



Recent Advances in MWCNT-Supported Metal Oxide Heterostructure Photocatalysts for Photocatalytic Degradation of Organic Pollutants: A Review

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Abstract: The increased industrial activities are associated with textile production, pharmaceutical production, food processing, and printing industries, which have caused the large discharge of organic pollutants into water bodies. The traditional processes of treating wastewater like biological treatment, adsorption, coagulation-flocculation, and membrane filtration fail frequently to eliminate these recalcitrant pollutants. Semiconductor photocatalysis has become an attractive advanced oxidation procedure which holds potential to mineralize complex organic compounds to harmless final products. Metal oxide semiconductors are just some of the many photocatalytic materials that have drawn considerable attention because of their high oxidative potential and chemical stability. The efficiency of their photocatalysts is however often constrained by rapid recombination of photogenerated electron-hole pairs, and low absorption of the visible light. MWCNTs have a high surface area, electrical conductivity, adsorption capacity and electron transport ability. MWCNT-supported heterostructures in the presence of metal oxides have the potential to allow a dramatic improvement in the photocatalytic performance of the supports by enabling the efficient separation of charges, enhancing light absorption, and the number of active catalytic sites. The review gives a thorough literature review of the formation of the MWCNT-based metal oxide heterostructure photocatalysts in promoting the photocatalytic degradation of organic pollutants. The nature of principles of photocatalysis, the use of carbon nanotube support and the mechanics that govern charge transfer in a heterostructured system are presented. Specific attention is given to the most popular metal oxides that are combined with MWCNTs. In this review the effects of the structural parameters: morphology, defect engineering, heterojunction formation, and synthesis methods on the photocatalytic activity are discussed in detail.

Keywords: MWCNT, heterostructures, dye degradation, advanced oxidation processes

1. INTRODUCTION

Like the release of untreated industrial wastewater has become one of the most critical environmental issues across the world. The textile dyeing, paper printing, leather processing, pharmaceuticals and cosmetic industries discharge huge amounts of toxic organic compounds into the aquatic environment. Some of these pollutants consist of dyes, phenolic compounds, antibiotics, pesticides and endocrine-disrupting chemicals. Most of these substances have complex aromatic structures and these are extremely resistant to natural degradation processes. Consequently, they linger in water bodies over extended durations which are very

dangerous to aquatic organisms and human wellbeing. The most dangerous pollutants of the industrial wastes include synthetic dyes. There are over 100,000 variously available dyes commercially and some 7×10^5 tons worth of dyes are produced on a global basis each year. In the dyeing processes, almost 10-15 percent of the dyes are lost and released to the wastewater streams. Dyes, even in low concentration, give water bodies a very strong color and therefore light penetration is limited and photosynthesis is inhibited in aquatic organisms. In addition, most dyes and their decomposition offshoots are cancer causing, mutagenic, and poisonous towards microorganisms and other organisms [1].



Conventional wastewater treatment process like adsorption, coagulation, biological, and membrane filtration have been used extensively in dye removal. The techniques have however a number of weaknesses such as incomplete degradation, secondary sludge formation, high costs of operation, and membrane foulage. As a result, the creation of new sophisticated treatment technologies which can fully decompose organic pollutants to harmless compounds has gained new significance [2]. The advanced oxidation processes (AOPs) have become one of the most useful technologies in the degradation of persistent organic contaminants. Such processes are based on the production of highly reactive oxygen species (ROS) including hydroxyl radical ($\cdot\text{OH}$), superoxide radical ($\text{O}_2^{\cdot-}$), and singlet oxygen ($^1\text{O}_2$). Among other AOPs, semiconductor photocatalysis has received a lot of interest because of its power to use solar energy in the degradation of pollutants.

There has been a wide research on semiconductor photocatalysts including titanium dioxide (TiO_2), zinc oxide (ZnO), copper oxide (CuO), nickel oxide (NiO), Cadmium oxide (CdO) and iron oxide (Fe_2O_3) as photocatalysts. When these materials are irradiated with light of appropriate strength, the electron-hole pairs formed in the materials cause oxidation and reduction reactions which result in the degradation of pollutants. Although these conventional semiconductor photocatalysts hold promise, they can be afflicted by quick recombination of the generated charge carriers, low visible light absorption, and low surface active sites [3-7]. To address these drawbacks, much research has been focused on the development of composite photocatalysts. Carbon nanotubes have been remarkably popular among the other supporting materials because of its outstanding physicochemical characteristics. Carbon nanotubes are multi-walled and are highly electrically conductive, have a high surface area, good mechanical strength, and high adsorption ability. Such characteristics render them the best support of metal oxide nanoparticles [8-9].

Combination between metal oxides and MWCNTs results in the development of heterostructured photocatalysts, which are better catalysts. MWCNTs when used in such systems serve as electron acceptors and conductive channels which enable high velocity charge movement. This decreases the recombination of electrons and holes and increases the efficiency of the catalyst under photocatalysis. Also, carbon nanotubes have a high surface area that offers many active sites that can be used to adsorb and react with pollutants [10-12]. Over the last several years, many studies have presented

the synthesis of MWCNT supported metal oxide heterostructures, such as $\text{TiO}_2/\text{MWCNT}$, ZnO/MWCNT , NiO/MWCNT , CuO/MWCNT , CdO/MWCNT and $\text{Fe}_2\text{O}_3/\text{MWCNT}$ composites. These materials have very high photocatalytic activities as compared to pure metal oxides. The enhancement is as a result of synergistic interactions of the semiconductor nanoparticles and the conductive carbon nanotube framework.

Thus, to learn about the processes that lead to the enhanced photocatalytic activity of MWCNT-supported metal oxide heterostructures and develop the methods of their further improvement, it is critical to thoroughly review these materials. This review is a summary of the current developments in the design, synthesis and photocatalytic application of these hybrid materials in the remediation of the environment.

II. FUNDAMENTALS OF PHOTOCATALYSIS IN MWCNT-SUPPORTED METAL OXIDE HETEROSTRUCTURES

Photocatalysis is a catalyzed reaction that uses light where semiconductor materials absorb photons and produce electron-hole pairs that undergo an oxidation and a reduction reaction. These charge carriers that are generated under photogenic conditions react with water and dissolved oxygen to form reactive oxygen species (ROS), including hydroxyl radicals ($\text{OH}^{\cdot}$), superoxide radicals ($\text{O}_2^{\cdot-}$), and hydrogen peroxide (H_2O_2). They can oxidize and mineralize complex organic pollutant to produce harmless end products like CO_2 and H_2O [13-14].

Metal oxide based semiconductors such as TiO_2 , ZnO , Fe_2O_3 , CuO , NiO and CdO have been extensively studied as photocatalysts due to their high oxidation potential, chemical stability and low cost. Nevertheless, there are a number of drawbacks in the photocatalytic efficiency of pure metal oxides which are inherent. These are high-speed recombination of electron-hole pairs that are produced by photo-generation, poor absorption of light at the visible wavelength range and inadequate sites where pollutants can be adsorbed. Consequently, different methods have been suggested in order to optimize photocatalytic activity, such as doping, heterojunction, surface, and conductive carbon material incorporation [15-16].

One of such methods is the incorporation of metal oxide nanoparticles into multi-walled carbon nanotubes, which have proved to be one of the most rewarding strategies to be used in enhancing photocatalytic functionality. The



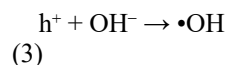
MWCNTs have a distinguishing feature of the tubular structure with more than one concentric layer of graphene. They are uniquely electrical conductors, have high surface areas, are strong mechanics and have good electron transportation properties. Such properties allow MWCNTs to act as effective electron acceptors and electron conduction in photocatalysts [17-18]. A heterostructures photocatalyst is created when the metal oxide nanoparticles are attached to the surface of MWCNTs. MWCNTs in such systems have a number of roles to play. To begin with, they increase adsorption capacity of organic pollutants because they have high surface area and p-p interactions between aromatic molecules. Second, they enable quick movement of photogenerated electrons thus inhibiting the recombination of electrons and holes. Third, they enhance the scope of light absorption of the composite photocatalyst by enhancing the response to visible light [19].

A. Basic Photocatalytic Mechanism

Photons cause the formation of a reactive-species on the surface of the photocatalyst layer, which in turn reacts to form a product. The semiconductor materials photocatalytic process starts when the catalyst absorbs photons whose energy is equal or higher than that of the band gap. This energy causes the valence band electrons to be excited to the conduction band (CB) and positively charged holes to remain in the valence band. The basic reaction may be expressed in the following form in equation (1):



These charge carriers then take part in redox reaction on the catalyst surface. The holes can be oxidized by water or hydroxide ions to form hydroxyl radicals by the photogenerated holes represents in equation (2-3):



Meanwhile, the electrons produced by photogeneration deactivate dissolved oxygen to produce superoxide radical shown in equation (4):



These reactive oxygen species are extremely oxidative and they are able to oxidize organic pollutants in a cascade of oxidation reactions.

B. Role of MWCNTs in Charge Separation

The main drawback of semiconductor photocatalysts is that the electrons and holes generated by the photocatalysts recombine quickly. This recombination greatly lowers the photocatalytic efficiency since fewer charge carriers will be available to produce the reactive oxygen species. MWCNTs are good in overcoming this problem because of their good electrical conductivity and electron storing capacity. The electrons produced in the metal oxide nanoparticles conduction band may be transferred to the arrangement of carbon nanotubes when the materials are coupled with MWCNTs. The charge recombination is inhibited by this electron migration and increases the lifetime of the photogenerated holes. As soon as the electrons are introduced to the nanotubes, they are easily reacted with oxygen molecules to produce superoxide radicals. In the meantime, the holes left within the semiconductor valence band just keep on oxidizing water or organic pollutants. Therefore, MWCNTs serve as electron reservoirs to increase the charge separation and photocatalytic performance.

C. Enhanced Adsorption of Pollutants

A second significant advantage of MWCNT-supported photocatalysts is that they have a good adsorption capacity. Carbon nanotubes have high surface areas and high p-electron systems which interrelate with aromatic organic molecules. Aromatic rings are found in many industrial dyes and pollutants and they are able to interact with the MWCNTs graphitic structure via p-p stacking interactions. The result of this is a higher rate of the adsorption of the pollutants on the catalyst surface which makes the pollutants get nearer to the reactive sites where the oxidation reactions will take place. Therefore, both the adsorption efficiency and the degradation rates enhance in the presence of MWCNTs in photocatalytic degradation.

D. Formation of Heterojunction Interfaces

The interface that forms between metal oxide nanoparticles and MWCNTs is very important in the determination of the photocatalytic performance. Different differences between the work function of and the energy band structures of the two materials make the electron transfer efficient at this interface. As the semiconductor is lit, the photogenerated electrons proceed to the carbon nanotube because of the



reasonable energy gradient. This forms an inherent electric field at the heterojunction interface which facilitates directional transfer of charge. Consequently, the heterostructure has enhanced charge separation, high recombination losses are minimized and enhanced catalytic photocatalytic ability. This interaction between metal oxides and MWCNTs is synergistic and has been attributed to the enhanced performance of these hybrid photocatalysts over their constituent units.

F. Generation of Reactive Oxygen Species

In photocatalysts prepared on MWCNT, the generation of reactive oxygen species is greatly increased because of the improved electron transfer. The major ROS formed in the process of photocatalysis are: Hydroxyl radicals ($\bullet\text{OH}$), Superoxide radicals ($\text{O}_2^{\bullet-}$), Hydrogen peroxide (HO_2) and Singlet oxygen ($^1\text{O}_2$). Such species attack organic pollutants by oxidation reactions that includes cleavage of aromatic rings, breaking of azo bonds in dyes, oxidation of functional groups and mineralization to CO_2 and H_2O . The general degradation cycle normally entails a number of intermediate processes before the total mineralization takes place.

G. Factors Affecting Photocatalytic Activity

The performance of MWCNT-based metal oxide photocatalysts is determined by a number of factors such as the composition of catalysts and the type of oxide in the metals, Nanostructure surface area and morphology surface area and morphology of nanostructures, settling of metal oxide nanoparticles on MWCNTs, The intensity of source of light and wavelength, Baseline concentration of pollutants, pH of the reaction medium, and availability of dissolved oxygen. These parameters are important to be optimized in order to have maximum photocatalytic performance.

III. SYNTHESIS STRATEGIES FOR MWCNT-SUPPORTED METAL OXIDE HETEROSTRUCTURE PHOTOCATALYSTS

The efficacy of photocatalysis of the MWCNT-based metal oxide heterostructures largely relies on the methodology that is adopted in preparing the catalysts. The synthesis pathway defines such significant physicochemical properties like particle size, metal oxide nanoparticles dispersion, crystallinity, surface area, defect density, and the interface between MWCNTs and metal oxides. These parameters should be properly controlled in order to reach efficient electron transfer and improved photocatalytic activity [20].

There have been a number of synthesis methods that have been devised to produce MWCNT-supported metal oxide heterostructures. They are sol-gel synthesis, hydrothermal and solvothermal methods, chemical vapour deposition, precipitation process, microwave-assisted synthesis, and in-situ growth plan. All of these approaches have their own benefits in the regulation of the structural and catalytic characteristics of the obtained nanocomposites photocatalysts [21-23].

A. Sol-Gel Method

The sol-gel technique is among the prevalent methods to prepare metal oxide nanoparticles on the MWCNTs. This procedure takes into account hydrolysis and condensation of metal or metal salt precursors into a colloidal suspension that is further developed into a three dimensional gel system with the required metal oxide particles. During a common sol-gel process, the metal precursors (titanium isopropoxide, zinc acetate or iron nitrate) are first dissolved in a solvent. The precursor solution is then used to disperse functionally modified MWCNTs to accomplish uniform distribution. The hydrolysis reaction results in the creation of metal hydroxide intermediates that are reacting through condensation reaction in order to create metal oxide networks that are deposited at the surface of the nanotube. Once the gel is formed, it is dried and subsequently burned in high temperatures to produce crystalline metal oxide nanoparticles attached on the surface of the MWCNT.

Sol-gel method has the following benefits like non-clumping of nanoparticles on carbon nanotubes, accurate regulation of particle size and composition, relatively low temperature of synthesis, and final photocatalyst have high purity. Nevertheless, when the calcification temperatures are too high, it can destroy the carbon nanotube structure and a lot of attention needs to be paid to the optimization of thermal treatment.

B. Hydrothermal Synthesis

Another technique that has become popular in the production of high crystallinity of MWCNT-metal oxide composites is hydrothermal synthesis. This technique is the execution of the chemical reactions within aqueous solutions under high temperature and pressure conditions in closed autoclaves. In the hydrothermal synthesis, the metal salts are dissolved in water as well as dispersed MWCNTs. The mixture is moved to a Teflon lined autoclave and at a temperature that is normally between $120\text{--}200^\circ\text{C}$. In such circumstances, the metal ions are subjected to controlled



nucleation and crystal growth cycles, and the metal oxide nanostructures well-defined on the surface of MWCNTs are formed. The hydrothermal conditions have a number of advantages such as enhanced metal oxide nanoparticles crystallinity, high affinity of metal oxides and MWCNTs, regulated morphology nano rods, nano flowers and nano sheets, and less aggregation of particles. As an illustration, ZnO/MWCNT and TiO₂/MWCNT nanocomposites prepared by hydrothermal processes tend to have a higher rate of photocatalysis because of their high crystallinity and particle dispersion.

C. Solvothermal Method

Solvothermal technique resembles hydrothermal synthesis except that organic solvents are used in place of water. The reaction environment is controlled by the use of organic solvents like ethanol, ethylene glycol, or dimethylformamide which determine the crystal growth. In solvothermal synthesis, precursors of metals and MWCNTs are combined in an organic solvent after which it is heated in occupied autoclaves. The solvent is a reaction medium and a structure-directing agent, which allows creation of nanostructures with a desired morphology. This technology has a number of benefits in synthesizing photocatalysts like enhanced particles size and morphology, improved metal oxide nanoparticles dispersion, hierarchical nanostructures formation, and enhanced interfacial contact of metal oxides and MWCNTs. Solvothermal methods are especially useful in the production of the complex heterostructures of NiO/MWCNT, CuO/MWCNT, and Fe₂O₃/MWCNT photocatalysts.

D. Chemical Vapour Deposition (CVD)

Chemical vapour deposition is one of the most stringent processes of synthesizing nanostructured materials on composition and morphology. The high-temperature decomposition of volatile metal precursors in CVD processes has been used to coating metal oxide nanoparticle onto the surface of MWCNTs. In the CVD process, the gases that have been made into its precursors are fed into a reaction chamber which holds MWCNT substrates. When the precursor is thermally degraded, it forms metal oxide nanoparticles which conditions and proliferate on the surface of the nanotube. CVD approach has a number of strengths such as existence of pure materials synthesized, good attachment of metal oxide nanoparticles and nanotubes, accurate size and thickness regulation of nanoparticles, and coatings of homogenous layers on the surfaces of MWCNTs.

Nonetheless, this method usually involves very special equipment and comparatively high temperatures of operation that can raise the cost of synthesis.

E. Precipitation and Co-Precipitation Methods

Simple and low cost methods are precipitation and co-precipitation, which is widely practiced in the synthesis of MWCNT-supported metal oxide composites. Under these procedures, metal salts are dissolved in aqueous medium and then precipitated by including alkaline reagents like NaOH or NH₄OH. In the case of dispersible functionalized MWCNTs in the solution, the nucleation of the metal hydroxide precipitates on the surface of the nanotube. The intermediates of hydroxide are then dried and calcinated to produce crystallized metal oxide nanoparticles. The benefits of precipitation methods are such as simplicity and low cost, large scale production, good nanotube dispersion of nanoparticles, and selectivity in the preparation of mixed metal oxide catalysts. Fe₂O₃/MWCNT, CuO/MWCNT, and NiO/MWCNT photocatalysts have been prepared using this method.

F. Microwave-Assisted Synthesis

Recently, microwave-assisted synthesis is one of the energy-efficient and rapid techniques of preparing nanostructured photocatalysts. In this method, the reaction mixtures are heated by means of microwave radiation evenly and thus, nucleation and crystal growth are hastened. Microwave heating has a number of benefits over classical thermal heating like immensely lowered reaction time, heating of reaction mixture uniformly, increased dispersion of nanoparticles, and reduction of particle sizes. By using the technique on MWCNT-based metal oxide systems, it is possible to create nanocomposites that are highly uniform and have improved photocatalytic activity.

G. In-Situ Growth Strategies

In-situ growth techniques entail the direct growth of metal oxide nanoparticles on MWCNTs as they are being produced instead of adsorbing the two constituents together afterward. This will result in good interfacial interactions between the metal oxide and the carbon nanotube framework. Oxygen-containing groups like -COOH and -OH are incorporated in functionalized MWCNTs in these strategies which serve as the nucleation points of forming metal oxide. These functional groups are bound by metal ions which are then hydrolyzed and oxidized to produce nanoparticles bound tightly to the surface of the nanotube. In-situ synthesis has a



number of benefits such as strong interfacial bonding, enhanced component inter-transfer, increased structural integrity, avoidance of nanoparticles agglomeration. This has led heterostructures synthesized in situ to be typically better photocatalysts than physically mixed composites.

H. Influence of Synthesis Method on Photocatalytic Performance

The way the catalytic process is synthesized affects the catalytic activity of the MWCNT-supported metal oxide photocatalysts. The efficiency of charge separation and reactive oxygen species generation depends on parameters like the size of nanoparticles, crystallinity of the particles, the density of defects and the interfacial contact with the particle. For instance such as hydrothermal synthesis normally yields highly crystalline nanostructures that are highly catalytic, sol-gel techniques permit accurate composition and particle size control, Microwave synthesis produces smaller nanoparticles and has increased reaction kinetics, and in-situ growth techniques help to increase electron transfer at the interface. Thus, in order to maximize the photocatalytic performance, a suitable synthesis strategy must be chosen.

IV. CHARGE TRANSFER MECHANISMS IN MWCNT-SUPPORTED METAL OXIDE HETEROSTRUCTURE PHOTOCATALYSTS

The rate of charge separation and transfer is one of the most important aspects of photocatalyst performance of semiconductor materials. Under the conventional photocatalysts, fast recombination of the photogenerated electron-hole pairs may greatly deter the catalytic performance since fewer charge carriers can produce the reactive oxygen species. Combination of metal oxide semiconductors and multi-walled carbon nanotubes is a viable means of increasing charge transport and inhibiting recombination. MWCNT-based metal oxide heterostructure has a high photocatalytic activity owing to the synergistic interaction between the conductive carbon nanotube structure and the semiconductor nanoparticles. Carbon nanotubes are highly electrical conductors and a good transporter of electrons with high mobility which means that they can be used as a form of electricity acceptor and conductor. Consequently, photogenerated electrons may move out of the conduction band of the semiconductor to the surface of the nanotube, which is effectively increasing the lifetime of photogenerated charge carriers. A number of charge transfer processes have been postulated to demonstrate the increased

photocatalytic activity of MWCNT-bound heterostructures. These are the formation of Schottky junction, Type-II heterojunction mechanisms, Z-scheme photocatalytic systems and conductive electron transport via the nanotube network [24-25].

A. Schottky Junction Formation

In most of MWCNT-metal oxide photocatalytic systems, the interface between the semiconductor and the conductive carbon nanotube formation exhibits a Schottky junction. Whenever a semiconductor material touches a conductive material of a different work function, a Schottky junction is formed. When metal oxide nanoparticles are applied onto MWCNTs, electrons are likely to flow out of the semiconductor to the carbon nanotube up to equilibrium. The transfer of electrons forms a built in electric field across the interface, which allows directional flow of photogenerated electrons. With light irradiation the electrons excited to a conduction band of the semiconductor are transferred rapidly to the surface of the MWCNT. In the meantime, the holes are left in the semiconductor valence band where they are involved in oxidation reactions. The benefits of the Schottky junction formation are such as effective separation of electronic-hole pairs generated by photogenic processes, repression of recombination of charge, increased movement of electrons toward oxygen molecules, and enhanced degradation performance of photocatalysts. MWCNTs are thus electron sinks which absorb electrons and inhibit their combination with holes.

B. Type-II Heterojunction Mechanism

The heterojunctions are usually type-II whereby two different semiconductor materials are combined with different band structures. Type-II band alignments can occur in MWCNT-supported photocatalysts, which is starting to occur between the metal oxide nanoparticles and/or between the modified carbon structures. Staggered conduction band edges and staggered valence band edges of the two materials are found in a Type-II heterojunction system. In the contribution of electron-hole pairs by light irradiation, the electrons move out of the higher conduction band into the lower conduction band of the receiving material. Simultaneously, holes move counter intuitively towards the high valence band. Such a spatial distance between electrons and holes decreases recombination considerably and increases the efficiency of photocatalysis. Carbon nanotubes become the electron transportation channels in MWCNT supported systems which transport electrons off the



semiconductor surface. Electrons, therefore, build up on the nanotubes leaving holes in the semiconductor lattice. This process enables the catalyst to have a greater number of reactive charge carriers that can be used in degrading pollutants.

C. Z-Scheme Photocatalytic Mechanism

Z-Scheme mechanism is also a relatively new concept in the design of advanced photocatalytic systems and has been given much attention recently. This system resembles natural photosynthesis and consists of the interaction two semiconductor materials, which collaborate with each other to increase the efficiency of photocatalysis. With Z-scheme photocatalytic systems, the electrons in the conduction band of one semiconductor are recombined with the holes in the valence band of the other semiconductor. The result of this process is the fact that highly energetic electrons and holes are obtained in separate materials with high reducing and oxidizing powers. Adding MWCNTs to Z-scheme systems makes them conductive mediators facilitating high speed electron transfer between semiconductor components. The nanotube network is an electron bridge which enhances the rapidity of transporting charges and the overall catalytic activity. Consequently, the system has a high oxidation and reduction potential besides efficient charge separation. The Z-scheme photocatalysis has the following benefits such as greater redox ability than the traditional heterojunctions, enhanced separation of charge carriers, improved usage of visible light, and enhanced degradation efficiency of photocatalysts. MWCNTs thus are of great importance in stabilizing Z-scheme photocatalytic systems.

D. Electron Transport through the Carbon Nanotube Network

Carbon nanotubes are remarkably electrically conductive and their rate of conducting electrons is very high and therefore, charge can be transported rapidly throughout the photocatalyst structure. The MWCNT-based heterostructures have the nanotube framework to create interconnected conductive network enabling the movement of electrons. When a semiconductor conduction band has transferred electrons to the nanotubes, the electrons are able to move fast along the network of nanotubes and come in contact with dissolved oxygen molecules in the surrounding solution. These radicals undergo additional reactions to generate hydroxyl radicals and other reactive oxygen species that cause the degradation of the pollutant. The existence of the carbon nanotubes thus greatly increases the production of

reactive species in that it increases the efficiency of the electron transport.

E. Role of Surface Defects and Functional Groups

Surface defects and functional groups on nanotube surface are also found to have a strong effect on the photocatalytic behaviour of MWCNT-supported heterostructures. Oxygen-containing functions like hydroxyl (-OH), carboxyl (-COOH), and carbonyl (C=O) groups of carbon nanotubes enhance the dispersion of metal oxide nanoparticles. These functional groups become the nucleation centers whereby during the synthesis metal ions can bind themselves and develop into nanoparticles. This causes the metal oxide nanoparticles to be well-bound to the nanotube surface forming good contact at the interface, which improves charge transfer. Surface defects in MWCNTs serve, too, as active catalytic sites and enhance the adsorption of pollutant molecules and reactions in electron transfer. In turn, carbon nanotube defect engineering is a useful approach to the enhancement of photocatalytic behaviour.

F. Generation of Reactive Oxygen Species

Enhanced reactive oxygen species (ROS) is achieved by the better charge separation and transfer of electrons in MWCNT-immobilized photocatalysts. The oxidation and degradation of organic pollutants is done by these species. The ROS that are primarily produced in the process of photocatalysis are Hydroxyl radicals ($\bullet\text{OH}$), Superoxide radicals ($\text{O}_2^{\bullet-}$), Hydrogen peroxide (H_2O_2), and Singlet oxygen ($^1\text{O}_2$). The degradation process is normally in a series of oxidation reactions as ROS react with pollutant molecules to degrade complex aromatic structures to smaller intermediates. These intermediates are then further oxidized till they are totally mineralized.

G. Factors Influencing Charge Transfer Efficiency

The efficiency of charge transfer involving MWCNT-supported photocatalyst is determined by several factors such as size of metal oxide nanoparticles, surface area of MWCNTs, quality of contact between components of interfaces, defect density of carbon nanotubes, band Gap of semiconductor materials, scattering of nanoparticles on surfaces of nanotubes. The maximization of these parameters is necessary to attain maximum photocatalytic efficiency.

V. PHOTOCATALYTIC DEGRADATION MECHANISMS OF ORGANIC POLLUTANTS USING



MWCNT-SUPPORTED METAL OXIDE PHOTOCATALYSTS

The enhancement and degradation of organic contaminants in wastewater by photocatalytic systems using MWCNT-supported metal oxide heterostructures as catalysts are the major goal of the system. Such pollutants are synthetic dyes, pharmaceuticals, pesticides, phenolic compounds and endocrine-disrupting chemicals. These contaminants are so hard to treat with the established treatment methods because of their elaborate molecular constructions and high chemical stability [26]. A viable approach to photocatalytic degradation with the help of semiconductor-based catalysts is that it implies the accomplishment of highly reactive oxygen species that can destroy complex organic compounds to simple and environmentally harmless products. Photocatalysts of the MWCNT supported leads to enhanced reactive oxygen species production by better separation of charge and better electron transportation, leading to more efficient degradation of pollutants. The mechanism of degradation is usually a sequence of steps such as adsorption of the pollutants on the catalyst surface, the production of reactive oxygen species, the oxidative attack of the pollutant molecules, the production of intermediate products and the ultimate mineralization of the products into carbon dioxide and water.

A. Degradation of Synthetic Dyes

The pollutants that are most common in industrial wastewater are synthetic dyes. Printing industries, cosmetic industries, textile industries, and leather industries release significant amounts of wastewater containing dyes to the water bodies. Such dyes usually have aromatic rings and azo bonds which render them unbiological degradable [27-28]. The application of metal oxide photocatalysts that are supported by MWCNTs has been reported to be highly efficient in the process of degrading different types of dye molecules such as methylene blue, rhodamine B, methyl orange, and crystal violet.

1) Methylene Blue Degradation: Methylene blue is a cationic dye that finds a lot of applications in textile and pharmaceutical industries. In the photocatalytic degradation, the heterocyclic structures and the aromatic rings of the methylene blue are attacked by the hydroxyl radicals. The degradation route encompasses N-demethylation reactions, cleavage of aromatic rings, formation of lower organic intermediates, and total mineralization to CO₂ and H₂O.

MWCNTs improve adsorption of methylene blue as there are p-p interactions between the aromatic dye molecules and the graphitic face of the carbon nanotubes. This enhancement of adsorption brings the dye molecules nearer to reactive sites causing faster degradation.

2) Rhodamine B Degradation: Another dye that is widely researched in photocatalytic studies is rhodamine B. The degradation process normally starts with the sequential elimination of ethyl groups of the dye molecule then accompanied by the destruction of the chromophoric structure. Conjugated ring system of rhodamine B is attacked by reactive oxygen species to form smaller organic compounds. The further oxidation will eventually result in total mineralization.

3) Azo Dye Degradation: Azo dyes like methyl orange, reactive black have azo bonds -N=N- which are chromophoric groups of color. These azo bonds are susceptible to hydroxyl radicals which cause decolorization to occur very fast. The biodegradation mechanism usually follows cleavage of azo bonds, preparation of aromatic amines, intermediate products oxidation, and to carbon dioxide and water, mineralization. MWCNT-based catalysts improve the process of azo dye degradation because of the greater separation of charge and higher production of ROS.

B. Degradation of Phenolic Compounds

Uses in industry Phenolic compounds find extensive use in industrial processes in the manufacture of plastics, pharmaceuticals, pesticides and petroleum refining. These are very toxic compounds and are persistent volumes in waters. In photocatalytic degradation, hydroxyl radicals assault the aromatic ring of phenolic compounds resulting in intermediate products that are catechol, hydroquinone, and benzoquinone. The additional oxidation of the above intermediates causes the opening of the ring reaction and the production of smaller organic acids like oxalic acid and formic acid. These compounds are finally mineralized into carbon dioxide and water. MWCNT-based metal oxide photocatalysts exhibit improved phenol degradation because they are able to produce more concentrations of reactive oxygen species.

C. Degradation of Pharmaceutical Pollutants

Drugs such as antibiotics, painkiller and hormones are also being found in wastewater and natural water. These pollutants are not easily eliminated through the normal



treatment procedures due to their complicated chemical makeup and great stability. Pharmaceutical degradation through photocatalytic degradation is characterized by the use of oxidative attacks on functional groups of pharmaceuticals, including amide bonds, aromatic rings, and heterocyclic compounds. These compounds are degraded by the reactive oxygen species in a chain of oxidation reactions to form intermediate products. The further oxidation will eventually result in total mineralization. MWCNT-based photocatalysts improve the degradation of pharmaceuticals by improving the transportation of electrons and formation of reactive species.

D. Role of Reactive Oxygen Species in Pollutant Degradation

Photocatalytic degradation of the pollutants occurs due to the presence of the key oxidizing agents, which are reactive oxygen species. Primary ROS that are engaged in these reactions are Hydroxyl radicals ($\bullet\text{OH}$), Superoxide radicals ($\text{O}_2^{\bullet-}$), Hydrogen peroxide (H_2O_2), and Singlet oxygen ($^1\text{O}_2$). Among these species, hydroxyl radicals are considered the most powerful oxidants because of their extremely high redox potential. They can rapidly attack organic molecules and initiate degradation reactions. Superoxide radicals also contribute to pollutant degradation by forming additional reactive species such as hydrogen peroxide and hydroxyl radicals. The enhanced charge separation in MWCNT-supported photocatalysts leads to increased ROS generation, thereby improving degradation efficiency.

E. Factors Affecting Photocatalytic Degradation Efficiency

There are only a few parameters that determine the photocatalytic degradation process, which are catalyst concentration, concentration of pollutants at the beginning of the year, solution pH, intensity of light and wavelength, dissolved oxygen concentration, presence of inorganic ions. As an illustration, hydroxyl radical formation can be favored in alkaline environments, whereas adsorption of some pollutants on the catalyst surface can also be increased in acidic environment. These parameters of operation should be optimized in order to have a high level of photocatalytic efficiency.

VI. COMPARATIVE PERFORMANCE OF DIFFERENT MWCNT-METAL OXIDE HETEROSTRUCTURE PHOTOCATALYSTS

The photocatalytic activities of metal oxide heterostructures that are supported by MWCNTs are strongly influenced by the nature of the semiconductor applied, characteristics of the composite material, and nature of the interaction between the metal oxide nanoparticles and the support of carbon nanotubes. Many metal oxide such as TiO_2 , ZnO , NiO , CuO , Fe_2O_3 and CdO have been explored extensively in photocatalytic degradation of organic contaminants when complexed with multi-walled carbon nanotubes [29]. The addition of the MWCNTs to metal oxide photocatalysts enhance most of the important properties such as surface area, adsorption capacity, electron transport efficiency, and visible-light absorption. Nonetheless, the degree of performance improvement is determined not only by the inherent characteristics of the metal oxide semiconductor but also by the synthesis method through which the heterostructure is to be made. In this section, a comparative analysis of the photocatalytic activity of various MWCNT-metal oxide systems to degrade organic contaminants is given [30-34].

A. TiO_2 /MWCNT Photocatalysts

One of the most commonly investigated photocatalysts comes in the form of titanium dioxide since it is immensely stable chemically, highly oxidative, non-toxic, as well as inexpensive. Nevertheless, pure TiO_2 has two significant deficiencies namely, recombination of the photogenerated charge carriers is fast and, secondly, limitation in light absorption that is confined to the ultraviolet region. In the case of TiO_2 nano particles supported on MWCNTs, the photocatalytic performance is enhanced greatly. The carbon nanotubes are electron acceptors and conduction channels which enable quick electron transfer between TiO_2 conduction band and nanotube surface. This inhibits the electron-hole recombination and enhances the production of the reactive oxygen species. Composites of TiO_2 /MWCNT have proved to be very efficient to degrade dyes like methylene blue, rhodamine B and methyl orange under UV and visible light irradiation. The presence of carbon nanotubes is credited to the improved charge separation, increased surface adsorption of pollutants, and the increased light absorption which results in the improved activity.

B. ZnO /MWCNT Photocatalysts

Zinc oxide is another common semiconductor photocatalyst that is under intense research and the band gap is analogous to TiO_2 but with better electron mobility and greater absorption in the UV. ZnO is also a good



photocatalyst in the degradation of organic contaminants. Nevertheless, ZnO nanoparticles are usually subject to photocorrosion and instability exposure in the presence of long-term irradiation. ZnO-based photocatalysts are enhanced with the incorporation of MWCNTs in their structure and catalytic activity. The impact of nanotubes in ZnO/MWCNT heterostructures is to improve the conduction of electrons and minimise recombination losses. Moreover, MWCNTs have a high surface area which facilitates the adsorption of pollutant molecules, and thus enhances the likelihood of oxidation reaction at the catalyst surface. ZnO/MWCNT photocatalysts have already been used in studies of degradation of dye, antibiotics, and phenolic pollutants in wastewater.

C. NiO/MWCNT Photocatalysts

Nickel oxide is a p-type semiconductor which has been of interest in photocatalytic and electrochemical uses. NiO nanoparticles produce heterostructural composites when mixed with MWCNTs and are more photocatalytically active. The composites of NiO/MWCNTs promote effective separation of the photogenerated charge carriers because of strong interfacial interactions between the semiconductor and carbon nanotubes. Conductive nanotube network increases the speed of movement of electrons and oxygen molecules can quickly transfer electrons. Such materials have shown usefulness in photocatalytic degradation of dyes including methylene blue and rhodamine B under the irradiation of visible light. The increased performance is a result of the better charge transportation and the augmentation of the development of the reactive oxygen species.

D. CuO/MWCNT Photocatalysts

Copper oxide is a narrow band gap semiconductor which carries a high absorption in the visible segment of the electromagnetic spectrum. A consequence of this property is that CuO is an especially promising material to be used in solar-driven photocatalysis. The heterostructure produced when CuO nanoparticles are mounted over MWCNTs show a better performance in terms of photocatalysis because there is an increase in charge separation and electron transport. The carbon nanotubes act as the conductive channels which facilitate the spread of the electrons off the semiconductor surface in a faster way. CuO/MWCNT composites have shown encouraging performances as regards to degradation of organic dye as well as pharmaceutical pollutants under visible light irradiation. The increase of the activity is explained by the increase of the light acquisition, the increase

of the cellular surface and the effective production of the reactive oxygen species.

E. Fe₂O₃/MWCNT Photocatalysts

The semiconductor Iron oxide (Fe₂O₃) is an environmentally friendly semiconductor with a narrow band gap that enables the absorption of the visible light. It is cheap, abundant, and non-toxic hence the possibility of its use in large scale environmental applications. Nevertheless, pure Fe₂O₃ photocatalysts are mainly characterized by a low electric conductivity and quick recombination of charge carriers. The presence of MWCNTs enhances the photocatalytic capabilities by accomplishing the movement of electrons and also increasing charge separation. Composites of Fe₂O₃/MWCNT have been demonstrated to be effective photocatalyst in the degradation of phenolic compounds as well as organic dyes. Secondly, iron oxide has magnetic properties which make it easy to recover the catalyst following treatment procedures.

F. CdO/MWCNT Photocatalysts

Cadmium oxide (CdO) is a n-type semiconductor with a narrow band gap usually with a range of 2.2 to 2.5 eV. The small band gap facilitates intense absorption of the visible light implying that CdO is a potential solar-driven photocatalyst. Combining CdO nanoparticles with multi-walled carbon nanotubes, the CdO/MWCNT heterostructures have a higher photocatalytic performance because of the improved separation of charges and the electron motion. The conductive network of nanotubes also enhances quick transport of the photogenerated electrons in CdO conduction band to the carbon nanotube surface, and hence this inhibits the electron-hole recombination. A few studies have indicated that CdO-based nanocomposites combined with other metal oxides like Fe₂O₃ and NiO exhibit high photocatalytic degradation of organic pollutants like methylene blue and herbicide compounds. The synergist effect between CdO, transition metal oxides and MWCNTs enhances the absorption of light, catalysis stability, and production of active oxygen species that cause degradation of pollutants.

G. Comparative Evaluation of Photocatalytic Efficiency

Metal oxide photocatalysts on MWCNT display various photocatalytic characteristics with respect to band gap energy, electron mobility and the coupling between them and the carbon nanotubes. A couple of them (TiO₂/MWCNT and ZnO/MWCNT) are the most widely researched as they are



highly catalytically stable and exhibit high photocatalytic efficiency. Nevertheless, CuO/MWCNT and Fe₂O₃/MWCNT systems are receiving more interest as visible-light-driven photocatalysts. Also, CdO-based heterostructures that are in combination with MWCNTs have gained some attention in the recent past because of their narrow band gap and high visible-light absorptions, making them efficient in the photocatalytic degradation of organic pollutants.

H. Influence of Structural Parameters on Photocatalytic Performance

It also relates to a number of structural parameters such as the photocatalytic performance of MWCNT-supported metal oxide composites depends on size of metal oxide nanoparticles, scattering of nanoparticles on the MWCNT surfaces, contact between nanotubes and semiconductor, carbon nanotubes: defect density, and porosity and surface area of the composite material. Smaller nanoparticles tend to offer more active sites and surface areas in which they are more likely to catalyze photoreactions. Even distribution of nanoparticles on the surface of the nanotube avoids aggregation and the availability of maximum interaction between pollutants and catalytic sites. A good interfacial contact between the metal oxides and MWCNTs improves the electron transfer and efficiency in charge separation.

VII. ADVANTAGES, LIMITATIONS, AND FUTURE PERSPECTIVES OF MWCNT-SUPPORTED METAL OXIDE PHOTOCATALYSTS

MWCNT-based metal oxide heterostructures are now considered to be the most promising photocatalytic materials to be used in the area of environmental remediation. Photocatalytic efficiency with the synergistic effect between conductive carbon nanotubes and semiconductor metal oxides is far greater than with the traditional photocatalysts. These are hybrid nanostructures that have the good electrical conductivity and adsorption potential of MWCNTs, and the high oxidative potential of semiconductor metal oxides. [35-37]. Although they have good performance, there are still some challenges that restrict their use in large scale wastewater treatment plants. Knowledge of the pros and cons of these materials is key to developing new generation photocatalysts that are more efficient, stable and greener. [38-42].

A. Advantages of MWCNT-Supported Photocatalysts

1) Enhanced Charge Separation: Among the key benefits of MWCNT-supported photocatalysts is the fact that they enhance photogenerated electron-hole pairs separation. Rapid recombination of charge carriers in conventional semiconductor photocatalysts can greatly impact negatively when it comes to photocatalytic efficiency. Carbon nanotubes are however, excellent conductors of electricity and have the ability to serve as electron acceptors. Photogenerated electrons are transferred between the semiconductor conduction band and the nanotube surface when nanoparticles of metal oxide are supported on MWCNTs. This movement of electrons inhibits the process of recombination and increases the lifetime of holes that were generated by photogeneration. This leads to an increased number of charge carriers to produce reactive oxygen species that leads to the degradation of pollutants.

2) Increased Surface Area and Adsorption Capacity: MWCNTs have very high surface area and adsorption of organic molecules. They have a graphitic structure that enables them to interact with aromatic pollutants like dyes and pharmaceutical compounds with strong p-p interactions. This increased adsorption leads to a closer approach of the pollutant molecules towards catalytic active sites thus increasing likelihood of oxidation reactions. As a result, the degradation efficiency of MWCNT-based photocatalysts can achieve significantly higher values than that of single semiconductor material.

3) Improved Electron Transport: The network of MWCNTs forms an interconnected tubular network, which offers highly conductive channels of transport of electrons. This network enables the electrons to move very fast through the structure of photocatalyst and reacts with dissolved oxygen molecules to produce reactive oxygen species. Enhanced electron transportation enhances photocatalytic reactions by encouraging sustained production of oxidizing radicals including hydroxyl radicals and superoxide radicals.

4) Enhanced Visible Light Absorption: A great number of metal oxide semiconductors have poor absorption in the visible part of the solar spectrum. MWCNTs can be incorporated to increase the use of visible light because of its high light absorption characteristics and a photosensitizer. This enhances light absorption leading to the photocatalytic reactions under the solar light and thus these materials are more applicable in a sustainable environmental environment.



5) *Structural Stability and Durability*: The photocatalysts based on MWCNTs have a high structural stability relative to pure semiconductor nanoparticles. The nanotube structure has a mechanical support that avoids aggregation of metal oxide nanoparticles. Moreover, the high affinity between MWCNTs and metal oxides promotes the life span of catalysts in such a way that it strengthens the catalysts every time the photocatalytic cycle is repeated, which results in high stability of the catalysts in the long run.

B. Limitations and Challenges

Irrespective of all the benefits, there are still numerous obstacles to the real implementation of MWCNT-supported photocatalysts.

VIII) High Production Cost: Production of high quality carbon nanotubes may involve complex processes like chemical vapor deposition that may make it expensive. This is an economic constraint which limits the use of MWCNT-based photocatalysts in large scale industrial use. Creation of low-cost techniques to synthesize carbon nanotubes is a valuable research agenda.

2) *Agglomeration of Nanoparticles*: Also, metal oxide nanoparticles can aggregate into the surface of MWCNTs in the process of the synthesis, resulting in the decrease in surface area and the number of the active catalytic sites. The efficiency of transfer of the electron between the semiconductor and the nanotubes is also lowered by the agglomeration. To achieve homogenous dispersal of nanoparticles one needs careful management of their synthesis conditions and surface functionalization of MWCNTs.

3) *Difficulty in Catalyst Recovery*: Even though carbon nanotubes are good catalysts, it may be difficult to separate and recover nanoscale photocatalysts in treated water. Catalyst particles can be suspended in water without the necessary recovery procedures, and they lead to the secondary contamination. One way to solve this problem has been suggested to be the magnetic alteration of photocatalysts or their immobilization on solid substrates. One way to solve this problem has been suggested to be the magnetic alteration of photocatalysts or their immobilization on solid substrates.

4) *Environmental and Toxicological Concerns*: The environmental effects of carbon nanotubes have taken its toll on the toxicity and ecological effects of this material in the long term. Though, according to multiple research, immobilized nanotubes remain relatively stable, the research deserves additional impact to learn more about their safety in environment. One of the issues of future research is to develop environmentally benign nanomaterials.

C. Future Research Directions

In a bid to overcome the existing limitations and to even improve on the photocatalytic performance, a number of research directions have been put forward on MWCNT-supported photocatalysts.

VIII) Development of Advanced Heterostructures: The future studies must be aimed at the fabrication of multi-component heterostructures that incorporate MWCNTs with several semiconductor materials. These hybrid systems can have a synergistic effect that can lead to improved charge separation and expansion of the light absorption spectrum. Such ternary composites as $\text{TiO}_2\text{-ZnO/MWCNT}$ or $\text{CuO-Fe}_2\text{O}_3\text{/MWCNT}$ photocatalysts are examples.

2) *Defect Engineering and Surface Modification*: Defects or doping elements on the surface of metal oxide nanoparticles can be added with a significant impact on photocatalytic activities. Defect engineering has the potential to enhance the charge carrier mobility and to enhance the number of active catalytic sites. Nanoparticle dispersion and enhancing the interfacial interactions can also be achieved by functionalizing MWCNTs on their surface.

3) *Development of Visible-Light Photocatalysts*: The majority of photocatalytic systems that exists today depends on ultraviolet radiation, which cuts across a minor portion of the solar spectrum. Future studies are supposed to focus on the design of visible-light-reactive photocatalysts that can use solar energy in a more efficient manner. Integration of narrow band gap semiconductors with MWCNTs could offer a strategy that is effective in accomplishing this objective.

4) *Integration with Other Advanced Oxidation Processes*: Incorporating photocatalysis with other developed oxidation



methods including electrochemical oxidation, Fenton reaction or persulfate activation can also be used to increase the level of efficacy in pollutant degradation. Complex wastewater treatment can be better salvaged using hybrid treatment systems.

5) *Large-Scale Application and Reactor Design:* The majority of photocatalytic experiments are done at the lab level. The work in the future needs to aim at coming up with reactor systems that can be scaled and the performance of the catalyst in the presence of actual wastewater. To scale down laboratory research into environmental technological work, pilot-scale demonstrations are required.

VIII. CONCLUSION

Metal oxide heterostructure photocatalysts on MWCNTs have become one of the most promising materials towards the development of superior photocatalytic degradation processes of organic pollutants in water and wastewater systems. Combining multi-walled carbon nanotubes with semiconductor metal oxides is an effective approach to address the fundamental drawbacks of traditional photocatalysts, which include quick recombination of photogenerated charge carriers and inability to absorb visible light. MWCNTs exhibit an impressive electrical conductivity, a high level of surface area, and high ability to adsorb different substances, which explains why they are highly effective at improving the photocatalytic activity of metal oxide semiconductors by enabling the efficient separation of charges and accelerating electron transport. The heterostructure interface between MWCNTs and metal oxide nanoparticles is important in enhancing the photocatalytic efficiency. Other charge transfer mechanisms, such as the formation of Schottky junction, Type-II heterojunction phasing, and Z-scheme photocatalyst system, play a role in improved separation of photogenic electrons and holes. These processes enhance the formation of reactive oxygen species like hydroxyl radicals, superoxide radicals and singlet oxygen that cause degradation and mineralization of organic pollutants.

Many synthesis techniques have been established in the production of MWCNT-based metal oxide composite and they include sol-gel, hydrothermal and solvothermal, chemical vapor deposition, precipitation, microwave-assisted and in-situ growth. These methods enable the accurate regulation of the structural characteristics, including particle size, morphology, surface area, and contact point between the

carbon nanotubes and the metal oxides. It is necessary to optimize these parameters to have high photocatalytic efficiency. Based on comparative analysis of various metal oxide-MWCNT systems, it is found that the $\text{TiO}_2/\text{MWCNT}$ and ZnO/MWCNT composite have good oxidation capacity and catalytic stability in degradation of dye pollutants. In the meantime, the CuO/MWCNT and $\text{Fe}_2\text{O}_3/\text{MWCNT}$ photocatalysts exhibit high potential photocatalytic activities when they are irradiated with visible light owing to their low band-gap energies. Enhanced photocatalytic activity of NiO/MWCNT composites is also exhibited due to the increase in charge carrier mobility and effective electron transport over the nanotube network. CdO based heterostructures in combination with the MWCNTs have small bandgap and high absorption in the visible light which is capable of effectively degrading organic pollutants through photocatalytic mechanisms. Even though they have great benefits, not all challenges are resolved yet and, therefore, before large-scale practical applications may be realized. These obstacles are the prohibitive price of carbon nanotubes synthesis, the possible agglomeration of nanoparticles when preparing the catalysts, the challenge in the recovery of the catalysts in the treated water, and the issue of the effect of nanomaterials on the environment. These shortcomings will need additional study on low cost synthesis protocols, immobilization process of catalysts, as well as the design of nanomaterials that would be environmental friendly.

Further studies on the subject matter should consider the creation of superior multi-component heterostructures, which incorporate MWCNTs with other types of semiconductor materials to increase the efficiency of photocatalysis and extend the range of light absorption. Besides, new opportunities to enhance charge transfer and catalytic activity can be offered by defect engineering, functionalization of surfaces and doping strategies. The combination of photocatalytic systems with other sophisticated oxidation processes can also provide good solutions to efficient treatment of complex streams of wastewater.

To sum up, metal oxide heterostructures on top of MWCNTs constitute a highly effective and highly versatile type of photocatalytic material that has become extremely promising in the area of environmental remediation. Further development of these nanocomposites can be achieved through continued enhancement of material design, synthesis processes and improvement of reactors, and hence these nanocomposites are likely to perform even better and become more quickly utilized in sustainable wastewater treatment technologies.



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