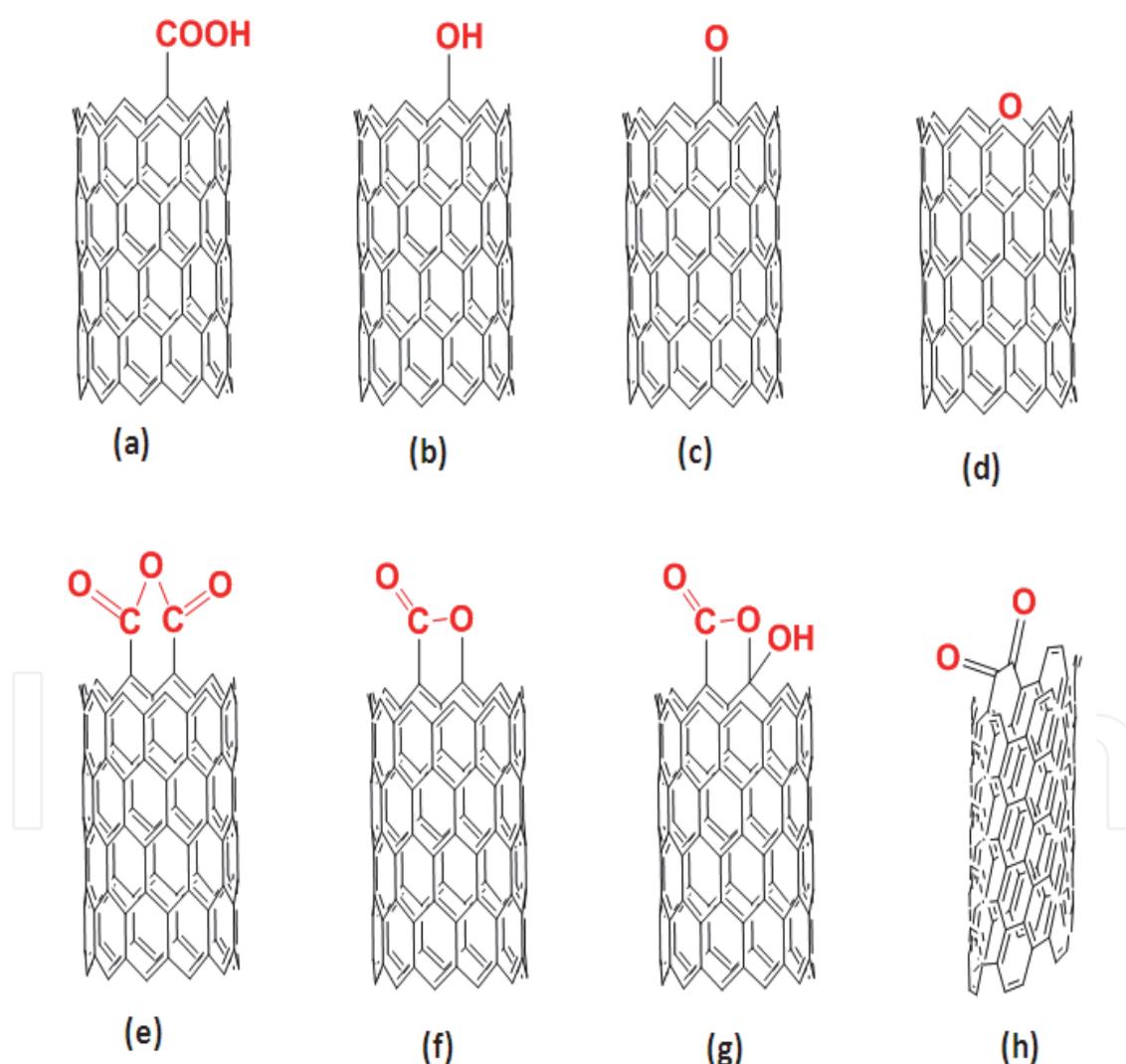


Fig. 1. Possible structures of oxygen-containing groups on the carbon nanotube surface

Synthesis of CNT/MO requires the nanotubes' surface to have mainly alcoholic and carboxylic functional groups which can facilitate the binding of the nanoparticles into the

nanotubes. Over other methods, treatment of CNTs by nitric acid or mixtures of sulfuric acid and nitric acid have been expected to mainly graft carboxylic and alcoholic functional groups onto the CNTs surface (Martinez et al., 2003; Chiang et al., 2011). It is also worth mentioning that the contents of carboxylic and alcoholic groups increase with increasing oxidation time.

The characterization of the presence of functional groups on the surface of nanotube and the efficiency of functionalization on nanotubes can be professionally carried out by various instruments like transmission electron microscope (TEM), field emission scanning electron microscope (FESEM), energy dispersive X-ray (EDX), Raman spectroscopy, thermogravimeter (TGA), and fourier transformed infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS).

Morphology and structure of CNTs is characterized by TEM and FESEM. The impurities and defects such as carbonaceous materials, amorphous carbon coatings and catalyst particles are observed as black dots inside the body of nanotubes or on its surface. TEM provides sufficient resolution for the nanotubes' length and diameter distribution; and opening of the ends of nanotubes. TEM and SEM can allow observing if damage to the surface of CNTs after chemical treatment has occurred and observing the presence of different materials around nanotubes, if any. EDX measurements are used for quantitative representation of the components in the CNTs sample. After oxidation process of CNTs, it is expected that EDX reflect more oxygen on the CNTs sample as a result of grafting new oxygen-containing functional groups.

FT-IR is used to analyze the chemical bonding and type of functional groups grafted onto the nanotubes. The application of FTIR in the study of the surface chemistry of nanotubes can provide direct means to observe the interactions occurring at the surface during adsorption and to determine the structure of the adsorbed species. The FTIR spectra of oxidized CNTs (o-CNTs) exhibit various characteristic bands. Example of FTIR spectra of o-MWCNTs is shown in Fig. 2.

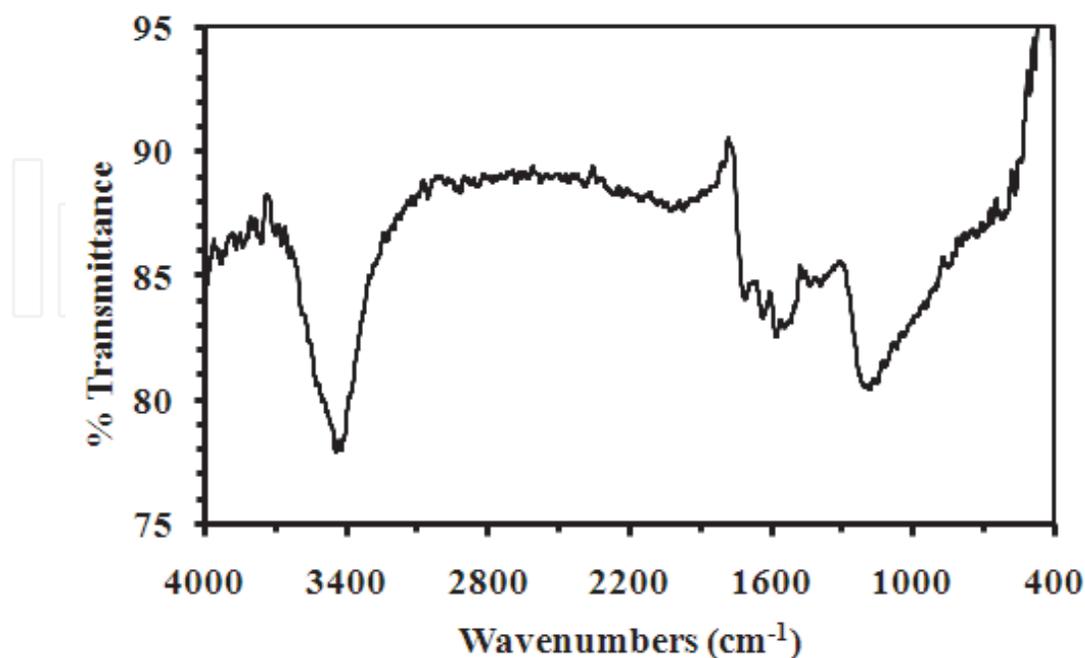


Fig. 2. FTIR spectra of MWCNT oxidized with mixtures of $\text{H}_2\text{SO}_4/\text{HNO}_3$ at 100 °C.

The IR spectrum of o-MWCNTs, Fig. 2, shows absorption peak at 1715 cm^{-1} corresponding to the stretching vibration of C=O from the carboxylic groups (-COOH). The carbonyl characteristic peak is also observed at about 1636 cm^{-1} and can be assigned to the carbonyl group from quinine or ring structure. The broad peaks at 1180 cm^{-1} could be assigned to C-O stretch from phenol or lactone groups; and also to C-C bonds. The band at 2910 cm^{-1} and 2850 cm^{-1} corresponds to CH stretching. The peak at around 3400 cm^{-1} corresponds to OH stretching. This peak can be assigned to the hydroxylic group of moisture, alcohol, or carboxylic groups. The aromatic C=C stretch is observed at around 1580 cm^{-1} in spectra of both pristine CNTs and o-CNTs.

XRD is used in order to ascertain the quality and crystalline nature of nanotubes as opposed to amorphous carbon materials. Fig. 3 shows the X-ray diffraction pattern of the o-MWCNTs. The intensity counts versus two theta. The angle is between the incident and scattered beams. The pattern shows intense peak at $2\theta = 25.9^\circ$ corresponding to the (002) reflection. Compared to the normal graphite, $2\theta = 26.5^\circ$, this peak shows a downward shift; which is attributed to an increase in the sp^2 , C=C layers spacing (Zhang et al., 2002). The other diffraction peaks, are at the angles 2θ of 42.7° , 43.9° , 53.5° and 77.5° and indexed to the (100), (101), (004) and (110) reflections.

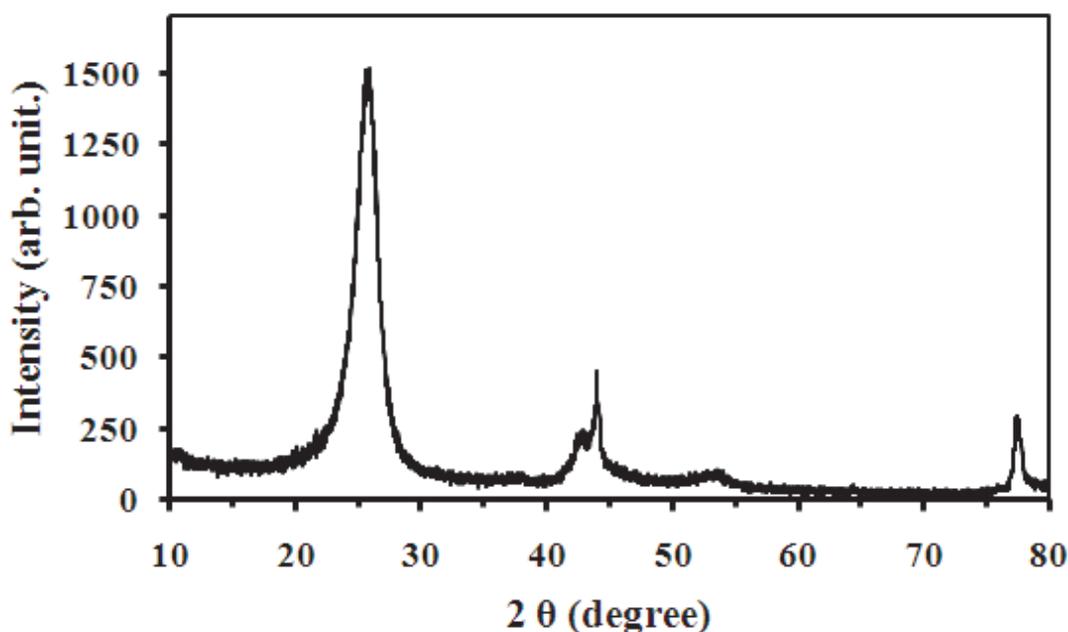


Fig. 3. XRD patterns of MWCNT oxidized with HNO_3 at $120\text{ }^\circ\text{C}$

Raman spectroscopy is frequently used to characterize CNTs. It reflects different characteristic spectra for sp^3 , sp^2 , and sp carbons, as well as for disordered sp^2 . Two bands is usually observed showing the characteristics of CNTs. The bands point the graphite band (G band), at about 1580 cm^{-1} , and the disorder and defects of the structure, named D band, at around 1330 cm^{-1} . The ratio between the intensity of D band and G bands ($I_{D/G}$), is related to the degree of disorder of the CNTs. When oxidation treatment of CNTs is performed, these characteristic peaks should still be identified to indicate that the treatment process does not damage the nanotube structure. An increase of the ratio values ($I_{D/G}$), of CNTs after oxidation treatment, ensures that the functional groups are covalently grafted with the CNTs. It indicates clearly that the oxidation treatments of CNTs breaks some of its bonds

and inserts new chemical bonds, interpreted as defects on the nanotube structure (Osorio et al., 2008).

The TGA analysis of CNTs presents good indication of the functionality. o-CNTs starts decomposing earlier than the pristine-CNTs. The thermal stability of the pristine CNTs decreases with increasing oxidative functionalisation. The decrease of the initial burning temperature of the o-CNTs is closely related to the introduction of the defects and functional groups upon oxidation treatments. This is attributed to the earlier decomposition of the grafted carboxylic groups on the nanotubes. For example, the decomposition of the pristine-MWCNTs occur (TGA under flowing nitrogen, temperature range of 90–860 °C, at rate of 15 °C/min) at the onset temperature of 639 °C while of o-MWCNTs, it occurs at 627 °C (Okpalugo et al., 2005).

The XPS survey scan of CNTs is used to reveal the chemical compositions of the uppermost surface of the nanotubes. The major peaks due to the C1s and O1s photoelectrons can be observed in the scan. For example, the change in the C1s and O1s can be monitored and the O/C atomic ratios can be calculated to indicate the degree of surface oxidation. General conclusion is that the higher the O/C ratio, the more the oxygen atoms are bound to the nanotubes in the oxidation treatment. In addition, XPS O1s peaks demonstrate additional information on the nature of the surface oxygen-containing groups including the contribution of chemisorbed H₂O.

2.2 Synthesis and characterization of carbon nanotube/metal oxides composites

Carbon nanotubes/metal oxide (CNT/MO) composites can be prepared by various methods as mentioned earlier in this section. Here, the focus is on the wet chemistry methods where the CNTs act as nucleation sites for the metal oxides. In the first section, the synthesis of CNT/MO will be discussed. In the second section, the characterization of the CNT/MO nanocomposites using different characterization tools will be described with highlight on the interpretation of some experimental data.

2.2.1 Synthesis of CNT/MO composites

Generally, the o-CNTs are dispersed in an appropriate solvent like acetone, ethanol, propanol or n-methyl-2-pyrrolidone; until well homogeneous suspension is formed. The dispersion can be achieved via sonication; some surfactants are used for dispersion. At the same, the precursor of the metal oxide is dissolved in a suitable solvent. Then, the latter is drop-wise added into the dispersed o-CNTs; and the mixture is sonicated for a while, then, magnetically stirred for some time. After that, the suspensions' mixture is transferred into round-bottomed flask and refluxed at high temperature; say 120- 200 °C, in oil bath or hot plate, with magnetic stirring, for specific time depends on the type of metal oxide. After that, the system is allowed to cool naturally to room temperature. Then, the mixture is filtered and washed with suitable solvent like distilled water and ethanol several times. After that, the resulted composite is dried at 100 °C. Final step in the strategy of synthesis is the calcinations process of the composite at various temperatures and for different times. The end product consists of CNTs coated, or embedded with nano-sized metal oxide; see the visualization illustration in Fig. 4.

The ratio of MO nanoparticles on CNTs is controlled by the initial concentrations and the type of the precursors of the metal ions. It is worth mentioning that the high ratio of MO would result in the agglomerating of the nanoparticles on the nanotubes. Additionally, the

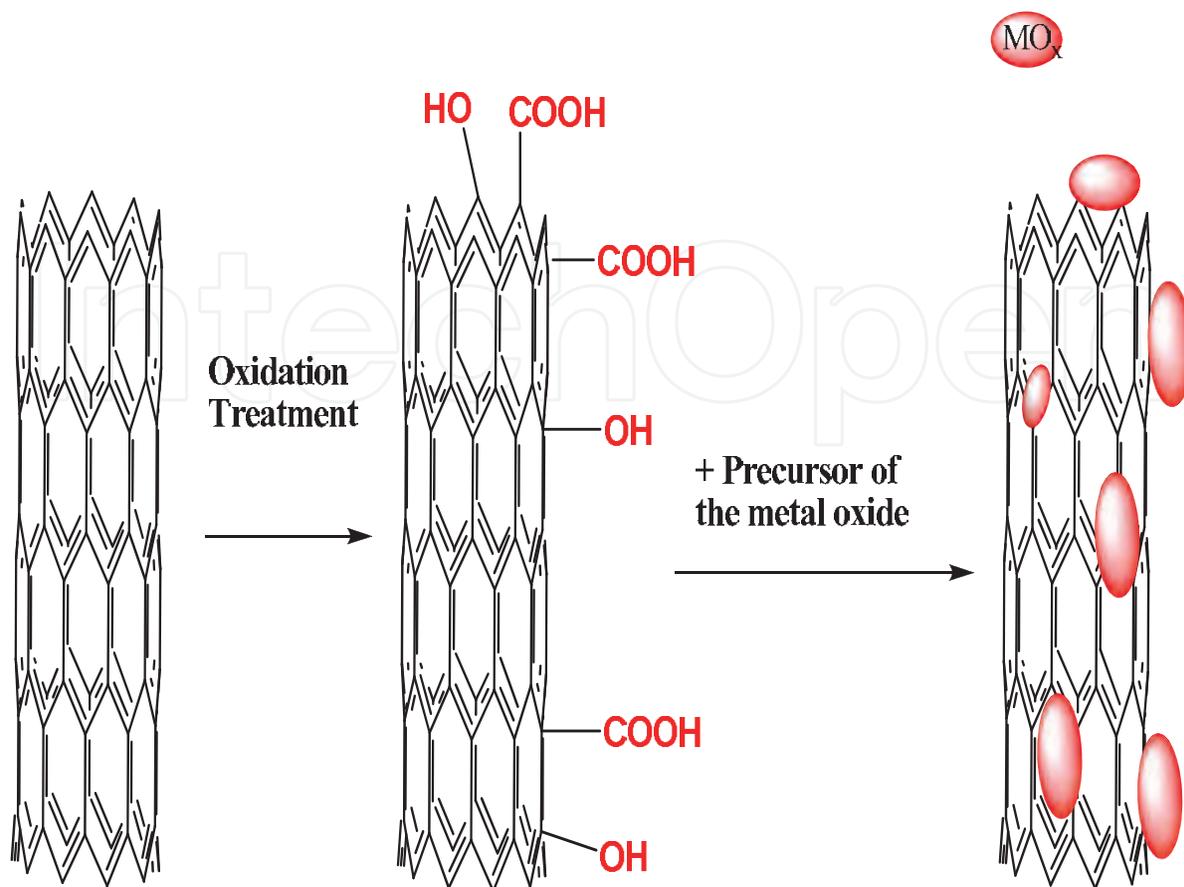


Fig. 4. Illustration representation of the synthesis of Carbon nanotubes/metal oxide (CNT/MO) composites

distribution of nanoparticles on the surface of the nanotubes is controlled by the synthesis treatment including the addition of the precursors into well dispersed o-CNTs, the extent of treatment oxidation of pristine CNTs. The nanoparticle size is controlled by the calcinations temperature and time. The rate of increasing the calcinations temperatures can also have an effect on the nanoparticle size. Controlling these parameters can yield a composite of uniformly dispersed metal oxide nanoparticles on the surface of the nanotubes.

As illustrated in Fig. 5, the nanotube surface presents polar groups like hydroxyl or carboxyl groups which are able to interact with the oxygen of the metal oxide, like aluminum oxide. The interaction could be through hydrogen bonding, or the oxygen atoms of hydroxyl or carboxyl groups interact with aluminum atoms through the pair of electrons on the oxygen atoms. The formation of chemical bond is also possible.

2.2.2 Characterization of CNT/MO composites

Characterization of the as-prepared carbon nanotube/metal oxides (CNT/MO) nanocomposite is performed by means of different characterization tools like high resolution transmission electron microscope (HRTEM), field emission scanning electron microscope (FESEM), energy dispersive X-ray spectroscopy (EDX), thermogravimetric analysis (TGA), Raman spectroscopy, UV-vis spectrometer and fourier transformed infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL) technique; in addition to electrochemical techniques. The techniques are complementary.

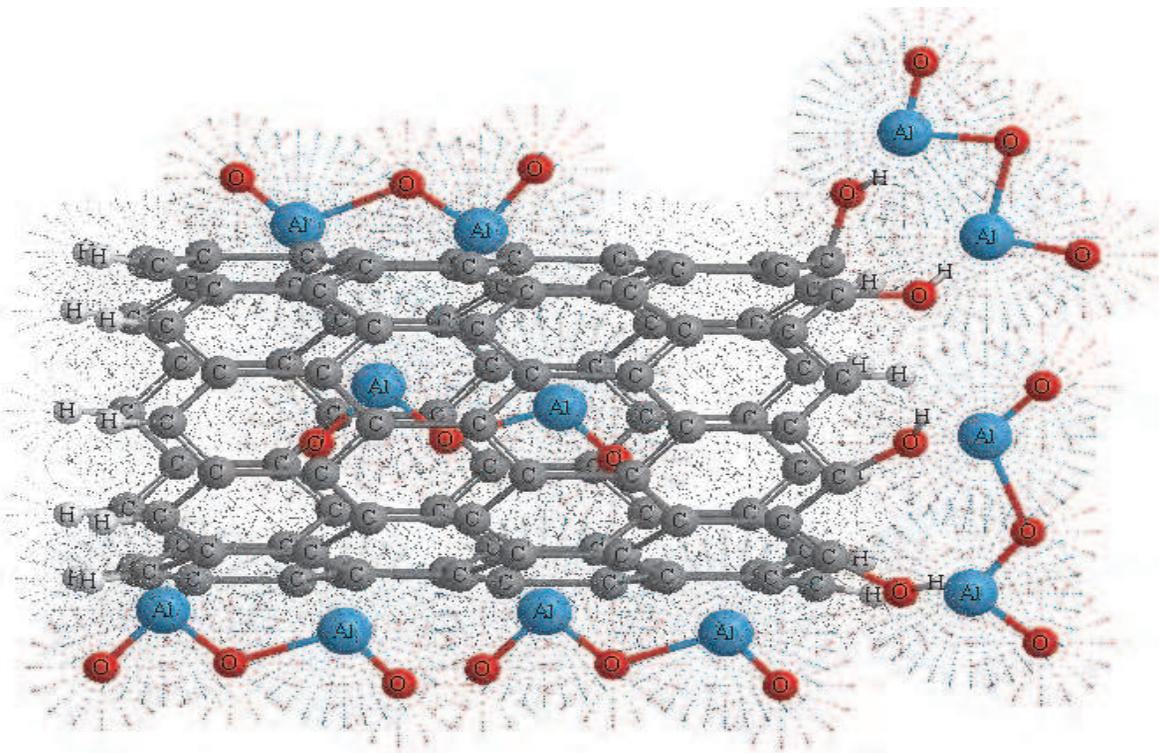


Fig. 5. Structural representative of possible interaction between Al_2O_3 and carbon nanotube in MWCNT/ Al_2O_3 nanocomposite.

They can be used to investigate the chemical and physical properties of the nanocomposites. In the following paragraphs, the importance of each technique for the characterization of the composites will be highlighted with detailed examples of some experimental results.

HRTEM image indicates the shape and distribution of nanoparticles on the surface of the nanotubes. The average size and diameters of the nanoparticles can also be determined from the TEM images. Particularly, TEM is employed to observe the loading state of the nanocomposites. Specifically, TEM images show the surface of the nanotubes coated, decorated or embedded with the nanoparticles. It might be also used to compare the surfaces o-CNTs with that of CNT/MO nanocomposite in term of the roughness and compact.

SEM micrograph is used to investigate the surface morphology and the general morphological features of the prepared composites nanomaterials. It also reveals the uniformity of dispersion of the nanoparticles on the nanotubes. The average particle size can also be calculated. SEM image can be taken with low or high magnification. As an example, Fig. 6 presents the low magnification SEM to reflect the morphology of the CNT/alumina nanocomposite in which CNTs seem to be decorated with aluminum oxide nanomaterial.

The EDX or EDS measurements are usually used to confirm the percentage, the atomic ratio, of components on the surface of the nanocomposites. It should be noticed that EDX spectrum is better to be measured for large surface area of the sample for better representation, in other words, lower errors. That means the SEM image from which EDX is measured could be in μm scale, as shown in the inset of Fig. 7. However, it is not expected to get the exact atomic ratio of the metal oxides since some oxygen contribution comes from the oxygen-containing functional groups, such as carbonyl or carboxyl groups, on the surface of CNTs.

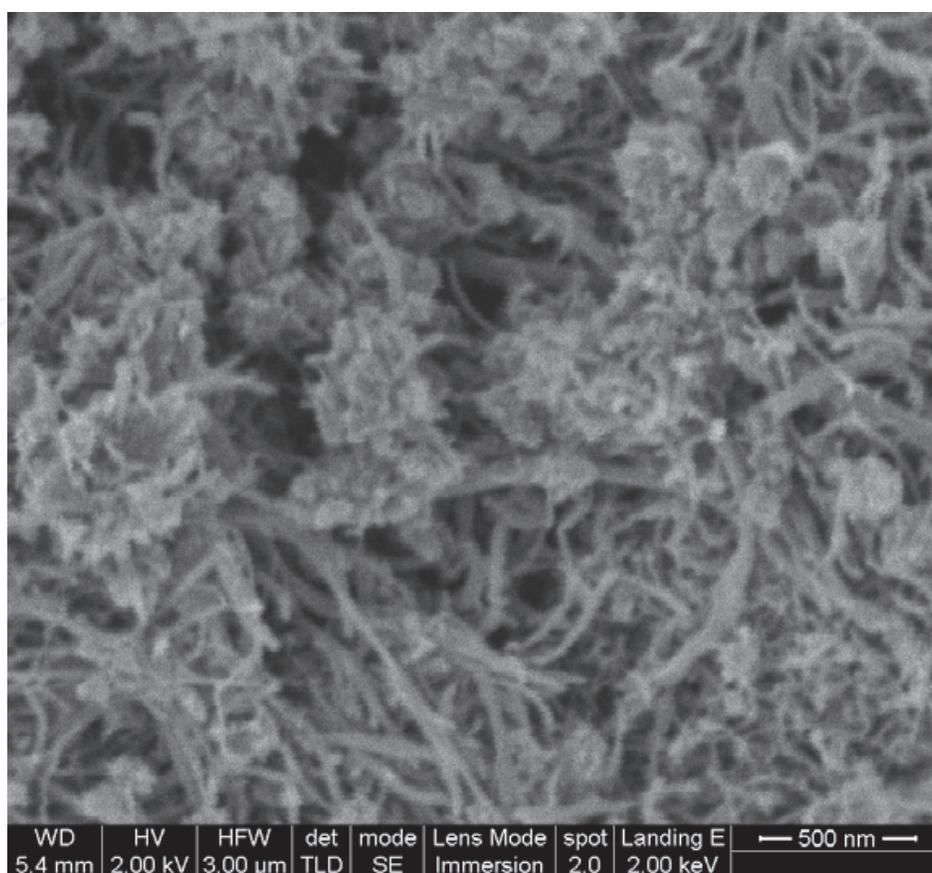


Fig. 6. Field emission scanning electron microscope (FESEM) of MWCNT/ Al_2O_3 nanocomposite

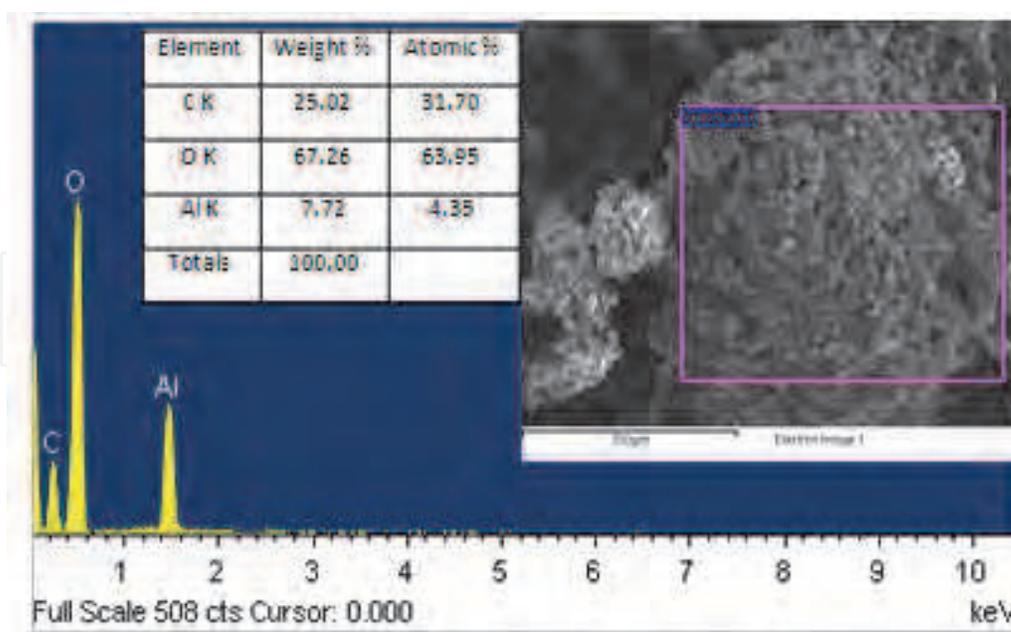


Fig. 7. Energy dispersive X-ray (EDX) spectrum of the area indicated in the Inset: low magnification scanning electron microscope (SEM) of MWCNT/ Al_2O_3 nanocomposite; Inset: Table presents the atomic ratio, percentage of the components in the nanocomposite.

Thermogravimetric analysis is used to confirm the presence of metal oxides particles in the nanocomposite. From TGA of CNT/MO nanocomposites, it is expected to have initial weight loss between 250 to 500 °C and can be attributed to condensation reactions of metal-hydroxyl residual groups on the surface of the prepared nanocomposites materials (Amais et al., 2007).

XPS analysis is also of important. In the C1s XPS spectra, the main peak is usually observed at 284.6 eV which is attributed to the C-C bonds. Additional peaks are observed at 285.8 eV, 286.8 eV and 289.3 eV; and are assigned to C-O and C=O bonds; and COO groups (Jitianu et al., 2004). The shift of these peaks to higher binding energy could be indicative of binding of metal oxide to the nanotubes.

The XRD patterns are used to characterize the crystalline structure of the CNT/MO nanocomposites. Comparing the XRD patterns of o-CNTs and CNT/MO nanocomposite, the characteristic peaks for o-CNTs at the positions of 25.9° and 43.9°, see Fig. 3, might disappear or become thinner in the XRD pattern of the nanocomposites. The reason is that these peaks in the nanocomposites are overlapped by the peaks of the metal oxide nanoparticles. For example, in the XRD pattern of MWCN/TiO₂ composites, only anatase and brookite phases attributed to TiO₂ have been observed. The possible explanation is that the main peak of nanotube at 25.9° is masked with the main peak of anatase TiO₂ at 25.4° since their positions are so close. Additional is that the crystalline extent of carbon nanotube is lower than the crystalline extent of TiO₂, leading to the shielding of the peaks of CNTs by those of TiO₂ (Yu et al., 2005). Example is the XRD pattern, Fig. 8, of MWCNT/WO₃ nanocomposite. In this pattern the diffraction peaks revealed the presence of hexagonal and orthorhombic tungsten oxide nanoparticles. Therefore, the presence of tungsten oxide nanoparticles peaks might lead to the mask the characteristic peak of the nanotubes at 2θ equal to 25.8 degree.

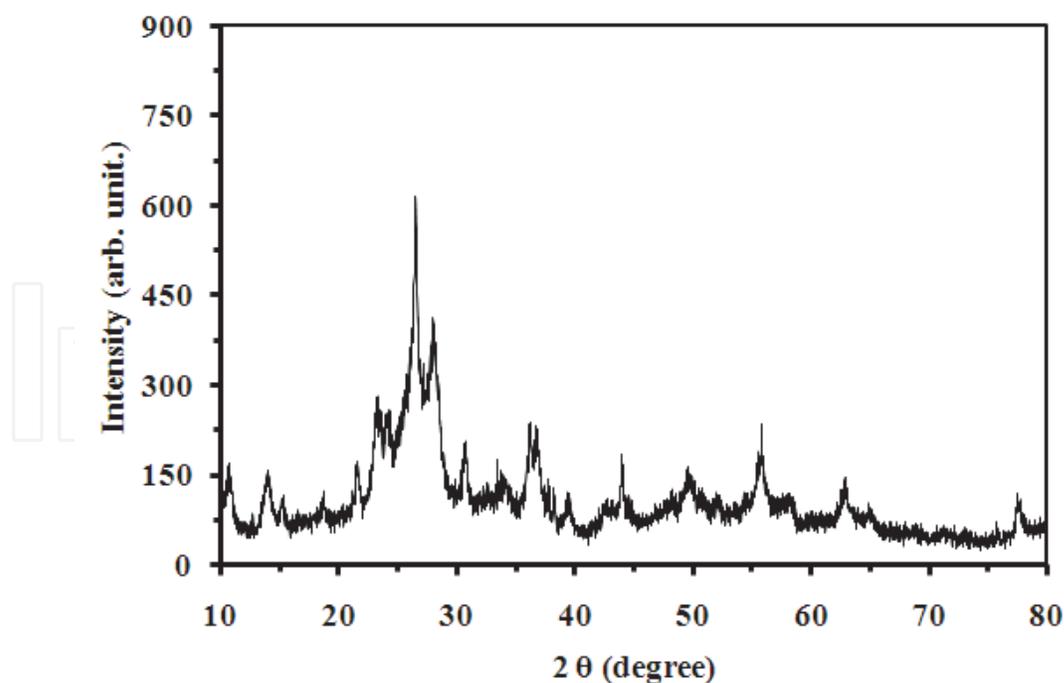


Fig. 8. XRD patterns of MWCNT/WO₃ nanocomposite.

Raman spectroscopy is a powerful characteristic technique that is employed to distinguish between the characteristic peaks of TiO₂ and those of CNTs since peaks from each

components; nanotube and metal oxide are in most cases separated in frequency, and thus the phases are distinguishable. It is worth mentioning that to run samples on Raman, the energy power should be as low as possible to prevent the effect on the nanotube absorption and get good results. The energy power is preferably to be selected between 10 and 100 mW.

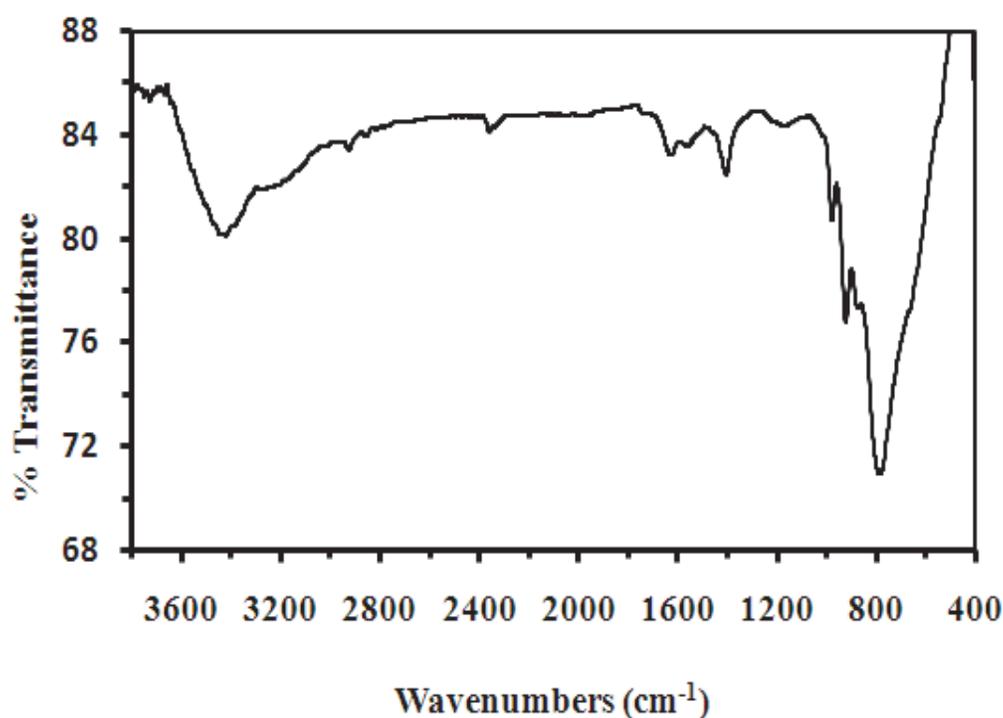


Fig. 9. FTIR spectra of MWCNT/WO₃ nanocomposite.

Comparing the IR spectra of o-CNTs and the nanocomposite is of interest. The comparison should focus on two characteristic peaks. The first peak is the characteristic peak of the pure metal oxide nanoparticles, which is usually appear between around 400 and 700 cm⁻¹ depends on the type of metal oxide. For example this peak appear at 700 cm⁻¹ in the IR spectrum of WO₃ nanoparticles. The shift of this peak in the spectra of nanocomposite could be attributed to strong bond between the metal and the nanotube through oxygen-containing group. The second peak is the band assigned to C=O stretching vibration. The shift of this peak toward lower wavenumber is an indication of the carboxylic ion binding between nanoparticles and the nanotube. Example is the IR spectrum of MWCNT/WO₃ nanocomposite, depicted in Fig. 9. This spectrum shows the shift of the peak of W-O covalent bond from 701cm⁻¹ to 770cm⁻¹. It also shows the shift of the band assigned to C=O stretching vibration from 1670 to 1606 cm⁻¹, reader can compare Fig. 9 with Fig. 2.

3. Applications of CNT/MO nanocomposites

CNT/MO nanocomposites are new generation with interesting properties that not only combine the properties CNTs and MO_x but also hold new properties caused by the interaction between them. In addition, combine these materials in a composite can overcome some disadvantages. For example, metal oxide nanoparticles have a tendency to agglomerate because of their dangling bonds. In the composite, dispersion of the nanoparticles on the surface of the nanotube prevents their agglomeration. It should be

noticed that the aggregation of nanotubes in aqueous media is solved by functionalization. As a result, the composites attractive wide applications compared with the isolated nanoparticles because CNTs act as carrier to stabilize the nanoparticles, maintaining their integrity. Examples of the fields of applications are water treatment, environment, catalysis and others. Examples of the nanocomposites that can be prepared are Ti_2O_3 , ZnO , WO_3 , Fe_2O_3 , SnO_2 , CeO_2 , Al_2O_3 , ZrO_2 , SiO_2 , V_2O_4 and Er_2O_3 on CNTs. In the next section, we will discuss the application of the composites as adsorbents followed by the discussion of their applications to enhance catalytic activity in the second section. A mechanism will be discussed to explain the enhancement of the photocatalytic properties of the nanocomposite.

3.1 Nanocomposites as sorbents

The sorption applications of CNT/MO nanocomposites to tackle environmental pollution problems have received considerable attention. The nanocomposites provide chemically inert surfaces with high specific surface areas for physical adsorption. They have relatively uniform structure, providing more adsorption sites.

For the application of the nanocomposite as sorbents in batch sorption experiments, different parameters need to be optimized, such as agitation speed, contact time and adsorbent dosage, pH of the aqueous media, initial concentration of the pollutant, effect of presence of other cations and anions in the media. Also, for the application of the nano-composite as adsorbents in fixed bed column experiments, different parameters need to be optimized, such as flow rate, the bed thickness and diameters, pH of the aqueous media, initial concentration of the pollutant, effect of the presence of other cations and anions in the media.

For example, MWCNT/alumina nanocomposite has been reported to be an effective sorbent for the removal of lead ions from aqueous solution with pH range of 3-7. The efficiency of the nanocomposite has been tested in batch mode and fixed bed, column mode. It has been reported that by increasing agitation speed, contact time and adsorbent dosage the amount of the removal is increased. The percentage of lead removal increases by decreasing the flow rate and increasing the bed thickness (Gupta et al., 2011). CNT-iron oxides magnetic composites has been successfully applied as adsorbent for removal of different targets from water such as Pb(II) , Cu(II) (Peng et al., 2005), Ni(II) , Sr(II) (Chen et al., 2009b) and Cr(III) (Gupta et al., 2011). The incorporation of iron oxide magnetite with CNTs has been used for europium adsorption. This composite is potentially a promising to facilitate the separation and recovery of CNTs from solution with magnetic separation technique. The beauty of this method is that CNTs do not become another source of contamination (Chen et al., 2009a). Also, the magnetic MMWCNT nanocomposite has successfully utilized as an adsorbent for removal of cationic dyes from aqueous solutions (Gong et al., 2009).

The adsorption ability of manganese oxide-coated carbon nanotubes has been utilized for the removal of lead(II) from aqueous solution. The effect of metal oxide nanoparticels loading level has been investigated. It has been reported that the adsorption capacity of Pb(II) increased with increasing MnO_2 load because of the availability of more binding sites. The optimum reported load is 30 wt% (Wang et al., 2007).

3.2 Nanocomposites as catalysts

CNTs have been widely used to support and enhance the catalytic activity of metal oxides. CNT/ WO_3 nanocomposite has been utilized as catalysts for C6 olefin skeletal isomerization in different activation conditions. Comparing with tungstated zirconia, the nanocomposite

shows higher skeletal isomerization selectivity at 200 °C with higher conversion level without deactivation. The optimum load of WO_3 on CNTs was reported to be 5% (Pietruszka et al., 2005). Such composite shows also higher photocatalytic activity comparing with WO_3 nanoparticles. The composite has been applied for the degradation of dye. It could be concluded that doping WO_3 into CNTs enhances the photocatalytic activity (Wang et al., 2008).

Another comparison of the photocatalytic activity has been conducted between TiO_2 and TiO_2/CNTs composites for acetone degradation. It has been noticed that the presence of a small amount of CNTs can enhance photocatalytic activity of TiO_2 (Yu et al., 2005). This is supported by another study in which photocatalytic activity of $\text{TiO}_2/\text{SWCNT}$ composite has been investigated degradation of organic dyes and 2,6-dinitro-p-cresol. High photocatalytic activity of the $\text{TiO}_2/\text{SWCNT}$ composite has been observed comparing with that of TiO_2 nanoparticles. This could be attributed to the synthetic effect of larger surface area, smaller crystalline size, and the formation of the chemical bond between TiO_2 and the nanotube which improve interface contact (Zhou et al., 2010; Wang et al., 2009). It has been reported that the bond of carbon-oxygen-titanium can extend the light absorption to longer wavelengths and therefore potentially leading to the improvement of the photocatalytic activity (Woan et al., 2009).

MWCNTs has been used to enhance the catalytic activity of zinc oxide for the acetaldehyde removal (Saleh et al., 2011) and cyanide degradation in aqueous media (Saleh et al., 2010) under UV irradiation. Zinc oxide nanoparticles are embedded on multiwall carbon nanotubes via thermal hydrolysis method. Great enhancement in photocatalytic activity has been recorded by the MWCNT/ZnO nanocomposite.

3.2.1 Mechanism

The enhancement in photocatalytic performance of the CNT/MO nanocomposites can be rationally explained in a mechanism based on two criteria. The first is adsorption ability of the nanotubes since the adsorption is a key process in the catalytic destruction of organic pollutants. While the second is the electron transfer from nanoparticles into the nanotubes, in other words the electron injection (Xu et al., 2010 & Martinez et al., 2011). In general, irradiation of metal oxide semiconductor with a photon of sufficient energy, greater or equal to band gap energy could promote an electron from valence band (VB) to conduction band (CB). The promoted electron leaves a vacancy in the valence band creating positive hole which can react with hydroxyl forming a powerful oxidant or a hydroxyl radical. The promoted electrons reduce dissolved oxygen to produce superoxide anion radical. The hydroxyl radical ($\cdot\text{OH}$) and superoxide anion radical ($\text{O}_2\cdot^-$) oxidize the target.

CNTs can adsorb oxygen molecule on its surface thus the promoted electrons in CB might directly react with the adsorbed oxygen molecule and form superoxide anion radical. This will increase the number of radicals ready for reacting with the target. Also CNTs can adsorb the target which is considered to be the first step in the degradation since the pre-adsorption of the target on the surface of catalyst particles is a prerequisite for efficient photo-degradation (Zhao et al., 1998).

On the other hand, the strong interaction and formation of ester bonds between the metal and the nanotube leading in a close contact which offers an effective route of electron transfer from the CB in to the nanotube. This can reduce the recombination of photo-generated electron-hole pairs. This conclusion is supported by the higher activity of the

CNT/MO composites and by being CNTs relatively good electron acceptors while semiconductors as good electron donor under illumination (Subramanian et al., 2004; Geng et al., 2008).

4. Conclusion

In this chapter we discuss the preparation of the new class of CNT/MO nanomaterials that offer great potential applications in different fields. The chapter has analyzed the methodology of functionalization and activation of the nanotubes as a first step for preparation of CNT/MO nanocomposites. The details of functional groups characterization have also been discussed. The synthesis of CNT/MO nanocomposites is detailed with the characterization interpretation. Some case-studies have been carried out referring to a realistic use of CNT/MO nanocomposites as adsorbents that have excellent adsorption ability for many kinds of pollutants like inorganic and organic compounds.

The advantage is that CNTs provide large number of nucleation centers available on its surface for receiving the nanoparticles and preventing their agglomeration. This makes such material not only good in adsorption but also in enhancement of the catalytic activity. The reason given for the high catalytic performance is the optimum dispersion of MO on the CNTs. The mechanism of enhancing the photo-catalytic activity is discussed based on adsorption ability of the nanotube and the transfer of promoted electrons from metal oxide to CNT. The most important processing issue is the interfacial strength between the CNTs and the MO nanoparticles.

Over the last years, much progress has been made in adsorption applications of CNT/MO nanocomposites. In spite of high costs, using CNTs as adsorbents may be advantageous in future owing to their high adsorption capacities. However, there are still much to do to enhance CNT/MO nanocomposites' adsorption properties in future. Efforts in synthesis methods to develop a cost effective way of CNTs production are required. Investigations on CNT/MO nanocomposites on applications in adsorption and catalysis are recommended.

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Since their discovery in 1991, carbon nanotubes have been considered as one of the most promising materials for a wide range of applications, in virtue of their outstanding properties. During the last two decades, both single-walled and multi-walled CNTs probably represented the hottest research topic concerning materials science, equally from a fundamental and from an applicative point of view. There is a prevailing opinion among the research community that CNTs are now ready for application in everyday world. This book provides an (obviously not exhaustive) overview on some of the amazing possible applications of CNT-based materials in the near future.

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