Chapter 3

Carbon Nanotubes based Nanocomposites as Photocatalysts in Water Treatment

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Abstract

The shortage of worldwide clean water and the increasing water demand are now ubiquitous problems around the world. Thus, efficient water treatment is an important research topic, of which photocatalysis is known as simplest and efficient technique utilized in the photocatalytic degradation of all major water pollutants, including heavy metal ion, organic and inorganic pollutants. In this context, the use of one- dimensional carbon nanotubes-based nanocomposites in water treatment have been widely demonstrated to be capable of removing persistent organic compounds due to their unique physical and electronic properties, large surface area, tunable morphology, biocompatible and chemical-environmental-thermal stability. This chapter begins with the discussion of the importance and properties of carbon nanotubes, and then briefs about the types and methods of preparation of carbon nanotubes-based nanocomposites in detail. The next section emphasizes the fundamentals of photocatalysis phenomenon and its proposed mechanism for the photocatalytic degradation of pollutants. The last section highlights the recent development in the carbon-based nanocomposites as photocatalyst in water treatment systems, supported by comprehensive literature account. Finally, the remaining challenges and perspectives for using carbon nanotubes-based nanocomposites are discussed.

Keywords

Carbon Nanotubes, Nanocomposites, Photocatalyst, Water Treatment

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1. Introduction

Water covers more than 70% of the Earth's surface and is the major constituent for all living organisms' well-being and sustenance. Today, an inadequate access to clean water and increasing levels of water pollution are among the most concerning global issues around the world [1]. The water pollution in our environment was aggravated by the rapid population growth and intense urbanization which degrading the water quality of lakes, rivers and coastal shorelines [2-4]. The unsafe water is jeopardizing our health and causes about 2 million deaths a year, either through dehydration or acute toxicity [5, 6]. As reported by United Nations, it is estimated that by 2025, two-thirds of the world population would be under water stress conditions and more than 2.8 billion people in 48 countries will be facing absolute water scarcity, and by 2050, 4 billion people in 54 countries will be suffering from water-insufficient conditions [7] as shown in Figure 1.

Figure 1: Freshwater stress map displayed percentage ranges of water withdrawal with respect to the total available water. Reprinted (adapted) from <http://www.grida.no/resources/5625> with permission of the GRID-Arendal.

Meanwhile, the water shortage is exacerbated by water pollution. There are various water pollutants, namely heavy metals, organic and inorganic contaminants to emerging endocrine disrupting pollutants that can provoke carcinogenic and even mutagenic effects in aquatic organisms and humans [8-11]. Based on the United Nation- Water statistic report, 70% of the industrial wastes are dumped untreated into water in the developing countries while 2 million tons of human waste are disposed of in water courses every day resulting in a limited clean water supply [12]. Therefore, intensive efforts are needed in engineered water treatments systems to overcome the clean water pollution problems.

There are various physico-chemical methods including membrane filtration, coagulation, flocculation, ozonation, adsorption and photocatalytic degradation for removing water pollutants from wastewater [13-16]. Among these processes, the photocatalytic degradation method is recognized as a high potential alternative technology for alleviating the refractory organic pollutants and hazardous waste in water. This is due to advantages such as simple, environmental-friendly, inexpensive technology and ease of application at ambient temperature and pressure [17-19]. Generally, the principle of photocatalysis is to convert the photon energy by using light absorption into the chemical energy in the forms of products. It involves the acceleration of photoreaction with the presence of semiconducting oxide photocatalysts (e.g: TiO_2 , ZnO , WO_3 , Fe_2O_3 , CdS , ZnS , SrTiO_3 , etc.)

[11, 20, 21]. However, the photocatalytic efficiency of the semiconductor photocatalyst has been limited by the two common factors which are the fastest recombination of photogenerated electron-hole pairs and large energy band gap. Therefore, in order to significantly overcome the limited visible-light absorption and rapid charge recombination of semiconductor photocatalysts, an effective method is by combining the semiconductor with the carbonaceous materials into a nanocomposite. Carbonaceous-metal oxide nanocomposites have been proposed over the past few years for application in the water treatment. Among different carbonaceous materials, carbon nanotubes have shown significant key role in the nanocomposite for the photocatalysis process, because of their several merits: high surface area, high mechanical strength, chemical inertness and good adsorbent properties, which are beneficial to improve water treatment [1, 2, 14].

This chapter provides insight into the properties of carbon nanotubes as well as the fundamental principle of the photocatalysis mechanism, followed by the summary of the various synthesis techniques for carbon-nanotube-based nanocomposites. The characteristics and advantages of existing synthesis methods are discussed. Detailed discussions are provided on the summary of recent advances of water treatment using carbon nanotubes-based nanocomposites as photocatalyst. The remaining challenges are also mentioned.

2. Properties of carbon nanotubes

Carbon nanotubes (CNT) is a carbon family member with one dimensional (1D) structure that rolled up into tubular with diameter of a few nanometers and up to few millimeters in length. It has highly organized helical arrangement of hexagonal arrays with open or closed ends capped with a hemisphere of the fullerene structure. Since the first discovery by Iijima in 1991, CNT have gained much attention due to their high surface to volume ratio, high aspect ratio, tunable physical, chemical, electrical, and structural properties [22, 23]. CNTs possess good structural integrity and chemical inertness support with relatively high oxidation stability which could endow CNTs more excellent performances as support for photocatalytic active materials [24, 25]. Eventually, the remarkable properties of CNT make them potentially valuable to be applied in a wide range of applications (sensors, electronics, water treatment etc.).

Figure 2: Structure representations of (a) MWCNTs and (b) SWCNTs. Reprinted (adapted) with permission from [26]. Copyright (2009) American Chemical Society.

The oxygen functional groups such as hydroxyl and carboxyl are introduced onto the CNTs surface during the synthesis and purification process. These functional groups can influence the maximum adsorption capacity of CNTs and make them more hydrophilic and suitable for the adsorption. Up to now, CNTs can be easily scaled-up to batch-scale production by chemical vapor deposition (CVD) method due to simplicity and economy.

Moreover, CNTs may act as effective electron sinks with a high electrical conductivity and high electron storage capacity which can store up to 1 electron per 32 carbon atoms during photoexcitation [27-30].

Basically, there are two main types of CNTs: Single walled carbon nanotubes (SWCNTs) and Multi walled carbon nanotubes (MWCNTs) that differ in the arrangement of their graphene cylinders (Figure 2). SWCNTs consist of a single layer of graphene cylinders; while MWCNTs consist of multiple layers of graphite rolled into form a tube shape. There are three different crystallographic configurations of SWCNTs such as zigzag, armchair, and chiral structure, depending on how the graphene sheet is rolled up to a cylinder way as shown in Figure 3. A pair of indices (n, m) is used to describe the chiral vector in the honeycomb crystal lattice for the SWCNTs structure along the two directions. The SWCNTs are named as zigzag nanotubes when $m=0$ which means the C-C bonds are parallel to the tube axis; while the SWCNTs are named as armchair nanotubes when $n=m$ (C-C bonds of each hexagonal are perpendicular to the tube axis). For the chiral nanotubes, C-C bonds are adjoining at an angle to the tube axis.

Figure 3: Three different types of single walled carbon nanotubes. Reprinted (adapted) with permission from [32]. Copyright (2011) IntechOpen.

MWCNTs structures can be categorized into two structural models based on their arrangements of graphite layers: Russian doll model and Parchment model. For Russian doll model, the layers of graphene sheets are arranged within a concentric structure and the inner nanotube has a smaller diameter than the outer nanotube. On the other hand, for Parchment model, a graphene sheet is rolled up around itself manifold times exactly like rolled up scroll of paper. Typically, SWCNTs can have diameters of 0.8 to 2 nm while MWCNTs having diameters of 5 to 20 nm. As reported, the total specific surface area of SWCNTs are in the range of 400-900 m²/g while for MWCNTs are between 200-400 m²/g, which provides CNTs with high surface active site to volume ratio as compared to conventional granular carbon [29, 31]. Nonetheless, MWCNTs exhibit advantages over SWCNTs, such as low cost per unit since the synthesis process of SWCNTs is extremely complicated and the yields are small as compared to MWCNTs. The properties of SWCNTs and MWCNTs are summarized in Table 1.

Table 1: Characteristics and textural properties of SWCNTs and MWCNTs [33].

Properties	SWCNTs	MWCNTs
Layer of graphite	Single layer	Multiple layers
Diameters	0.8-2 nm	5-20 nm
Specific gravity, g/cm ³	0.8	1.8
Elastic Modulus, TPa	~1	~0.3-1
Strength, GPa	50-500	10-60
Thermal conductivity, W m ⁻¹ K ⁻¹	3000	3000
Total specific surface area, m ² /g	400-900	200-400
Cost	High	Low

Environmental applications based on CNTs offer more realistic possibilities and have many advantages over other carbon materials in terms of costs, structural and electrical properties. Indeed, the adsorption capability and high adsorption efficiency of CNTs makes them excellent prospects for widespread use in a variety of industries all around the world. Based on the intrinsic properties (high thermal conductivity, good chemical and environmental stability) of CNTs shown in Figure 4, CNTs can act as promising blocks for carbon-based composite, giving great potential in water treatment applications. Nano-scaled composite materials of MWCNTs are in great interest due to its high chemical inert nature, non-swelling effect and rigidity [28, 29, 34].

Figure 4: Properties of CNTs.

3. Synthesis Methods of CNTs-based Nanocomposites

Over the past few years, various synthesis methods to form CNTs-based nanocomposites have been explored. The incorporation of the CNTs can control the physiochemical properties of metal oxide nanoparticle photocatalyst to meet the specific requirement for a given application purpose. Additionally, it may also exhibit some new properties caused by the interaction between the two types of components. To date, there are several synthesis methods that can be utilized to produce CNTs-based nanocomposites photocatalyst. These techniques include liquid phase deposition method, simple mixing, ultrasonic irradiation, chemical vapor deposition, electrodeposition, hydrothermal, solvothermal and sol-gel method. However, in these methods, functionalization of CNTs is a crucial step that should be carried out before the synthesis and preparation of CNT-based nanocomposites material. This step is essential to remove the impurities, like metal catalyst and amorphous carbon as the adsorption ability of CNTs can be influenced by coating with CNTs. Usually, the functionalization of CNTs are executed by oxidation treatment with the oxidizing agents, namely nitric acid, sulfuric acid, a mixture of sulfuric acid and nitric acid, potassium permanganate, hydrogen peroxide and so forth. Different oxidizing agents used would resulting in creating different functional groups on the CNT surface such as carboxylic (-COOH), alcoholic (-OH), aldehydic (-COH), ketonic (-C=O), and esteric (-C=O-O) oxygenated functional groups as shown in Figure 5 [35].

Figure 5: Three different types of single walled carbon nanotubes. Reprinted (adapted) with permission from [35] Copyright (2011) IntechOpen.

The chemical affinity of CNTs to metal oxide can be enhanced after the chemical functionalization of the CNTs sidewalls and tips. An example is the fabrication of CNTs/metal oxide nanocomposites with good interface adhesion after oxidizing treatment of

CNTs as illustrated in Figure 6. Metal oxides particles are well-attached on the surface of oxidized CNTs.

To date, researchers are looking for the facile and greener methods especially with shorten reaction time, minimal steps involved, less energy and less toxic by-products for the synthesis of nanocomposites materials. Therefore, different synthesis techniques applied will result in different structure and morphology of the CNTs-based nanocomposites. In the following section, the most commonly techniques such as simple mixing, chemical vapor deposition, electrodeposition, hydrothermal and sol-gel methods to yield the desired CNTs-based nanocomposites are briefly described.

Figure 6: Schematic representation of the preparation of treated CNTs/metal oxide nanocomposites. Reprinted (adapted) with permission from [35] Copyright (2011) IntechOpen.

3.1 Simple mixing

Simple mixing has been reported as one of the most fundamental routes for the synthesis of CNTs based Metal oxide (MO) nanocomposites. Under simple mixing method, a certain amount of MO powder and CNTs were dispersed and mixed in water under slow stirring rate at room temperature. This method usually performed in solution and water is used to be solvent. According to Ashkarran et al., they have prepared CNT-TiO₂ using three

different simple mixing methods: (i) simple mixing of CNTs with TiO₂ nanoparticles, (ii) simple mixing of CNTs with TiO₂ nanoparticles followed by heat treatment and (iii) simple mixing of CNTs with TiO₂ nanoparticles followed by UV illumination. From the TEM image, they have found that TiO₂ nanoparticles are well decorated on the CNTs surface in all three simple mixing methods [36].

Thus, this implies that it is possible to decorate CNTs with TiO₂ nanoparticles by simple mixing. The attachment of MO onto the surface of CNTs is through van der Waals interactions. Xu et al. synthesized CNTs/MO nanocomposites using simple mechanical mixing method for gas phase degradation of benzene. In respect to this method, it is simple and less time-consuming; however, it has been criticized for the low level of interaction where there is no intimate contact or chemical bonding between CNTs and MO. The type of bonding exists between CNTs and MO in this method is physisorption and MO may detach from CNTs surface through mechanical process such as sonication as reported by Yu et al. Significantly, the interaction between CNTs and MO is one of the key factors for controlling electron transfer and photocatalytic activity in CNTs/metal oxide nanocomposite structure [37-39].

3.2 Chemical vapor deposition (CVD)

Chemical vapor deposition (CVD) techniques are among the most common methods to synthesis CNTs based MO nanocomposites that utilize the growth of a solid material from gaseous phase through chemical reaction at the surface of a substrate at controlled flow rates. The chemical reactions that occurred on the heated surface of the substrate resulting in the deposition of coated thin on the surface. Due to the high purity of reagent used in this method, it can provide MO with a good control of the size, shape, purity, composition and easy scalability. In contrast to high pressure or high temperature synthesis, medium temperature at around 600-800 °C and a slightly reduced atmospheric pressure is required by this technique.

According to Tavakkoli et al., maghemite (γ -Fe₂O₃) nanoparticles are decorated on carbon nanotubes (CNTs) in a one-step synthesis using a low cost floating catalyst vapor deposition method for hydrogen evolution reaction. This study shows the growth of carbon encapsulated iron nanoparticles are highly dependent on the amount of iron source, ferrocene and an average size of 5.4 nm for the carbon encapsulated metallic iron nanoparticles are obtained from the HRTEM image [40]. Uniform coating of MO on CNTs can be achieved by this technique but when it scaled down to few nanometers, uniformity and defect-free coatings are difficult to be achieved due to the fast deposition. Moreover, this technique is not simple and specialized equipment is needed [41, 42].

3.3 Electrodeposition

Electrodeposition is one of the most powerful techniques for the deposition of MO nanoparticles via reduction of metal complexes by electrons. The nanocomposites can be produced through the migration of charged particles dispersed in a liquid medium under an electric field, followed by the particles are coagulated at an electrode. In the early stages of electrodeposition, the limiting step corresponds to electron transfer from work electrode for metallic ions in solution. The size and the coverage of MO nanoparticles on the sidewalls of CNTs can be controlled by electrodeposition parameters, including concentration of the metal salt, nucleation potential and deposition time. The main advantage of this technique is that the electrodeposited nanoparticles show higher purity as well as a good adhesion to the surface of CNTs. In detail, a strong adhesion could be provided via a simple van der Waals interaction between the CNTs and the MO nanoparticles.

The work done by Zhao et al., showed that, the deposition of TiO_2 is carried out by using TiCl_3 as a precursor and electrolyte through galvanostatic oxidation with 1 mA/cm^2 at pH 2.5 with $\text{HCl}/\text{Na}_2\text{CO}_3$. As a result, it has been reported that this technique occurs to the same extent on both the sidewalls of the tubes and the tips [43]. Another work done by Nguyen and Bui, high density gold nanoparticles are electrodeposited into a three dimensional framework attached CNTs in 0.2 M hydrogen tetrachlororoaurate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) solution at an applied potential of -1.2 V for 200 s. The SEM image indicated that the gold nanoparticles are densely distributed on the whole surface of the CNTs [44]. However, electrodeposition technique is difficult to produce bulk quantities of samples and this becoming the major drawback of this method.

3.4 Hydrothermal

Hydrothermal techniques have been employed in the synthesis of CNTs based MO nanocomposites in recent years. This method is highly dependent on the chemical reactions and solubility changes of precursors in a Teflon-sealed autoclave under controlled temperature and/or pressure for growing the nanocrystals [45].

Kalubarme et al., synthesized CNT/cerium oxide (CeO_2) composite with one-pot hydrothermal method in the presence of potassium hydroxide (KOH) and capping agent polyvinylpyrrolidone. The precursor solutions (functionalized CNTs, Cerium nitrate, KOH and polyvinylpyrrolidone) were mixed and put in a Teflon stainless steel autoclave at 170°C for 24 h reaction. They indicated that two steps of reaction are involved for the growth of CeO_2 ; (1) Ce^{3+} is oxidized into Ce^{4+} when reacting with hydroxyl ion followed by (2) spherical particles of CeO_2 will grow as hexagonal nanocrystals by the effect of capping agent under the hydrothermal condition. The capping agent will give control upon the

crystal size of the nanoparticles by hindering the crystal growth. The HRTEM image revealed that the CeO₂ nanoparticles exhibit hexagonal structure on the CNT support [46].

Another work done by Dai et al., stated that in a typical hydrothermal synthesis of MWCNTs/TiO₂ nanocomposites, the pristine or acid-treated CNTs were added to the aqueous solution of the titanium precursor and treated in an autoclave at temperature between 100-200 °C to produce crystalline films of TiO₂. As a result, a dense coating of spherical or slightly elongated nanoparticles are obtained. It is worth mentioning that the titanium precursors used for hydrothermal processes are mainly titanium tetrachloride (TiCl₄) and titanium oxysulfate (TiOSO₄). Typically, the final materials obtained are mostly amorphous TiO₂ with seeds of anatase regardless the chosen conditions and chemistry. Thus, a further heat treatment that occurs at 300-500 °C in air is required to fully crystallize the TiO₂ coating on CNTs and avoid the burnout of the CNTs [47]. In contrast with other methods, the advantages of the composites prepared by hydrothermal methods are found to give better results, including less agglomeration among particles, narrow particle size distribution, and controllable phase homogeneity and particle morphology. However, this method requires longer preparation times (several hours or a day) and acquires hydrothermal temperature and pressure [48, 49].

3.5 Sol-gel

Sol-gel is a versatile technique that involves the transition of a liquid colloidal sol, followed by hydrolysis and polymerization of the precursors which are usually metal alkoxides into a solid gel phase. The sol particles may interact by Van der Waals forces or hydrogen bonds while the interactions in gel system are of covalent nature and the gel process is irreversible.

The rate of hydrolysis and poly-condensation will significantly affect the structures and properties of MO. Generally, sol-gel method is the most common technique to synthesize MO on the CNTs surface because this method is cheap, easy to control the chemical composition, does not require complicated equipment and occur at ambient temperature that can produce materials with high purity and homogeneity. However, the major drawback of this synthesis is that the final product normally consists of an amorphous phase rather than the defined crystals and hence, crystallization and post annealing steps are required. Moreover, this method usually leads to heterogeneous, non-uniform coating and random aggregation of MO onto the CNTs surface. Significantly, the selection of precursor is crucial for sol-gel method due to the reason that homogeneous nucleation or heterogeneous on CNTs are influenced by the reactivity of the precursor with the solvent. The growth rate of nanoparticles is also affected where the fast condensation rates resulting in a large particle-size distribution. Kose et al., synthesized zinc oxide (ZnO)/ MWCNTs nanocomposites for lithium ion battery anodes by sol-gel technique using zinc acetate

dehydrate and functionalized MWCNTs as the starting materials. The authors studied the effect of two chelating agents, triethanolamine and glycerin used in the sol-gel synthesis on the structure of ZnO/ MWCNTs nanocomposites. Field emission gun-scanning electron microscopy (FEG-SEM) shows that a very fine layer of ZnO was homogeneously coated on the individual MWCNTs the ZnO/ MWCNTs nanocomposites prepared with chelating agents [50].

Another example by Ellis et al., indium oxide (In_2O_3) is grown on the surface of oxidized SWCNTs using a sol-gel synthesis for ethanol sensing at room temperature. The authors reported that the degree of calcination will provide a close contact between the In_2O_3 and the nanotube surface where the In_2O_3 can be crystallized and condensed on SWCNTs after calcination. HRTEM image indicated that the crystalline In_2O_3 are attached above a bundle of SWCNTs [51]. The most common titanium precursor used for preparing TiO_2 / CNTs is titanium isopropoxide since it readily dissolves in alcohol and is not overly sensitive as revealed from the work done by Rodriguez et al. Acids or bases are added for altering the reaction rate. TiO_2 are formed by hydrolysis and poly-condensation process of titanium alkoxides.

Soroodan and Fatemi synthesized TiO_2 / CNTs composites using sol-gel method for the degradation of acetaldehyde. Benzyl alcohol as the linking agent was added to the TiO_2 / CNTs composites resulting in homogeneously coating of TiO_2 sols over the CNTs [52-54]. The comparison between the unique features of simple mixing, chemical vapor deposition, electrodeposition, hydrothermal and sol-gel methods is summarized in Table 2. Synthesis routes covers the range of techniques are tabulated in Table 3.

Table 2: Comparison of the most widely used synthesis methods for preparing CNTs/MO composite.

Synthesis method	Advantage	Disadvantage
Simple mixing	<ul style="list-style-type: none"> •Simple •Less time-consuming 	<ul style="list-style-type: none"> •No intimate contact or chemical bonding between CNTs and MO nanoparticles
CVD	<ul style="list-style-type: none"> •Short processing time 	<ul style="list-style-type: none"> • Requires higher deposition temperature • Complicated steps
Electrodeposition	<ul style="list-style-type: none"> •Provide MO with a good control of size, the shape and purity •Uniform coating of MO on CNTs •Electrodeposited MO nanoparticles show higher purity as well as good adhesion to the surface of CNTs 	<ul style="list-style-type: none"> •Needs specialized equipment •Difficult to produce bulk quantities of CNTs/MO sample
Hydrothermal	<ul style="list-style-type: none"> •Reduce agglomeration among MO nanoparticles •Control phase homogeneity and particle morphology 	<ul style="list-style-type: none"> •Longer preparation time •Acquires hydrothermal temperature and pressure
Sol-gel	<ul style="list-style-type: none"> •Simple •Cheap •Occur at ambient temperature •Fine and well-dispersion of MO nanoparticles on CNTs surface 	<ul style="list-style-type: none"> •Difficult controlling of hydrolysis rate

Table 3: Representative summary of CNT/MO composite synthesis routes

Synthesis routes	CNTs	MO	Synthesis conditions	Remarks	Applications	Ref.
Simple mixing	CNTs	TiO ₂	<ul style="list-style-type: none"> •CNTs are purified with HCl •CNT/TiO₂ composite were prepared with the simple mixing, UV illumination and heat treatment 	<ul style="list-style-type: none"> •No observable formation of chemical bonds and the CNTs are wrapped around TiO₂ anatase grains 	Degradation of Rhodamine B	[36]
Simple mixing	MWCNTs	Commercial P25	<ul style="list-style-type: none"> •Purification of MWCNTs using HNO₃ •Dispersed in anhydrous ethanol solution 	<ul style="list-style-type: none"> •Less individual interfacial between MWCNTs and TiO₂ •Simple mixing cannot combine P25 and MWCNTs effectively 	Degradation of benzene	[38]
Simple mixing	MWCNTs	Titanium sulfate	<ul style="list-style-type: none"> •MWCNTs was treated using HNO₃/H₂SO₄ mixture •Acid-treated MWCNTs were dispersed in water and introduced into titanium sulfate solution 	<ul style="list-style-type: none"> •Unable to create effective interfacial contact between TiO₂ and CNTs 	Degradation of acetone	[39]

CVD	CNTs	Maghemite (γ - Fe_2O_3)	<ul style="list-style-type: none"> •Synthesis temperature of 1100 °C, atmospheric pressure and in laminar flow conditions •Toluene and ethylene as the carbon sources for the CNT •Ferrocene was decomposed to Fe nanoparticles at high temperature 	<ul style="list-style-type: none"> •A mixture of carbon encapsulated iron nanoparticles are decorated on the CNTs. 	Electrocatalysts for the oxygen evolution reaction	[40]
CVD	CNTs	Titanium tetrachloride	<ul style="list-style-type: none"> •CVD growth of CNTs was carried out using the supported Ni as the catalyst •CVD deposition of a TiO_2 layer on the CNTs 	<ul style="list-style-type: none"> •The conformal coverage of TiO_2 nanoparticles on the CNTs walls 	Photocatalytic antifungal activity	[41]
CVD	CNTs	Commercial anatase TiO_2	<ul style="list-style-type: none"> •CVD growth of CNTs was carried out using the supported Fe as the catalyst and a mixture of C_2H_4 and H_2 •CNTs directly grown on TiO_2 	<ul style="list-style-type: none"> •CNTs were found to be uniformly grown in TiO_2 particles without altering the crystalline structure 	Photocatalytic Hydrogen Production	[42]

Electrodeposition	CNTs	TiO ₂	<ul style="list-style-type: none"> •The electrodeposition of TiO₂ was performed in a three-electrode cell with resin as a working electrode, Pt wire and Ag/AgCl were used as counter and reference electrodes •KCl solution as the electrolyte 	<ul style="list-style-type: none"> •CNTs were coated with a uniform layer of highly crystalline anatase TiO₂ nanoparticles 	Photo degradation of organic pollutant	[43]
Electrodeposition	CNTs	Gold nanoparticles	Applied potential of -1.2 V for 200 s in 0.2 M hydrogen tetrachloroaurate solution	The TEM image showed that the gold nanoparticles are homogeneously dispersed onto CNTs surface after the electrodeposition process	Hydrazine detection	[44]
Hydrothermal	CNTs	Cerium oxide	<ul style="list-style-type: none"> •CNTs were treated with 30% HNO₃ with stirring for 6h at 120 °C • Hydrothermal treatment at 170 °C for 24 h in an 80 ml Teflon stainless steel. 	<ul style="list-style-type: none"> •The growth of CeO₂ taken place when come in contact with hydroxyl ion. •The hexagonal CeO₂ nanocrystals were observed to grow on the CNTs surface. 	Supercapacitor	[46]

Hydrothermal	SWCNTs	Titanium sulfate	<ul style="list-style-type: none"> •SWCNTs were treated in the boiled nitrate solution •Hydrothermal treatment at 140 °C for 24 h 	<ul style="list-style-type: none"> •Well-dispersed SWCNTs and TiO₂ nanoparticles having intimate contact, which inhibited the growth of TiO₂ grain 	Photocatalytic hydrogen evolution	[47]
Hydrothermal	MWCNTs	Titanium isopropoxide	<ul style="list-style-type: none"> •Purification and functionalization of MWCNTs using HCl and HNO₃ •Hydrothermal treatment at 140 °C for 24 h 	<ul style="list-style-type: none"> •Favors a decrease in agglomeration among particles and controlled particle morphology 	Degradation of methylene blue solution	[48]
Sol-gel	MWCNTs	ZnO	<ul style="list-style-type: none"> •MWCNTs were functionalized using an acid mixture of HNO₃:H₂SO₄ (1:3 v/v) •Triethanolamine and glycerin acts as chelating agents 	<ul style="list-style-type: none"> •The addition of chelating agents may result in enhancing thin film porosity and increasing solution viscosity. •The FEG-SEM image indicated that a mesoporous structure with a homogenous distribution of pores are formed 	Lithium ion battery anodes	[50]

Sol-gel	SWCN Ts	In ₂ O ₃	<ul style="list-style-type: none"> • SWCNTs are oxidized using HNO₃ • Oxidized SWCNTs, indium hydroxide (indium (III) chloride and ammonia) were sonicated, stirred and dialyzed in water for overnight. 	<ul style="list-style-type: none"> • A core-shell morphology of In₂O₃/SWCN Ts composite was observed where the CNTs are completely encapsulated by the indium oxide layer. 	Ethanol Sensing	[51]
Sol-gel	MWCN Ts	Titanium isopropoxide Titanium butoxide	<ul style="list-style-type: none"> • MWCNTs was treated using HNO₃/H₂SO₄ mixture • Titanium precursor, ethanol, H₂O, and HCl was mixed and stirred at ambient temperature 	<ul style="list-style-type: none"> • Dispersion of TiO₂ nanoparticles on the surface of CNTs 	Degradation of methylene blue solution	[52]
Sol-gel	MWCN Ts	Titanium isopropoxide	<ul style="list-style-type: none"> • CNT/TiO₂ composite were prepared with the aiding of benzyl alcohol as a linking agent 	<ul style="list-style-type: none"> • Homogeneous coating of TiO₂ sols over the CNTs 	Degradation of acetaldehyde	[54]

4. Fundamental principles of photocatalysis

Generally, photocatalysis has been considered as one of the most sustainable methodologies which has been the subject of a huge amount of studies for water purification treatment. According to International Union of Pure and Applied Chemistry (IUPAC) compendium of chemical terminology, a catalytic reaction involving light absorption by a catalyst can be defined as photocatalysis [55]. It can be carried out in various media, including gas phase, pure organic liquid phases or aqueous solutions. Among these AOPs, heterogeneous photocatalysis employing semiconductor catalysts has

demonstrated its efficiency in degrading a wide range of ambiguous refractory organics into readily biodegradable compounds and substantially, mineralization to innocuous carbon dioxide and water [56-58]. Taking into account the advance photocatalysis processes involved photodegradation under UV irradiation, the materials used as photocatalysts must satisfy several functional requirements with respect to band gap energy, morphology, surface area, stability and reusability [59]. Besides, light harvesting ability of a photocatalyst is an important criterion to produce maximum photo-induced charge carriers. The basic parameter that governs the light-harvesting ability of the photocatalyst is its electronic structure, which determines its band-gap energy [60, 61]. Figure 7 illustrates the E_g values and the positions of band edges of various semiconductors.

Figure 7: Schematic representation of E_g values (in eV) and position of band edges of various semiconductors Reprinted (adapted) with permission from [63] Copyright (2015) Springer Nature.

Among the advanced semiconducting materials (i.e. WO_3 , Fe_2O_3 , CeO_2 , ZnO , and ZnS) being reported for electronics, magnetic, optical and photocatalytic applications; TiO_2 is the most widely used photocatalyst for the removal of organic pollutants from drinking

water treatment, industrial and aqueous systems in environment clean-up. The extensive use of TiO₂ in photocatalytic building materials is attributed to the following characteristics: (a) relatively inexpensive, non-toxic and chemically stable; (b) high photocatalytic activity compared with other metal oxide photocatalysts and (c) the photogenerated holes are highly oxidizing [62].

From the literature, binary metal sulfides semiconductors such as CdS, CdSe or ZnS are regarded as toxic and insufficiently stable for catalysis in aqueous media due to photoanodic corrosion. Photo-corrosion occurs when the anion from the catalyst itself is oxidized by photogenerated holes instead of water. Besides, the band gap (3.2 eV) and band-edge positions of ZnO are similar to those of TiO₂ and it was reported that ZnO has a higher electron mobility than TiO₂. However, ZnO is unstable in water due to incongruous dissolution and will form Zn(OH)₂ on the ZnO particle surfaces and thus lead to catalyst inactivation. Moreover, ZnO suffer from photo corrosion induced by self-oxidation and they can react with the photogenerated holes giving the following reactions as shown in Equation 1:

The Zn²⁺ released by photo-corrosion may produce a new poisoning effect on the environment, bringing about further pollution. As a result, the utilization of ZnO in environmental purification is greatly limited by these disadvantages. Thus, TiO₂ proves to be more a suitable benchmark photocatalyst for photodegradation of organic pollutants due to its high photoactivity, resistance to photo corrosion and possess a good mechanical resistance in acidic and oxidative environments. The photocatalytic properties of TiO₂ nanoparticles are derived from the illumination with photons having energy greater than the band gap energy, the photons will excite the electrons from the valence band (VB) into the conduction band (CB), resulting in the formation of photogenerated charge carriers (hole and electron). The photogenerated holes in the valence band will react with adsorbed water molecules, forming hydroxyl radicals (•OH). •OH produced has the second highest oxidation potential which can non-selectively oxidize almost all electron rich organic molecules and eventually converting them into CO₂ and water. Therefore, the organic pollutants which are adsorbed on the surface of the catalyst will be oxidized by •OH. In the meantime, electrons in the conduction band will typically participate in reduction processes, which typically react with molecular oxygen to produce superoxide radical anion (O₂^{•-}). The presence of molecular oxygen plays a substantial role in the photoinduced processes on the irradiated TiO₂ surface, as effective charge carriers,

separation is enabled. In addition, $O_2^{\bullet-}$ may not only take place in the further oxidation process but also prevents the electron-hole recombination, hence electron neutrality within the TiO_2 is maintained. Therefore, both $\bullet OH$ and $O_2^{\bullet-}$ play such an important roles in the photocatalytic reaction mechanism. The Equation (2-5) represents the mechanism of the photocatalytic degradation by TiO_2 [62, 64, 65].

It is essential for effective photocatalytic degradation of organic pollutants that the oxidation of pollutant and the reduction process of oxygen occur simultaneously in order to prevent the accumulation of electron in the conduction band and hence, the rate of recombination of e_{CB}^- and h_{VB}^+ is reduced. A schematic diagram illustrating the mechanism of photocatalysis on TiO_2 nanoparticles is shown in Figure 8.

Figure 8: A schematic diagram illustrating the mechanism of photocatalysis on TiO_2 nanoparticles.

However, an obvious hindrance to the widespread use of TiO₂ nanoparticles as a photocatalyst is its poor visible light response, the rapid recombination rate of charge carriers, low adsorption capacity to hydrophobic contaminants, high aggregation tendency and difficulty of separation and recovery, which decreases the quantum efficiency of the overall reaction. CNTs is used as a one-dimensional photocatalyst for contributing to the routes of enhancing TiO₂ photocatalytic activities, e.g., TiO₂ is an n-type semiconductor, but with the presence of CNTs, photoinduced electrons may migrate freely in the direction to the CNTs surfaces where CNTs can act as extremely effective electron sinks, which might have a lower Fermi level like a metal for suppressing the electron-hole pairs recombination. [28, 29, 66, 67].

The general principles photocatalytic mechanism of CNT/MO nanocomposites are briefly introduced in the following section. Accordingly, the photocatalytic degradation process initiated via the absorption of photon by the MO semiconductor. Under such conditions, the electrons from valence band would be excited to the conduction band of MO creating the electron-hole pairs on the catalyst surface. The photogenerated electrons were then transferred to CNTs, (act as the electron acceptor). The trapped electrons would then react with the dissolved oxygen to form the reactive oxygen species, followed by suppressing the rate of electron-hole recombination. In the meantime, the photogenerated electrons on the MO surface tended to reduce the dissolved oxygen to form superoxide anion, which may subsequently react with the adsorbed water to form the hydroxyl radicals. The hydroxyl radicals (acted as a primary oxidant in the photocatalytic system) then reacted with organic pollutant molecules and mineralized it into CO₂, H₂O and mineral acids [68, 69]

The mechanism reactions are shown as below:

$$h\nu$$

5. Applications of CNTs-based nanocomposites in water treatment

CNTs-based nanocomposites have been being one popular type of photocatalyst for water treatment, since it combines the excellent performances of MO semiconductor with CNTs. To date, removal of heavy metal ion, organic, inorganic and emerging pollutants in water have been increasingly studied using CNTs-based nanocomposites. Therefore, the water treatment applications using several MO photocatalysts supported on CNTs used in degradation of organic pollutants are extensively discussed in the following sections. Table 4 summarizes the targeted organic pollutants, light sources, catalysts and the influences of various operational parameters on the photodegradation of organic pollutants based on the recently published work. It can be seen that most organic pollutants can be photocatalytically degraded by MO within minutes to several hours under UV or near UV-visible irradiation, while longer time was needed for visible irradiation. The combination of CNTs with MO will extend the wavelength from UV to visible light range. Wongaree et al., demonstrated that a highly removal efficiency of methylene blue solution with CNT/TiO₂ nanocomposites (70 %) within 90 min under visible light irradiation as compared with pristine TiO₂ (22 %). Based on this, the lower band gap energy of CNTs/TiO₂ as compared with pristine TiO₂ resulting in a better light absorption of the composites in visible region [52]. In the similar work presented by Zhang et al., showed that the as prepared (CNTs)/Bismuth (Bi₄VO₈Cl) composite photocatalysts exhibited 30 % higher photocatalytic degradation of methyl orange (MO), hexavalent chromium Cr(IV), and bisphenol A (BPA) in water under visible light irradiation than that of pure Bi₄VO₈Cl. The enhanced photocatalytic activity by the composites are due to the synergetic effects by increased adsorption efficiency of pollutant, increased light absorption and reduced recombination rate of photogenerated charge carriers [70]. Zouzelka et al., prepared MWCNTs/TiO₂ composites for the degradation of 4-chlorophenol as compared to a P25 reference layer. The authors found that the first order rate reaction constant increased by about 100 % for the MWCNTs/TiO₂ composites, which suggested, MWCNTs acts as an electron sink and favors for photogenerated charge separation [71]. Photocatalysis using MWCNTs/TiO₂ composites are completely removed tetracycline under UVC irradiation as reported by Ahmadi et al., The authors also carried out the removal of real pharmaceutical wastewater using MWCNTs/TiO₂ composites which obtained total organic carbon (TOC) removal of 82.3 % after 4 h. The finding also demonstrated that the MWCNTs/TiO₂ composites exhibited superior catalytic capabilities over TiO₂ nanoparticles for degradation of tetracycline [72]. Another work reported by Zhu et al., ZnO/CNTs hierarchical microsphere composites was prepared by chemical deposition route for the photocatalytic removal of methylene blue under UV and visible light irradiation. The maximum photocatalytic activity of the composites (92.3 %) is higher than

that of pure ZnO (70.4 %) which suggested that CNTs play an important role for the photocatalytic removal of methylene blue [73]. An interesting work done by Zaman et al., revealed that the sonocatalytic degradation efficiency of methylene blue by SnO₂/MWCNT nanocomposite. During the sonocatalytic process, MWCNTs acts as an electron sink for accepting sonogenerated electron from the SnO₂ to promote interfacial electron transfer process. A complete removal of methylene blue was achieved in 30 min in the presence of SnO₂/MWCNT nanocomposite as compared with the bare SnO₂. A simple hydrothermal synthesis of WO₃-CNTs composite for sulfamethoxazole degradation was constructed by Zhu et al. [74]. The as-synthesized WO₃-CNT (73.3%) possessed enhanced photocatalytic performance for the sulfamethoxazole degradation than bare WO₃ (25.4 %) under visible light irradiation. Payan et al. described the fabrication of titanate nanotube (TNT)/MWCNT nanocomposites via hydrothermal method for the photodegradation of 4-chlorophenol under solar and UV illumination. For both UV and solar irradiations, TNT/MWCNT nanocomposites exhibited higher photocatalytic efficiency compared to the bare TNTs, which provided that SWCNTs has high surface areas that can create more active sites on the surface of CNTs, leading to more effectual degradation of 4-chlorophenol [75]. In other recent work, Oveisi et al., explored the Materials Institute Lavoisier-125 (Ti) (MIL-125 (Ti))/carbon nanotube (CNT) nanocomposites synthesized by hydrothermal method and tested for photocatalytic reactive black 5 degradation. The photocatalytic result showed that MIL/CNT composite (60 %) had higher photocatalytic dye degradation as compared to only MIL 125 (Ti) alone (< 40 %) due to the generation of powerful oxidants which included free radicals in water [76]. Kamil et al., reported MWCNTs/TiO₂ nanocomposite was prepared using sol-gel method for the Bismarck brown R dye degradation. The maximum photocatalytic efficiency was achieved by MWCNTs/TiO₂ nanocomposite (82.7 %) compared to TiO₂ (47.3 %) respectively.

Table 4: Summary of organic pollutants removal by photocatalytic reaction under various operational parameters

Photocatalyst	Type of organic pollutants	Initial Conc. of Pollutant	Catalyst dosage	Light source	Irradiation time	Removal efficiency (%)	Ref.
CNT/TiO ₂	Methylene blue	1 x 10 ⁻⁵ M	1.0 g/L	Fluorescence lamp (15W)	1.5 h	70	[52]
CNTs)/Bi ₄ VO ₈ Cl	Methyl orange (MO) Hexavalent chromium Cr(VI) + Bisphenol A (BPA)	10 mg/L 8.6 mg/L	1.0 g/L 1.5 g/L	300 W Xenon lamp	10 h 4 h	74.8 100	[70]
MWCNT/TiO ₂	4-chlorophenol	0.1 mmol.L ⁻¹	N/A	UV light (365 nm)	5 h	70	[71]
MWCNT/TiO ₂	Tetracycline	10 mg/L	0.2 g/L	6W UVC lamps	100 min	100	[72]
CNT/ZnO	Methylene blue	30 mg/L	0.17 g/L	500W Hg lamp 500 W Xenon lamp	1 h	92.3 76	[73]
SnO ₂ /MWCNT	Methylene blue	0.02 mM	30 mg	n.d.	30 min	100	[77]
WO ₃ -CNT	Sulfamethoxazole	10 mg/L	0.50 g/L	300 W Xenon lamp	3	73.3	[74]
TNT/SWCNT	4-chlorophenol	50 mg/L	2 g/L	UVC lamp	8 h	92	[75]
MIL-125 (Ti /CNTs	Reactive black 5	20 mg/L	0. 1 g/L	UV lamp	3 h	60	[76]
MWCNT/TiO ₂	Bismarck brown R dye	5 × 10 ⁻⁵ M	0. 5 g/L	UV lamp	1.5 h	82.7	[78]
CuO/CNT	p-chloroaniline	10 mg/L	0.375 g/L	Metal halide lamp	3 h	97	[79]
C ₃ N ₄ /CNTs	Rhodamine B	10 mg/L	0. 6 g/L	500 W Xenon lamp	2 h	98.6	[80]
TiO ₂ /CNT	Methylene blue	10 mg/L	0. 4 g/L	UV lamp	1 h	> 90%	[81]

Conclusion and future directions

In conclusion, it is notable that the CNT-based MO nanocomposites act as a potential photocatalyst for the degradation of various organic pollutants. The photocatalytic effect of CNT/MO nanocomposites occurs not only because of the adsorption of CNTs, but also because of the electron transfer between CNTs and MO, removing the organic pollutant from the solution. Despite the advances, great opportunities still exist in the exploitation of carbon-based hybrid assemblies. In this chapter, we have summarized the recent advances in the synthesis and application of the CNT-based MO nanocomposites. Despite various exploitations and extensive studies of this MWCNTs/MO nanocomposites have been

undertaken, a number of great challenges still remain and require attention in the future works. In order to bring this technology to practical applications, further studies and developments are required. Many studies applying photocatalysis for water treatment have been conducted by taken into account the concentration of the targeted organic pollutant without taking their attention to the possible intermediate products produced after the degradation. In fact, some intermediate products formed during the photodegradation experiment might be more dangerous and toxic compared to the original pollutant. The underlying mechanism of the photocatalytic enhancement by CNTs/MO nanocomposites is not fully understood and need to be examined in details to gain the clear understanding and to prove guidelines for future water treatment design based on photocatalysis. Generally, this enhancement is ascribed to the extended absorption and improved charge transfer in the hybrids. Although some studies have suggested a different mechanism in the literature, the possible mechanism of photocatalytic reaction may depend on the interfacial status of CNTs/MO nanocomposites, type of bonding, type of CNTs, functionalization, surface area and so forth. Thus, all these aspects in the fundamental processing-structural-developments will need to be better understood and controlled. Broader environmental applications on this CNTs/MO nanocomposite shall be explored. For instance, the photocatalytic degradation of persistent organic pollutants that hardly found in the literature shall be investigated, which important to the environmental protection and human health. Although it is still in the infancy, a widespread and great progress in this area can be expected in the future. The previous work mainly focused on a batch scale of photocatalytic degradation for pollutant removal, but the lack of application in a larger scale. Thus, there is a need for the design of a prototype for the convenience of photocatalytic degradation of organic pollutants so that it can be applied in real practice.

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