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# Graphene-Semiconductor Composites as Visible Light-Induced Photocatalyst

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Additional information is available at the end of the chapter

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## Abstract

Graphene-based composites produced by the incorporation of graphene into suitable semiconductors doped with various metals enable to induce the unique properties of the graphene, such as extended light absorption range, charge separation, and so high dye adsorption capacity. Therefore, graphene-based composites can provide to enhance the overall photocatalytic performance of the base semiconductor under the visible-light, and to open up new pathways to high-performance photocatalyst for the future applications. This chapter of the book focuses on the structural and optical properties of the graphene-semiconductor-based composite structure. Furthermore, final photocatalytic properties of the graphene-based composites can be controlled by applying different synthesis routes. Common synthesis methods of the graphene-semiconductor composites such as sol-gel, solution mixing, *in situ* growth, hydrothermal growth, and solvothermal method are discussed on the resultant visible-light photocatalytic property of the these composites. At the same time, doping of the graphene-semiconductor material with metal ions also allows an improvement of the visible light-induced photocatalytic activity. Therefore, studies related with the effect of the dopant agent on the visible light photocatalytic activity are also reviewed in this chapter.

**Keywords:** graphene-semiconductor composites, photocatalyst, visible light degradation, structural-electronic properties, synthesis methods

## 1. Introduction

Environmental water contaminations originated from the organic dye compounds used in textile and paint industries and household chemicals are a continuous threat to human health. Generally, water treatment methods include primary and secondary treatment steps. While primary treatment of water is designed to physically remove organic solids by sedimentation and flotation, secondary treatment is aimed to biologically remove the residual organics from

wastewater by utilizing microorganisms in a controlled environment [1]. As an advanced treatment step, desalination technologies such as reverse osmosis, electrodialysis, ion exchange, and freeze desalination were applied. However, the above-listed traditional biological treatment techniques can be ineffective in decolorizing dye molecules. Due to the specific needs during the degradation of organic pollutants, there has been a strong interest in the development of efficient treatment method.

Recently, in order to degrade organic dye compounds, many researchers have studied on the photocatalyst material which is usually a wide band gap semiconductor in the presence of solar energy. The photocatalytic reaction mechanism is based on the ability to create electron-hole pairs under photo illumination. For photocatalytic devices, sunlight, which is abundantly available as natural irradiation energy, and UV irradiation sources can be conveniently exploited for the irradiation of semiconducting materials. For practical applications, development of an efficient, reproducible, and cost-effective visible light-induced photocatalyst is desirable for the large-scale production of catalyst. Recently, many research papers are dedicated to the semiconductor-based [zinc oxide (ZnO), cadmium sulfide (CdS), cadmium selenide (CdSe), iron oxide ( $\text{Fe}_2\text{O}_3$ ), tin oxide ( $\text{SnO}_2$ ), zinc sulfide (ZnS), etc.] [2], carbonaceous-based (nanotubes, fullerenes, graphene, etc.) [3], and semiconductor-carbonaceous composite photocatalysts [4]. Over the recent decades, semiconductor-based photocatalysts have attracted great attention in water purification because of their high photosensitivity, environment-friendly non-toxic nature, and low cost [5].

Although semiconductor-based photocatalysts, especially  $\text{TiO}_2$ , have been recognized as the most effective catalysts and are widely used in the removal of toxic or hazardous organic pollutants, several fundamental issues must be addressed before the photocatalysts are efficiently used for the industrial applications. For example, large bandgap of the  $\text{TiO}_2$  photocatalyst provides only absorbance of UV light with a wavelength of less than 385 nm, which accounts for less than 10% of solar irradiation. In addition, fast recombination of electron-hole pairs limits the applicability of  $\text{TiO}_2$  as photocatalyst. These problems are the cause of low photosensitivity and high cost, and makes these types of photocatalyst unfavorable for large scale production.

In the family of carbon nanomaterials, graphene-based photocatalyst activated under the visible light seems to be the preferred candidates because of their outstanding advantages such as low cost, innocuous nature, ease of availability/processing, and suitability of their structure to create composites with semiconductors [6]. Graphene is a two-dimensional material having  $\text{sp}^2$ -bonded carbon atoms tightly packed into a two-dimensional honeycomb structure. After discovering by Novoselov et al. in 2004 [7], graphene has been attracting more and more attention because of their unique properties such as excellent mobility of charge carriers at room temperature ( $100,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) [8], theoretically large surface area ( $2630 \text{ m}^2 \text{ g}^{-1}$ ) [9], optical transparency [10], excellent mechanical strength ( $2.4 \pm 0.4 \text{ TPa}$ ) [11], high thermal conductivity ( $\sim 5000 \text{ W m}^{-1} \text{ K}^{-1}$ ) [12], exhibiting half-integer room-temperature quantum Hall effect [13], capacity of sustaining large electrical current density ( $10^8 \text{ A cm}^{-2}$ ) [14], etc. It has attracted a great attention for their potential applications in variety fields such as catalyst

[15], sensors [16], nano electronics [17], energy conversion [18], and water treatment [4]. In the past few decades, there is an ever-increasing interest in the photocatalytic applications of graphene [19].

To improve the photocatalytic efficiency of the semiconductor-based metal oxides and graphene-based photocatalysts under the visible-light, integration of semiconductor metal oxides with graphene has been one the most popular approach due to theoretically large specific-surface area and high intrinsic electron mobility of graphene at room temperature [3]. Graphene behaves as an electron acceptor in this type composite photocatalysts. Generally, degradation of the organic dye molecules takes place with anchoring onto the surface of semiconducting particles by means of covalent bonding and ion-pair type association. In the literature, different types of graphene-based composites (graphene-semiconductor, graphene oxide (GO)-semiconductor, and reduced graphene oxide-semiconductor; as a semiconductor material  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{CdS}$ ,  $\text{Zn}_2\text{SnO}_4$ , etc.) can be found. Graphene-semiconductor composites have been fabricated through simple mixing and/or sonication, sol-gel process, liquid-phase, hydrothermal, and solvothermal methods. Furthermore, as a strategy to improve visible-light photocatalytic efficiency of graphene-based composites, doping semiconductor with metal ions is an effective way. In this chapter of the book, structural and optical properties of the graphene-semiconductor composites, general synthesis methods, and photocatalytic properties of these composites under the visible light are discussed. Finally, the effect of the doping on the resultant visible light-induced photocatalytic activity of graphene-semiconductor composites is reported.

## 2. The graphene-semiconductor composites; structural and optical properties

Over the last decades, spreading of diseases due to organic dye compounds caused by noxious chemicals has become a global public health issue. Thus, scientists have focused on the studies of the wastewater treatment and antibacterial applications required to use a photocatalyst material. In the studies to prevent the spreading of the dye molecules, carbonaceous materials draw attention because of offering high photocatalytic activity [6].

Carbon is one of the most abundant elements in the world and is necessary for life in the nature. Carbon has different forms or allotropes which include buckminsterfullerene (or just simply fullerene), diamond, graphite, etc. The discovery of buckminsterfullerene ( $\text{C}_{60}$ ) [20] which is a cluster of 60 carbon atoms brought the Nobel Prize in Chemistry in 1996 to Kroto, Curl, and Smalley. On the other hand, diamond is considered as the hardest material, whereas graphite is extremely soft. Graphite is a naturally occurring mineral and has parallel carbon atom layers which are named as graphene, so that graphene can be defined as a single and flat layer of graphite which consists of  $\text{sp}^2$ -bonded carbon atoms packed into a two-dimensional (2D) honeycomb lattice. Graphene was first isolated as a single-layer from graphite in 2004 by Novoselov et al. using the mechanical exfoliation technique [7]. This technique is based on the repeated peeling of thin flakes from a piece of graphite with a scotch tape. This success

has led to an incredible increase in theoretical and experimental studies about graphene in the recent years. Geim and Novoselov were awarded the Nobel Prize in Physics 2010 because of the producing, isolating, identifying and characterizing graphene.

Apart from the exfoliation method, alternative ways for the producing of graphene have been developed: epitaxial growth on silicon carbide is based on the evaporating silicon from SiC with heating and leaving a thin carbon layer [21]. Chemical vapor deposition on metal surfaces is one of the fabricate methods of graphene. A transition metal (nickel) film is exposed to a hydrocarbon gas at high temperature under ambient pressure. Cooling the sample, solubility of carbon in the transition metal film decreases and an ultrathin graphene layer is formed over the metal surface [22, 23].

Besides these methods, the chemical reduction of graphene oxide (GO) derived from chemical exfoliation of graphite is one of efficient and low cost ways in order to obtain large scale graphene which was first reported by Ruoff's group [24–27]. GO is a strongly oxidized form of graphene which can be obtained using oxidizing agents from graphite oxide. Graphite oxide is generally obtained with Hummers' method [28] which involves the oxidation of graphite powder in the mixture of concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ), sodium nitrate ( $\text{NaNO}_3$ ), and potassium permanganate ( $\text{KMnO}_4$ ). After oxidation, the layers of graphite oxide, which consists of GO sheets exhibit hydrophilicity, allows water to intercalate between the sheets and disperse them. So, the exfoliation of graphite oxide is facilitated and a layer graphene or GO is produced via ultrasonic treatment in aqueous media. GO contains various types of oxygen containing functional groups such as hydroxyl, epoxide, and carbonyl groups caused by heavily oxidation. Due to the disruption of the conjugated structure by functionalization, covalent bonds of carbon and oxygen atoms become more intense and the resistance of the layer increases, so the conductivity of GO decreases. For this reason, a more efficient chemical reduction method is required in order to obtain GO with high conductivity. In other words, GO needs to be reduced by removing the oxygen-bearing group. The term of the reduced GO (rGO) is used to refer to as chemically modified graphene, chemically derived graphene, or reduced graphene [29].

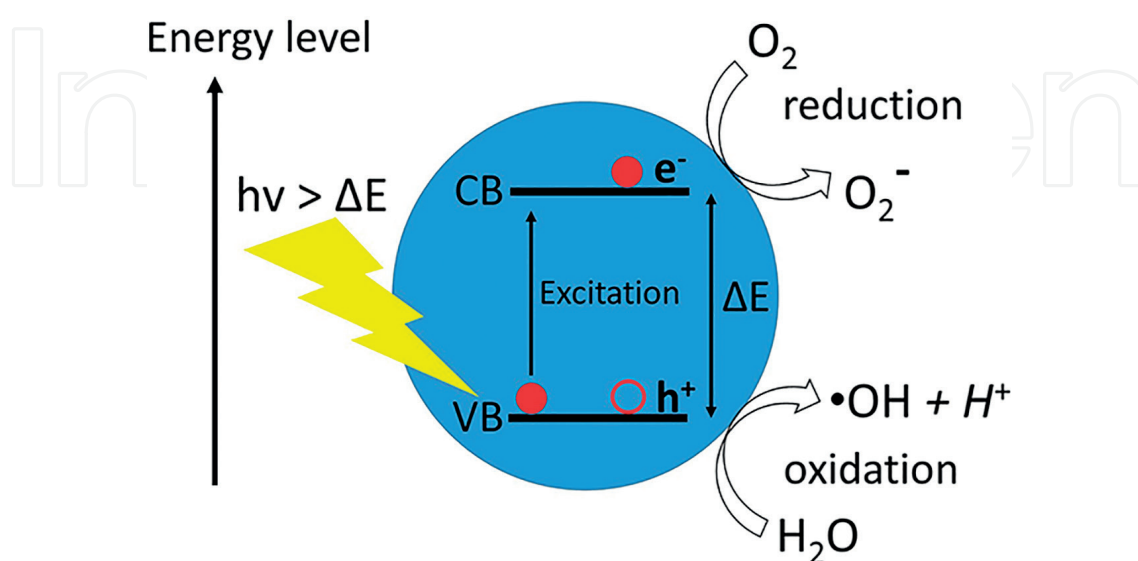
There are various GO reduction methods which can be achieved through chemical, thermal, or electrochemical ways [30, 31]. In order to obtain rGO with chemical way, reducing agents are used such as hydrazine ( $\text{N}_2\text{H}_4$ ) [27], hydroquinone (HQ) [32] sodium borohydride ( $\text{NaBH}_4$ ) [33], and hydriodic acid (HI) [34]. Hydrazine, which is one of the most widely used reducing agents, has been used to reduce GO in order to remove the functional groups. However, hydrazine is highly toxic and incorporates C–N groups which increase the resistance of GO sheets due to scattering electrons. During the thermal reduction, GO is exposed to a heating process with the evolved gases. Decomposing of the epoxy and hydroxyl groups with temperature generates high pressures that separate the graphene sheets [35–37]. However, thermal reduction damages the structure of graphene sheets and causes mass loss [31, 35].

Another method is electrochemical reduction, where the electron behaves as the reducing agent. In the electrochemical approach, a thin GO film is deposited onto the surface of the substrates such as flexible plastic, glass, indium tin oxide, and glassy carbon [38, 39]. Reference and auxiliary electrodes are placed and the electrochemical reduction process is performed on the GO with cyclic voltammetry in a buffer electrolyte. Oxygen-containing functional groups in GO can be reduced by the applying various voltages.



Exhibiting of the photocatalytic properties of the graphene-based materials depends on the creating free radicals in the photocatalytic reaction. However, fast recombination of the electron-hole pair, which is formed under the light source, is the major disadvantage of the using of the graphene as a photocatalyst material. In order to overcome this problem, chemical modification of the graphene is done with bioactive nanoparticles or light sensitive materials. Due to the expensive cost of gold and silver, which are commonly used as nanoparticles [40, 41], the applications of the photocatalyst composite formed with these elements and graphene is limited in large scale applications. The chemical modification of the graphene with light sensitive materials is another way to improve photocatalytic activity of graphene.  $\text{TiO}_2$  is the light sensitive material used most commonly up till now. However, an alternative material which will form a composite structure with graphene is still being sought due to small portion solar light usage of  $\text{TiO}_2$ .

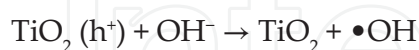
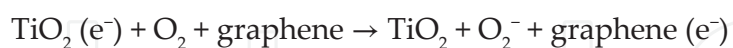
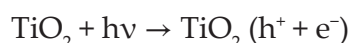
Since the seminal discovery of water splitting on  $\text{TiO}_2$  with photoelectrolysis by Fujishima and Honda in 1972 [42], there is a growing interest in the photocatalysis of semiconductors. Many types of semiconductor photocatalysts have been reported up to now including  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{CdS}$ ,  $\text{CdSe}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{SnO}_2$ ,  $\text{ZnS}$ , etc. Among the many different semiconductor materials,  $\text{TiO}_2$  has been widely used in the light-induced photochemical reactions because of its low cost, nontoxicity, chemical stability, and its highly oxidizing. However, the applications of  $\text{TiO}_2$  are restricted due to fast recombination rate of photogenerated electron-hole pairs and its large band gap (3.2 eV) that requires the UV light irradiation. **Figure 1** shows a schematic illustration of the photocatalytic reaction mechanism. With the absorption of the photon energy, which has greater than that of the band gap of the semiconductor material, electron in the valance band becomes excited and jumps to the conduction band. Hence, a positively charged hole forms in the valance band. As a result of the recombination with the electron, this the positively charged hole can oxidize water molecules and provide to form hyper-reactive hydroxyl free radicals ( $\bullet\text{OH}$ ). These radicals induce the photodegradation of the dye molecules.



**Figure 1.** A schematic illustration of the photocatalytic reaction mechanism.

There has been considerable interest on the enhancement of photocatalytic activity by the combination of carbonaceous materials with semiconductors because of its extraordinary structural and electronic properties. The pioneering work of Williams et al. about UV-induced photocatalytic reduction of GO [43] has increased the interest in graphene-based semiconductor photocatalysts. They exposed a mixture of graphene oxide and  $\text{TiO}_2$  to UV light in ethanol. When the holes that occur as a result of excitation are consumed to produce ethoxy radicals, the electrons accumulate within  $\text{TiO}_2$  particles and reduce the oxygen containing functional groups on GO surface. Zhang et al. observed a significant enhancement in the photocatalytic activity of the photodegradation of methylene blue (MB) with chemically bonded graphene  $\text{TiO}_2$  P25 (with particle size around 25 nm) nanocomposite photocatalyst [44]. These nanocomposite photocatalysts were obtained with the reduction of GO and loading of P25 using hydrothermal method.

Photocatalytic enhancement in the graphene-semiconductor composites can be explained with three mechanisms due to unique properties of graphene: (i) extension the wavelength of the absorbed light due to the chemical bonds which narrow the band gap of semiconductor and transparency of graphene; (ii) suppression of the recombination of photogenerated electron hole pairs. The excited electrons transfer from the conduction band of semiconductor to graphene which is an acceptor due to its long  $\pi$  conjugation structure [45]. With fast charge transportation and effective separation of electron-hole pairs, the charge recombination is suppressed; (iii) increasing absorptivity of pollutants. Model dyes or contaminant molecules usually have an aromatic structure and they could be conjugated to the aromatic regions of the graphene. This absorptivity increases the amount of contaminant molecules on the catalyst and improves a significant increase of photocatalytic degradation [44–46]. The role of adsorption of graphene in photocatalysis was studied by Liu et al. [47]. They have shown that rGO captures dye molecules from water through adsorption and photoinduced electrons from  $\text{TiO}_2$  through surface during photocatalytic process. The photocatalytic mechanism in graphene- $\text{TiO}_2$  composites can be briefly summarized as follows:



In order to increase the photocatalytic activity of  $\text{TiO}_2$ , it is required that the slowing of the charge recombination rate and the reduction of the energy band gap. These processes have been done with increasing the porosity and surface area [48], doping with metals [49] or non-metals [50], and surface coupling with metals [51] or semiconductors [52]. While there is a great challenge and effort to explain the mechanism of photocatalytic enhancement observed in graphene-semiconductor composites, it is still unclear.

Apart from  $\text{TiO}_2$ , there are some semiconductors which have been studied in the photocatalysis of graphene-semiconductors composites as photocatalysts. One of these semiconductors, ZnO, is a promising candidate for environmental contaminations due to its strong oxidizing power, good photocatalytic activity, and low cost. The crystal structures of ZnO exist in rock-salt, zinc blende, and wurtzite (hexagonal) forms. Wurtzite is the most commonly used and

thermodynamically stable phase of ZnO [53]. ZnO has similar characteristics to TiO<sub>2</sub> due to its large band gap (3.37 eV) and UV light sensitivity. ZnO has been used in the photocatalytic reduction of GO in ethanol by Williams and Kamat [54]. Similar to mechanism of graphene-TiO<sub>2</sub> composites, electron-hole pairs generated by UV excited ZnO create electron-hole pairs due to UV irradiation as a photocatalyst and degrade the pollutants [55].

Although there have been a lot progress in the photocatalysis of graphene-based semiconductor composites, very small portion of the solar spectrum is utilized due to UV light sensitive semiconductors. In recent years, semiconductors such as SnO<sub>2</sub> [56], BiVO<sub>4</sub> [57], CdS [58], and CdSe [59] have been used as photocatalysts in graphene-semiconductor composites under visible light. These semiconductors generally have been chosen due to their proportional narrow band gaps. For example, the energy band gap of CdSe is 1.67 eV, so it can be used under visible light in order to use solar spectrum efficiently. Also, use of graphene enhances the photoactivity of graphene-semiconductor composites due to separation of charges, suppression of the charge recombination, and facilitation of charge transfer. There is a great challenge to improve the efficient conversion of solar spectrum in the visible light region photocatalysis which will be mentioned in section 4.

### 3. Common synthesis methods of the graphene-semiconductor composites

At the present time, many different methods have been developed to synthesize graphene-semiconductor composites. Most commonly used synthesis methods are sol-gel, solution mixing, *in situ* growth, hydrothermal, and solvothermal methods. More detailed explanations of these syntheses are given below.

#### 3.1. Sol-gel method

Sol-gel method is the process of the suspending of particles in a liquid and placing of these particles onto a surface from a solution. Zhang et al. [60] synthesized graphene-TiO<sub>2</sub> composites employing a sol-gel method using tetrabutyl titanate (TBOT) and GO as starting materials. At first, they dispersed the graphene sheets into ethanol solvent, and then dropped TBOT into the suspension. The obtained sol was dried to form precursor. Finally, graphene/TiO<sub>2</sub> composites were synthesized by annealing the precursor for the crystallization. They investigated the photocatalytic activity of the graphene-TiO<sub>2</sub> composites using hydrogen evolution from water photo-splitting under UV-Vis illumination. Liu et al. [61] reported a preparation of graphene-TiO<sub>2</sub> composites using titanium precursors and rGO by a sol-gel method and observed an enhancement in the photocatalytic activity under visible light.

#### 3.2. Solution mixing method

Solution mixing method is one of the most common and easiest methods for the preparation of graphene/semiconductor composites which are prepared using the suspensions of graphene



and semiconductor nanoparticles. Paek et al. [62] prepared graphene-SnO<sub>2</sub> composites using solution mixing method. They first prepared graphene sheets via the chemical reduction of graphite oxide, and then obtained SnO<sub>2</sub> nanoparticles through the controlled hydrolysis of SnCl<sub>4</sub> with NaOH. Reduced graphene sheets were dispersed in the ethylene glycol, and reassembled in the presence of SnO<sub>2</sub> nanoparticles to form the composites. Bell et al. [63] prepared rGO-TiO<sub>2</sub> composites by mixing suspensions of TiO<sub>2</sub> powder with the GO suspension ultrasonically and exposing the suspension to UV light. Sonication has been used to dissolve GO in non-polar solvents. Using a similar technique, Akhavan and Ghaderi [64] prepared the graphene-TiO<sub>2</sub> thin films and studied the antibacterial activity of the graphene-TiO<sub>2</sub> composite thin films under solar light irradiation.

### 3.3. *In situ* growth method

*In situ* is derived from Latin meaning in the reaction mixture in chemistry. *In situ* growth is based on the direct reaction of graphene and semiconductor nanoparticles in solution, and widely used to prepare graphene-semiconductor composites. Lambert et al. [65] synthesized GO-TiO<sub>2</sub> composites via the hydrolysis of TiF<sub>4</sub> in the presence of aqueous dispersions of GO then obtained rGO-TiO<sub>2</sub> adding hydrazine after sonication. Zhang et al. [66] prepared rGO-SnO<sub>2</sub> and rGO-TiO<sub>2</sub> composites using *in situ* method. They reduced GO dispersion to rGO with adding SnCl<sub>2</sub> or TiCl<sub>3</sub>. Sn<sup>2+</sup> and Ti<sup>3+</sup> ions were converted to SnO<sub>2</sub> or TiO<sub>2</sub> nanoparticles and rGO-semiconductor composites were studied for the photocatalytic properties for degrading rhodamine B (RhB) under visible light. Li and Cao [67] obtained graphene-ZnO composites via a chemical deposition route. GO suspension was mixed with Zn<sup>2+</sup> ions containing solution then NaOH was added to the mixture. The powder obtained from the separated and dried solution was dispersed in NaBH<sub>4</sub> solution. After hydrothermal treatment, graphene-ZnO composites were obtained and used in the degradation of RhB under UV or visible light irradiation.

### 3.4. Hydrothermal growth method

Hydrothermal method can be defined as the process of growing crystals in the presence of water as a solvent at high temperature and pressure in an autoclave which is a closed reaction vessel. This method is one of the conventional methods in order to obtain graphene-semiconductor composites. Zhang et al. [44] obtained a chemically bonded graphene-TiO<sub>2</sub> (P25) nanocomposite with graphene oxide and P25, using a facile one-step hydrothermal method. In their work, GO was dissolved in a solution of distilled water and P25 was added to the solution. Then suspension was placed in an autoclave so GO was reduced and P25 nanoparticles were deposited on the graphene simultaneously. They measured an enhancement in the reaction rate of the photodegradation of MB using graphene-P25 nanocomposites under UV and visible light. Liu et al. [68] demonstrated a one-pot hydrothermal approach to prepare rGO-ZnO composites and applied these composites as photocatalyst in order to decompose MB under UV and visible light. GO was dispersed in aqueous solution with ultrasonication and then Zn powders were mixed with GO suspension. Zn powder was used as a reducing agent and a precursor of ZnO. Ye et al. [69] prepared CdS-graphene and CdS-carbon

nanotube nanocomposites prepared with hydrothermal method and used these nanocomposites as photocatalysts for the hydrogen evolution and the degradation of methyl orange under visible-light irradiation.

#### 4. Visible light photocatalytic activity of the graphene-semiconductor composites

In recent decades, graphene-semiconductor-assisted photocatalysts have attracted considerable attention in not only wastewater treatment but also antibacterial applications due to their high photosensitivity, low cost, and environment-friendly non-toxic nature [70]. Widely used photocatalyst semiconductors such as  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{CdS}$ ,  $\text{CdSe}$ , etc., do not fulfill all the practical needs as a photocatalytic material, since activation of these catalysts require high-energy UV light, resulting in low efficiency in the visible and near infrared regions. The low separation efficiency of electron-hole pairs and photo-corrosion are other principle problems that inhibit the photocatalytic activity of these semiconductors. In order to solve these limiting factors and enhance the visible light photocatalytic activity of the semiconductors, considerable efforts have been spent on the improvement of the photocatalytic activity by means of noble metal deposition [71], transition-metal doping [2], and semiconductor combination [72]. According to purely used semiconductor, better photocatalytic activities are obtained when the above listed methods are used. However, the recombination of electron-hole species in the semiconductors is still a problem for the photocatalytic applications.

Semiconductor-matrix system is another method to improve photocatalytic property due to impede the recombination of electron-hole species in the semiconductors by efficient electron transport matrices, such as carbon nanostructures or conductive polymer films, or by molecular electron delay semiconductor structures. Among these techniques, carbonaceous nanomaterials seems to be the most promising matrix system due to enhancement of the photocatalytic properties of semiconductors due to their unique structures that can bring attractive characteristic to photocatalyst materials. Photocatalyst and the delocalized conjugated carbonaceous materials have similar energy level providing an interface hybrid effect between these materials. This effect results in rapid charge separation and slow charge recombination in the electron-transfer process.

Among the various types of semiconductor materials,  $\text{TiO}_2$  has provoked great interest as photocatalyst due to its excellent photocatalytic performance, high stability, low cost, and relatively low toxicity, in comparison to other semiconductor metal oxides [73]. Recently,  $\text{TiO}_2$ -carbonaceous-based composites attract great attention for their potential applications in air and water purification due to their outstanding photocatalytic activity. These types of composites can be divided into three main groups; carbon-doped  $\text{TiO}_2$ ,  $\text{TiO}_2$  fixed activated carbon, and carbon-coated  $\text{TiO}_2$ . Although unique advantages of carbon-based materials as composite material such as chemical stability and inertness in acid and basic media, unusual tunable structural, electronic and chemical properties [74, 75], the lack of reproducibility, and the weakening of the light intensity at catalyst surface have still remained as challenges

[76, 77]. Great photocatalytic activity under the visible light is another limiting factor that impedes the photocatalytic marketing.

Zhang et al. synthesized  $\text{TiO}_2$  (P25)-graphene composite via a one-step hydrothermal method and investigated photocatalytic activity of the composites under the both UV and visible light [44]. They found that under both the light sources, the P25-graphene composite structure exhibited better photocatalytic degradation of the dye and enhanced charge separation and transportation properties than that of the pure P25 and P25-carbon nanoparticle structure. They also found that absorption spectra of pure P25 and P25-graphene composite structure shows a red shift to higher wavelength for composite structure exhibiting a photo-responding range at approximately 430–440 nm which corresponds to the violet-blue region in electromagnetic spectrum. Therefore, semiconductor-graphene composite structure offers a more efficient utilization of the solar spectrum under visible light irradiation and expected to assist its use in practical environmental protection issues. The improvement in the photocatalytic property of the P25-graphene composite structure can be attributed to its extended photo responding range by means of chemical bonds and selective adsorption of the aromatic dye on the catalyst. This noncovalent adsorption is driven by the  $\pi$ - $\pi$  stacking between aromatic regions of the graphene and dye molecule. Similar adsorption has also been reported for the conjugation between aromatic molecules and carbon nanotubes [78].

Li et al. reported that graphene-CdS visible light driven photocatalysts composites act as the clean and renewable hydrogen production path through water splitting [58]. They found that under the visible light, pure CdS exhibited little photocatalytic activity due to the rapid recombination of CB-electrons and VB-holes. The photocatalytic activity of CdS semiconductor was improved by the graphene addition since larger surface area of graphene provides more active adsorption sites acting as photocatalytic reaction centers. Graphene also provides a reduction in the recombination probability of the photo-excited electron-hole pairs and an increasing the number of the charge carriers to form reactive species. However, there is saturation graphene amount in the visible light-induced photocatalytic activity due to “shielding effect.” The high weight addition of graphene into composite structure reduces the light irradiation depth due to its opacity, thus and reaction medium restricts the efficiency of graphene in promoting the photocatalytic activity of graphene-semiconductor composites [44, 79, 80]. Due to intrinsic “shielding effect” leading to achieve an optimal photocatalytic activity enhancement with graphene addition into semiconductor material, generally 5 wt.% graphene is incorporated into composite structure.

For the investigation of visible light photocatalytic mechanism, Wang et al. reported synthesis of high-quality nanosized anatase ultra-thin  $\text{TiO}_2$  nanosheets grown on graphene nanosheets with {001} facets via a simple one-pot solvothermal synthetic route [81]. They proposed that  $\text{TiO}_2$ /graphene nanocomposites show better visible light photocatalytic activity than pure  $\text{TiO}_2$  and P25 due to prefer transferring of the photo-induced electrons via  $\text{Ti}-\text{O}-\text{C}$  between  $\text{TiO}_2$  and C interaction. This electron transection delays the recombination of photo-induced charge carriers and extends the carrier lifetime, therefore provides to the enhancement of photocatalytic performance of the composite structure under the visible light. For this enhancement of the visible light photocatalytic activity of the composite structure, Wang et al.

proposed that the effective separation of photo-induced charges induced by  $\text{TiO}_2$  nanosheets with exposed {001} facets and graphene plays an effective role.

## 5. Effects of doping on the visible light photocatalytic property of the graphene-semiconductor composites

Generally, in order to improve visible light-induced photocatalytic activity of the semiconductor-based, carbonaceous-based, and semiconductor-carbonaceous composite photocatalysts, the band gap energy of photocatalyst material should be reduced or split into several sub-gaps. Doping semiconductor-based photocatalyst material with various noble metals such as gold, palladium, and silver and transition metals such as cobalt, chrome, copper, iron, molybdenum, etc. become an exciting area in research [5, 82, 83]. Yildirim and Durucan reported that electronic band structure of the semiconductor ZnO nanoparticles can be tunable with substitutional incorporation of Cu ions into ZnO crystal lattice providing to the absorbing more photons [84]. Therefore, transition metal doping enables semiconductor photocatalyst to expand its photo response from the UV light region into the visible range and to decompose organic pollutants more effectively.

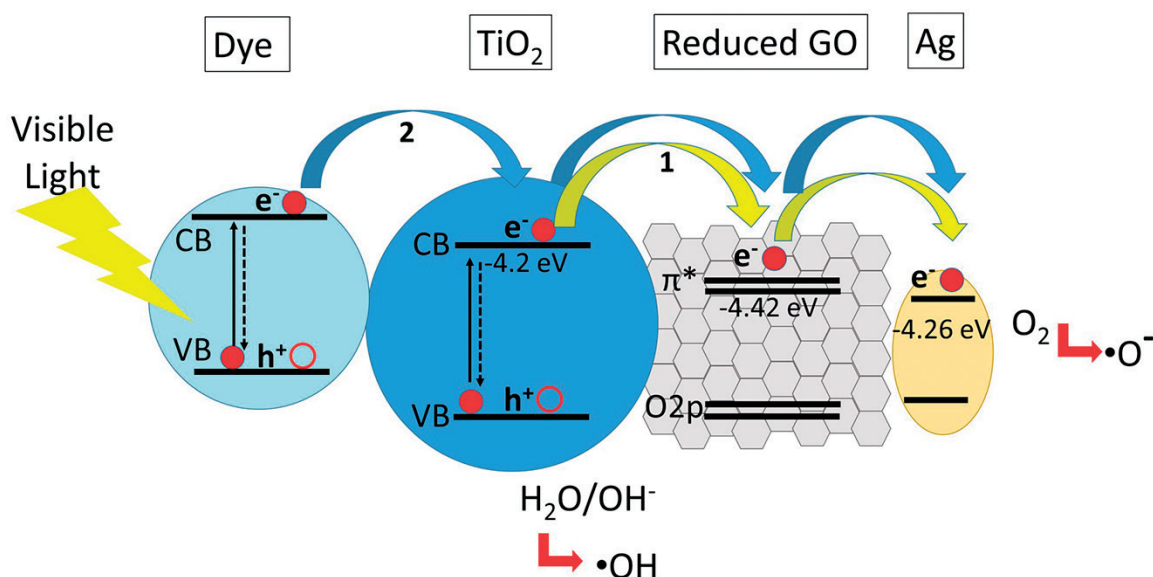
For the graphene-semiconductor-based composites, in order to improve the visible light-induced photocatalytic activity, the manipulation and optimization of charge carrier transfer across the interface between semiconductors and graphene is important [58]. Up to now, researchers have expressed an opinion that an intimate interfacial contact is a key aspect for the sufficient utilization of electron conductivity of graphene so enhancement of the photocatalytic activity of the graphene-semiconductor-based composites [85, 86]. However, tunable interfacial atomic charge carrier transfer pathways are also important for the photocatalytic activity of the composites. Atomic charge carrier transfer pathways can be controlled by means of the rational synergy interaction between incorporated individual components in graphene-semiconductor composites [3].

Zhang et al. reported a detailed study to investigate the effect of the various types of metal ion ( $\text{Ca}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$ ) addition into CdS which is a well-known II–VI semiconductor with suitable band gap (2.4 eV) matching well with the spectrum of sunlight [87]. Incorporation of the metal ions was performed by using the simple solvothermal method. They proposed a mechanism for the formation of the metal interfacial layer matrix between semiconductor CdS and graphene and found that incorporation of the small amount of metal ions into the interfacial layer matrix between the semiconductor and graphene considerably enhance the visible light-induced photocatalytic activity of graphene-semiconductor composites. Interfacial layer is maintained by the electrostatic attractive interaction between negatively charged oxygen atoms of the functional groups on the GO and positively charged metal ions. Furthermore, binding interaction between defect sites on the GO sheet and metal ions could also promote to more effectively attaching of metal ions onto the GO sheet. Zhang et al. also found that for the highest photocatalytic activity under the visible light irradiation, the optimal weight addition ratio of graphene is 5 wt.%. It is quite interesting to observe the best



catalytic activity from 5 wt.% graphene addition since generally less than 5 wt.% graphene containing graphene-semiconductor composites exhibit a proper synergy interaction between graphene and the semiconductor due to the shielding effect of graphene. Graphene addition maintains the intimate interfacial contact between the semiconductor and graphene transfer charge carriers and expands the lifetime more effectively under visible light irradiation. Therefore, with the introducing small amount of metal ions into composite structure, the photocatalytic activity of the composite is considerably improved. Under visible light irradiation, this composite structure can be used anaerobic reduction of nitro compound and the aerobic selective oxidation of alcohol.

In order to improve the visible light-induced photocatalytic activity, doping was found to be helpful due to tailoring the electronic properties of the composites. Mechanism of the organic dye degradation by the semiconductor catalyst is based on two photocatalytic routes for the excitation under visible-light irradiation. A schematic representation of the photocatalytic reaction mechanism for the Ag-doped  $\text{TiO}_2$ -rGO composite structure is shown in **Figure 2**. The first photocatalytic route is based on the excitation of the semiconductor  $\text{TiO}_2$ . Light irradiation causes to electron excitation forming photogenerated electron in the conduction band (CB)/hole in the valence band (VB). Photoinduced electron transfer could take place from CB of  $\text{TiO}_2$  ( $-4.2$  eV) to work function of the graphene oxide ( $-4.42$  eV) [88]. Furthermore, the work function of the Ag nanoparticles ( $-4.74$  eV) is located at a lower energy level than that of GO [89]. Therefore, photoinduced electrons could easily move from GO to Ag nanoparticle surface and chemical reactions with the dye molecules occur as photogenerated charges move to the particle surface. The recombination of photoinduced electrons and holes is minimized, thus reactive oxygen radicals ( $\cdot\text{O}_2^-$ ) is formed as a reaction of these electrons with adsorbed oxidants (usually  $\text{O}_2$ ). At the same time, the holes in the VB could react with  $\text{H}_2\text{O}/\text{OH}^-$  to generate hydroxyl radicals ( $\cdot\text{OH}$ ) which contribute to dye degradation.



**Figure 2.** A proposed mechanism for the photodegradation of dyes over  $\text{TiO}_2$ -Ag-rGO composite under visible light irradiation.



The second photocatalytic route includes the excitation of dye under visible-light irradiation. In this way, photogenerated electrons excited from dye could transfer to first  $\text{TiO}_2$ , then to graphene oxide, and to lastly Ag nanoparticle surface as shown in **Figure 2**. Therefore, dye molecules provide also to an improvement of the photocatalytic ability by means of acting as a visible light sensitizer and offering a self-degradation. For the both routes, while reaction of the excited electrons and dissolved oxygen molecules produces oxygen peroxide radicals, reaction between the positive charged hole and the hydroxide ion derived from water forms hydroxyl radicals. As a result of these reactions, an enhancement of the photocatalytic activity of  $\text{GO-TiO}_2\text{-Ag}$  nanocomposites is expected.

Lu et al. reported that manganese oxides supported on  $\text{TiO}_2$ -graphene nanocomposite catalysts [90].  $\text{MnO}_x$  active component was incorporated into  $\text{TiO}_2$ -graphene nanocomposites prepared with the sol-gel method and contained different amount of graphene (0–2 wt.%). These  $\text{MnO}_x$  incorporated  $\text{TiO}_2$ -graphene catalysts exhibit excellent structure and electrical properties, which favored the catalytic reaction. Due to different oxide states of Mn ( $\text{MnO}$ ,  $\text{MnO}_2$ ,  $\text{Mn}_2\text{O}_3$ , and nonstoichiometric  $\text{MnO}_x/\text{Mn}$ ) Mn incorporation provides multiple valence states which supports electron transfer and so redox reaction on the surface of the composite catalyst.

## 6. Conclusions

In recent decades, photocatalysis is attracting more and more attention due to their potential for solving environmental problems originated from organic dye compounds which cause to serious detrimental effects for living ecosystems as a result of water pollution. Up to now, many research papers and review articles are dedicated to development of the photocatalytic materials. Semiconductor metal oxide especially  $\text{TiO}_2$  and  $\text{ZnO}$  have been used as two most preferred materials widely used in the removal of toxic or hazardous organic pollutants. However, due to their wide band gap, semiconductor-based photocatalysts can only absorb UV light comprising for less than 10% of solar irradiation. Therefore, expanding the absorption spectral range to exploit the more abundant source of light energy and even poor illumination of interior lighting coming from the sun is critical in development of the photocatalyst. According to literature, the photocatalytic activity of semiconductor materials can be improved by the graphene addition since graphene with larger surface area provides more active adsorption sites acting as photocatalytic reaction centers. Graphene also provides a reduction in the recombination probability of the photo-excited electron-hole pairs and an increasing the number of the charge carriers to form reactive species. For this purpose, graphene-semiconductor-based composite structure is one of the most popular approach due to their outstanding/combining advantages such as theoretically large specific surface area and high intrinsic electron mobility of graphene at room temperature, low cost, innocuous nature, ease of availability/processing, and suitability of their structure to create composites with each other.

In literature, a wide variety of the growth methods have been reported such as sol-gel, solution mixing, *in situ* growth, hydrothermal growth, and solvothermal method. Among these methods, solution mixing technique is one of the most common and easiest the method for the fabrication of graphene-semiconductor composite structures which are synthesized by using

the suspensions of semiconductor nanoparticles and graphene. For the graphene-semiconductor-based composites, to enhance the visible light-induced photocatalytic activity, doping was found to be helpful due to tailoring the electronic properties of the composites providing the manipulation and optimization of charge carrier transfer across the interface between semiconductors and graphene and a reduction in the recombination probability of the photo-excited electron-hole pairs. This chapter of the book is a review of the studies for the development of highly photocatalytically active graphene-semiconductor composite under visible light irradiation.

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