Chapter 8

Immobilization Impact of Photocatalysts onto Graphene Oxide

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Additional information is available at the end of the chapter

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Abstract

The densely functionalized graphene oxide (GO) surface and the two-dimensional carbon structure had provided a unique opportunity for supporting photocatalysts. Concerning GO-based photocatalysis, GO plays the role of an electron acceptor that accelerates the interfacial electron-transfer process, recombination retardant of charge carriers, fine-tuner for the electronic and chemical properties of the supported photocatalysts, and finally, a carrier transport between different active sites. Moreover, standalone GO is a p-doped semiconductor material with the π* orbital of the oxygen remains as the conduction band minimum (CBM) while the valance band maximum (VBM) changes gradually from the p-orbital of carbon to the 2p orbital of oxygen upon oxidation. The outstanding features of the GO-based photocatalysis opened the way to serve the progress in many environmental applications including water treatment, air purification, water splitting, CO_2 conversion, and sensing applications.

Keywords: photocatalysts, graphene oxide (GO), immobilization, environmental applications, energy conversion

1. Introduction

Over the past two decades, advanced oxidation processes (AOP) have received great attention, especially photocatalysis. The term photocatalysis was generally used to describe materials activated with light photons of appropriate energy to modify the rate of a chemical reaction without itself being transformed giving it the character of a catalyst. The photocatalytic process has provided an environmentally friendly method in many environmental and even non-environmental fields such as energy storage and conversion. However, the applications

of photo-activated catalysts have been limited by the relatively low-efficiency resulting in a growing research activity to improve this technique.

The abundance of functional epoxide and hydroxyl groups on graphene oxide (GO) surfaces with the edges and rim sites around vacancies being decorated with pendant carboxylic acid, quinoidal, ketone, and lactone groups enables binding of active sites. Fortunately, the oxygenated groups can largely expand the structural/chemical diversity of GO by further chemical modification or functionalization, which offer an effective way to tailor the physical and chemical properties of GO to expected extents. Besides, GO also displays excellent optical and mechanical properties for a wide landscape of applications. Furthermore, the residual defects and holes arise through the reduction process of GO degrade the electronic quality of r-GO. As a consequence, GO, and GO-based composites have shown great potentials in the applications of energy storage/conversion and environment protection.

The properties of GO such as readily dispersible in water at the molecular level, biocompatibility, and tunable band gap motivated researchers to explore its potential as photocatalytic material. Furthermore, GO combines two complementary qualities, electrons imbibition, and consumption. The electrons imbibition property stimulates the interfacial electron-transfer process from TiO_2, actively limiting the chance of charge carriers recombination with a striking promoting of the photocatalytic response. Simultaneously, the consumption of the received electrons occurs during the partial reduction of GO to reconstruct the conjugated network of the graphene under ultraviolet (UV) assistance. This sensation leads to efficient charge separation and the possibility of more interactions between the composite and targeted organic compounds. In addition, TiO_2/GO composites extend the absorbable light range from the UV into the visible region.

2. Supported photocatalysts onto graphene oxide (GO)

Supported photocatalysts are a properly evolved concept in imparting progressed exposure of the catalysts to reactants and is common in industrial catalytic technologies. In this type of configuration, however, the nature of the photocatalyst-support interactions is important. For durable overall performance, a strong chemical bond is necessary, however, the influences of bonding on photocatalytic mechanisms are considered. The application of TiO_2 in suspension is effective in capturing sunlight due to the fact suspended TiO_2 powders have a high particular surface area within the range from 50 to 300 $m^2 g^{-1}$, which in turn helps in keeping off mass transfer limitation, ensuing in a high photocatalytic activity. Moreover, TiO_2 alone showed a very low photocatalytic activity because of the rapid recombination of conduction band (CB) electrons and valence band (VB) holes. However, a light transport limitation appears with excessive catalyst loading. Besides, it is difficult to separate the small TiO_2 particles from the water after the remedy. To overcome this, the catalyst particles can be immobilized on a surface. In addition, this may lower the oxidation capacity in keeping with volume of water as compared to the suspension of solid particles system, due to the mass transfer difficulty and

moderate transport limitation because of (i) a diminished catalyst surface-to-volume ratio, (ii) the presence of substrate that absorbs light and deteriorate its distribution, and (iii) a loss of movement of particles.

There are different kinds of materials that have been used as a support to fix photocatalysts. Among the different supports, GO is an excellent substrate material for many reasons due to its high specific surface area and superior electron mobility. There have been many efforts to immobilize TiO_2 photocatalyst over diverse structures of supports together with increasing the surface/volume ratio concurrently, which subsequently improves the photocatalytic oxidation efficiency. However, the surface area can only be productive if it allows efficient absorption of light. There is extensive attention to the preparation methods of GO-based material nanocomposites. GO-based material nanocomposites can be synthesized by numerous methods and approaches including the hydrothermal method, electrochemical co-deposition, in situ polymerization, microwave-assisted method, vacuum impregnation, and sol-gel technique. In the GO-based nanocomposite, GO presents either as a functional component or as a substrate for immobilizing the other components.

3. Heterogeneous GO-based photocatalytic materials

Research series conducted by Fujishima and Honda pull the trigger of scientific research of photocatalysis stimulation. Their initial demonstration was based on the activation of a semiconductor particulate material by the action of radiation with an appropriate wavelength to catalyze the dissociation of water. Since this time, several photocatalysts have been subject to extensive studies. In general, when a semiconductor photocatalyst material undergoes irradiation with a light of suitable wavelength, an electron gain a quantum of energy sufficient to its promotion to the CB. This electron transmission causes a positive hole in the VB. The electron in the CB and the hole in the VB are responsible for reduction or oxidation of any substrate, respectively, as shown in **Figure 1**. The role of graphene-metal oxide composites as photocatalysts, adsorbents, and disinfectants in water treatment was previously reviewed [1].

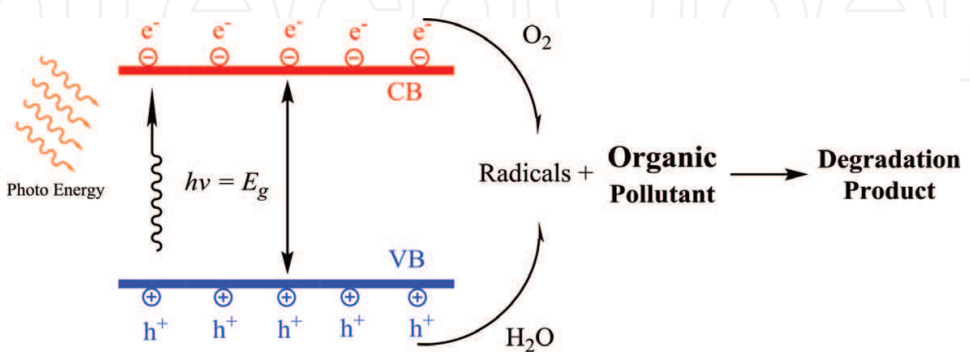

Figure 1. Simplification of photocatalysis mechanism.

3.1. Binary metal oxides

Titanium oxide (TiO_2) is the first and most important binary transition metal oxides that have been studied in the field of photocatalysis. TiO_2 is characterized by chemical stability and non-solubility in the aqueous medium, which facilitates the process of separation after the desired reactions. Moreover, photocatalytic stimulation is primarily aimed at environmental applications; therefore, non-toxicity of titanium dioxide is also favorable. Other n-type semiconductor binary oxides with a d-transition metal such as WO_3, Fe_2O_3, Nb_2O_5, V_2O_5, NiO, Ta_2O_5, ZrO_2, CuO, and Cu_2O have been studied. In addition, binary metal oxides of elements other than transition metals such as ZnO, Ga_2O_3, Sb_2O_3, Bi_2O_3, and CeO_2 had also some attention. Although ZnO suffers from photocorrosion, it is photocatalytic activity is comparable with TiO_2. Furthermore, the photocorrosion process can be controlled by monitoring of the operational factors such as the pH, additives, and ZnO crystal growth.

GO has been explored as electron acceptor molecule for making composite with TiO_2. The effects of particle size GO content and targeted pollutants for different TiO_2 and GO composites have been represented by examples in **Table 1**. Moreover, other metal oxides such as ZnO,

Composites	TiO_2 particle size	GO content	Pollutant	Ref.
Pt-GO-TiO_2/GR	30 nm	0.5 wt%	Dodecylbenzenesulfonate	[9]
TiO_2-GO and TiO_2-GR	5–15 nm	90 wt%	Methylene blue	[10]
TiO_2/GO	—	10 mg	Methylene blue	[11]
TiO_2GO	57 nm	3.3 wt%	Diphenhydramine methyl	[12]
TiO_2/GO	50 nm thickness	10 wt%	Methylene blue	[13]
TiO_2/GO	20–40nm	4.6 wt%	Methyl orange	[14]
TiO_2/GO	30 nm	10 wt%	Methylene blue	[15]
TiO_2/GO	—	GO:TiO_2 = 1.5 wt	Methyl orange	[16]
TiO_2/GO	10 nm	0.03 mg GO	Methylene blue	[17]
TiO_2/GO	4–5 nm	3.3–4.0 wt%	Diphenhydramine and methyl orange	[18]
TiO_2/GO	15 nm	~10%	Rhodamine B	[19]
TiO_2/GO	10 nm	GO:TiO_2 = 3:2 wt	Methyl orange	[20]
TiO_2/GO	6–9 nm	1 wt%	Methylene blue	[21]
Co_3O_4/TiO_2/GO	30–50 nm	3–4 wt%	Oxytetracycline and Congo Red	[22]
Fe_3O_4/TiO_2/GO	17 nm		Enrofloxacin	[23]
B/GO/TiO_2	51 nm		4-Nitrophenol	[24]
La/TiO_2/GO			Acid Blue 40	[25]

Table 1. Summary of TiO_2 and GO composites used as photocatalyst.

[2–4] NiO, [5] WO_3, [6] CuO, [7], and Mn_3O_4, [8] have been also incorporated with GO to serve as an enhanced photocatalyst.

3.2. Non-oxidic binary compounds

Many photocatalytic substances contain no oxygen, but still have another element of group 16 in the periodic table. Chalcogenide such as CdS, ZnS, Sb_2S_3, Bi_2S_3, MoS, CdSe, and CdTe give a good example of such materials. Sulfides other than zinc sulfide have an absorption edge compatible with solar energy utilization rather than photocatalytic processes. Unfortunately, sulfides have the disadvantage of photo-induced corrosion. Cadmium selenides and tellurides have a valence band redox potential lower than 1.23 V. This explains their poor photocatalytic activity for oxidation of organic pollutants [26].

A simple and high-yield room-temperature solid-state method was employed for the first time to fabricate GO/ZnS, GO/CdS, and GO/Bi_2S_3 composites [27]. The synthesized GO/metal sulfide composites were used as photocatalysts for the degradation of methyl orange under UV irradiation. The composites exhibited superior photocatalytic activity to pure metal sulfides, owing to the high specific surface area, and the reduction of photo-induced electron-hole pair recombination in metal sulfides due to the introduction of GO.

However, incorporation of non-oxidic binary compounds alone with GO is superfluous. They are often introduced to the GO surface with each other or with different photocatalytic materials. The association of ZnS-CdS with GO to form the ZnS-CdS/GO heterostructure for the photocatalytic H_2 gas generation result in the duplication of the recorded production rate. Moreover, doping ZnS-CdS/GO heterostructure with 2 wt% Pt nanoparticles to serve as co-catalysts, the hydrogen generation rate is significantly elevated to 1.68 and 0.78 mmol h^{-1} upon irradiation with UV-visible or visible light, respectively [28].

3.3. Multiple compounds

Metallates of elements of the middle region of the periodic table and cations with filled or partially filled orbitals in their outer shell, which may hybridize with the oxygen 2p orbitals. Aluminates, ferrites, niobates, tantalates, titanates, tungstates, and vanadates are some examples of these metallates. While the examples of those cations are 6 s orbitals in Pb^{2+} and Bi^{3+}, and 5 s in Sn^{2+} or 4d in Ag^{+}. Various ternary and quaternary oxides, oxynitrides, oxysulfides, and oxyhalides have also been investigated for evaluation of their activity in the degradation of organic pollutants and water splitting.

Incorporation of metallates with GO has also been investigated as an enhanced photocatalyst. For instance, the Bi_2WO_6/GO photocatalysts were successfully prepared via in situ refluxing method in the presence of GO. The photocatalytic degradation of rhodamine B under visible light irradiation was utilized to evaluate the photocatalytic performance. The photocatalytic activity of Bi_2WO_6/graphene was greatly enhanced compared to pure Bi_2WO_6. The enhanced photocatalytic activity could be attributed to that GO as charge transfer channel [29].

4. Photocatalytic roles of graphene oxide (GO)

4.1. Intrinsic photocatalytic activity

Most of the photocatalytic materials are wide band gap semiconductors. GO is a p-doped material because oxygen atoms are more electronegative than carbon atoms [30]. The band gap of GO can be tunable by just varying the oxidation level. The fully oxidized GO can act as an electrical insulator while the partially oxidized GO can act as a semiconductor [31]. Introducing more oxygen enlarges the band gap, and the valence band maximum (VBM) gradually changes from the p-orbital of graphene to the 2p orbital of oxygen; the π^* orbital remains as the conduction band minimum (CBM), **Figure 2**.

The photocatalytic characteristics of GO nanostructures were confirmed by measuring reduction rate of resazurin into resorufin as a function of UV irradiation time [32]. The band gap of GO locates between 2.4 and 4.3 eV. Upon excitation, the electron-hole pairs will be generated at the GO surface. Hence, the localized defects on the GO nanosheets trap the produced electrons and limit their recombination process with the counter-currently produced holes.

4.2. Photocatalyst support

Since GO was rediscovered in 2004, it represents the top of carbon materials in many of its properties including outstanding electronic, thermal, and mechanical properties. GO as a support has many distinctive features including two-dimensional structure with the large specific surface area, high adsorption capacity, and excellent dispersibility in both aqueous and organic solvents [33]. Furthermore, the spread of the oxygenated functional groups facilitates the decoration of its surface with photoactive spots. As GO can add many advantages to the photocatalyst, it can also avoid many special problems related to the active site. The photocorrosion of ZnO was inhibited to a large extent upon incorporation with GO [34].

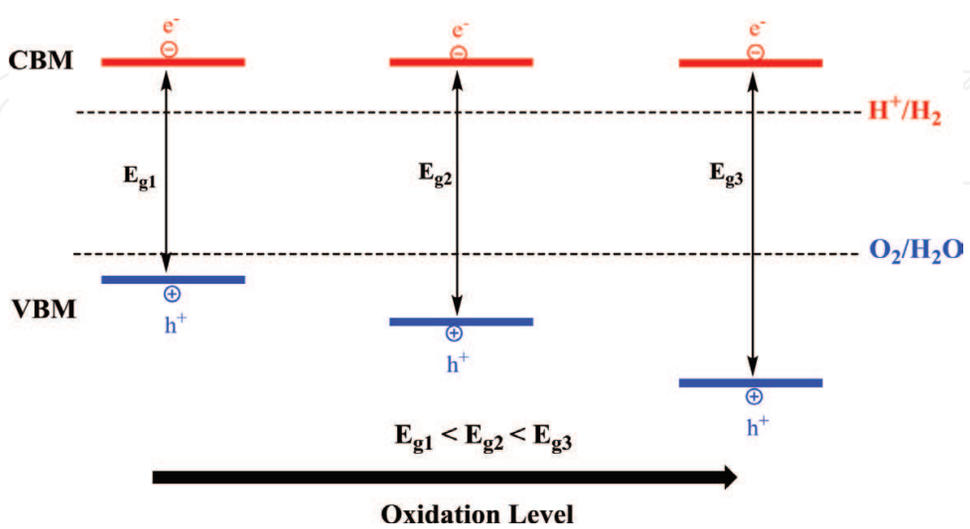

Figure 2. The VBM and CBM positions of GO sheets with varying oxidation level.

We cannot overlook some of the constraints that may limit the use of GO in supporting photocatalysts. The first thing to issue is the operating temperature range. The temperature between 150 and 200°C is usually sufficient for the start of the GO labile oxygen-containing groups decomposition [35]. The second issue that there is a claim that the $OH^{\bullet}$ radicals generated at the TiO_2 surface could lead to an oxidative attack on the carbon-rich structure, which is ultimately mineralized as evident from the decreased total organic carbon (TOC) concentration with increasing irradiation time [36].

4.3. Charge separation and gap control

It is expected that the chemical bonding and associated charge transfer at the interface between the photocatalyst and GO support can be used to fine-tune the electronic and chemical properties of the active sites. For instance, TiO_2 is the widely used photocatalyst, however, its activity is restricted to the ultraviolet region because of its wide band gap, and the photo-generated electron-hole pairs in experience rapid recombination [37, 38]. GO sheets are particularly effective in separating charges on TiO_2 as the photo-generated electrons will move toward the GO support, leaving behind the holes in the supported semiconductor particles. Thus, the GO support acts as an electron acceptor to enhance the separation between the photo-generated electron and holes, thereby suppressing their recombination, and consequently enhancing the photocatalytic efficiency. In addition, the unpaired π-electrons on GO can interact with TiO_2 to extend the light absorption range of TiO_2 (**Figure 3**). The GO/TiO_2 composites exhibited excellent photochemical activity under visible light irradiation.

The photocatalytic activity of the gap controlled composite is governed by other factors including GO to active sites ratio. After the threshold limit, the photocatalytic activity decrease with increasing the absorption and scattering of photons by the excess carbon content in the composite. Photocatalytic activity of hybrid material also depends on the interface between TiO_2 and graphene an intense coupling between TiO_2 and GO facilitates charge separation and so retards recombination. Liang et al. [19] reported the growth of uniform TiO_2 nanocrystals directly on GO substrate via hydrolysis with subsequent hydrothermal treatment.

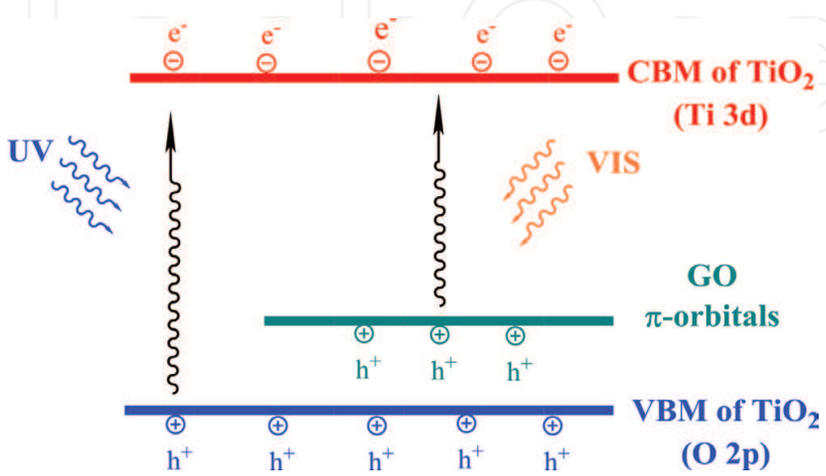

Figure 3. The interaction between unpaired π-electrons on GO with surface TiO_2.

The resultant GO/TiO_2 hybrids were tested in the photocatalytic degradation of the well-known rhodamine B dye. In comparison with commercial P25 TiO_2, the prepared hybrids showed a three time faster degradation rate due to the enhanced electronic combination between GO and TiO_2 in addition to the remarkable higher gross surface area.

4.4. Heterojunction formation

Incorporating GO with metal-containing semiconductors can initiate a p-n junction, which considerably improves the separation of photo-generated charges. This is a possible way to fabricate GO/semiconductor composites with different properties by using a tunable semiconductor [39]. GO/TiO_2 composites were prepared by using $TiCl_3$ and GO as reactants. Again, the concentration of GO in starting solution played an important role in the photocatalytic performance of the composites. The heterojunction between p-type GO and n-type TiO_2 semiconductors functioned as the separator for the photo-generated electron-hole pairs, **Figure 4**. These semiconductors could be excited by visible light with wavelengths longer than 510 nm for the degradation of methyl orange. Also, the integration of GO with TiO_2 will significantly increase the photovoltaic response and significantly prolong its mean life-time of electron-hole pairs compared with that of TiO_2 [40]. Similar to TiO_2, ZnO also can form a p-n heterojunction with GO for visible light absorption. Quantum dot sized ZnO nanoparticles deposited on graphene sheets with a p-n heterojunction interface were demonstrated by a change of photocurrent direction at different bias potential that significantly enhanced photo-response properties under solar light irradiation [41].

4.5. Coupling multiple active sites

GO can act as a common platform for more than one active site to produce enhanced heterostructure for photocatalytic activity. For example, ZnS-CdS/GO shows a twice activity toward photocatalytic hydrogen generation compared with ZnS-CdS standalone heterostructures [28].

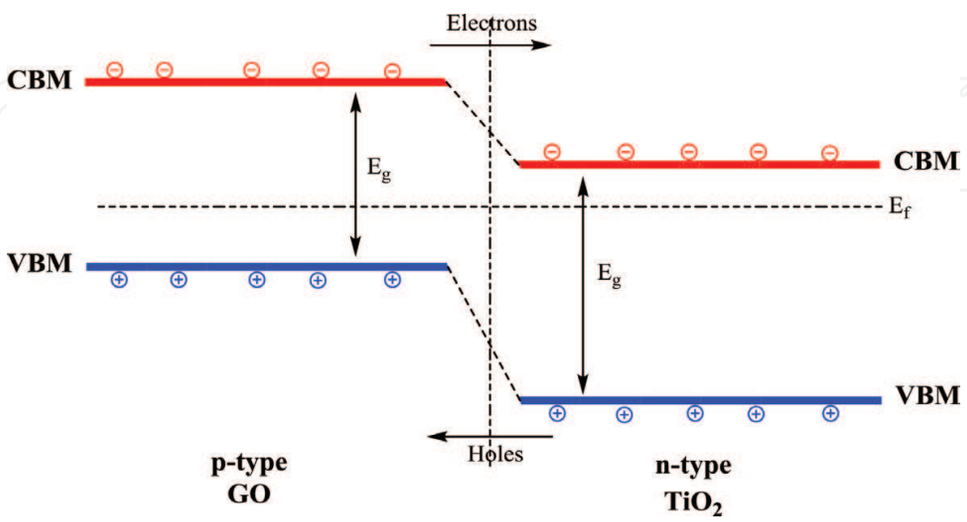

Figure 4. p–n heterojunction formation at the interface between GO and TiO2.

Hence, GO construct a carrier transport channel between ZnS and CdS to enhance cooperative effects. In addition, GO oxide platform allow the loading of 2 wt% Pt nanoparticles as co-catalysts for the ZnS-CdS/GO heterostructures. Under UV-visible and visible light irradiation the hydrogen generation rate of the resultant heterostructure is significantly improved to 1.68 and 0.78 mmol h^{-1}, respectively.

5. Environmental applications

5.1. Water treatment

The contamination problem of natural water resources with pollutants of different forms is a problem that threatens public health. The photocatalysis is expected to play a major role in the water purification process because it has a great ability to exploit solar energy in pollutants degradation in the moderate temperature range. Visible light-responsive photocatalysis has been widely investigated for the treatment of inorganic, organic, and biological contaminated water. However, the application of photocatalysis in water treatment is still in the research stage.

5.1.1. Degradation of organic pollutants

Since organic dyes pharmaceuticals are usually leakage with a significant part to the industrial wastewater during manufacture processes; it has received a lot of attention in terms of treatment processes, including photocatalysis. Because of the easy tracing of dye decolonization process, it has left a great scientific legacy of published scientific papers. In general, when the photocatalyst is irradiated with photon with energy compatible with the band gap energy (Eg), an electron is transferred from the VB to the CB, leaving behind a hole. Accordingly, the produced electron-hole pairs are involved in a series of chain oxidative-reductive reactions, Eqs. (1)–(10) [42].

$$\text{Photocatalyst} + h\nu \longrightarrow h^+ + e^- \tag{1}$$

$$h^+ + H_2O \longrightarrow {}^{\bullet}OH + H^+ \tag{2}$$

$$h^+ + OH^- \longrightarrow {}^{\bullet}OH \tag{3}$$

$$h^+ + \text{pollutant} \longrightarrow (\text{pollutant})^+ \tag{4}$$

$$e^- + O_2 \longrightarrow {}^{\bullet}O_2^- \tag{5}$$

$$O_2^- + H^+ \longrightarrow {}^{\bullet}OOH \tag{6}$$

$$2\,{}^{\bullet}OOH \longrightarrow O_2 + H_2O_2 \tag{7}$$

$$H_2O_2 + {}^{\bullet}O_2^- \longrightarrow {}^{\bullet}OH + OH^- + O_2 \tag{8}$$

$$H_2O_2 + h\nu \longrightarrow 2\,{}^{\bullet}OH \tag{9}$$

$$\text{pollutant} + \left({}^{\bullet}OH, h^+, {}^{\bullet}OOH \text{ or } {}^{\bullet}O_2^-\right) \longrightarrow \text{degradation product} \tag{10}$$

Recently, enhanced photocatalytic ZnO/GO nanocomposite was introduced for the degradation of methyl orange under UV irradiation [43]. The reaction proceeds for 2 h to achieve 95% degradation from the initial dye concentration of 10 mg/L. Pseudo-first-order kinetics were recorded with respect to methyl orange with an apparent reaction rate constants in the range of 0.009–0.030 min^{-1}. Moreover, the aforementioned ZnO/GO photocatalyst passed the stability and reusability test.

5.1.2. Stalemate of inorganic pollutants

Chromium is one of the common cationic pollutants in wastewater. Chromium exists in two main oxidation states in the environment, Cr(VI) and Cr(III). Compared with Cr(III), Cr(VI) is more toxic [44]. Hexagonal nanoflowers of Tin(IV) sulfide/GO was synthesized by hydrothermal method [45]. The composite showed a high photocatalytic activity toward the oxidation of hexavalent chromium upon contact with the SnS_2/GO under visible light irradiation, Eqs. (11)–(13).

$$SnS_2/GO + h\nu \longrightarrow h^+ + e^- \tag{11}$$

$$2\,h^+ + H_2O \longrightarrow \tfrac{1}{2}\,O_2 + 2\,H^+ \tag{12}$$

$$CrO_4^{2-} + 8\,H^+ + 3\,e^- \longrightarrow Cr^{3+} + 4\,H_2O \tag{13}$$

5.1.3. Membrane purification

Membrane fouling and poor water flux are the main problems facing water treatment by membrane technique. However, incorporation of photocatalysis onto the membrane surface is expected to increase the water flux as result of the photo-enhanced hydrophilicity and contaminant degradation. Surface modification by photocatalyst grafting provides a very promising route to the fabrication of high-performance photocatalytic membranes for sustainable water treatment.

Deposition of TiO_2 and GO nanosheets on the polysulfone-base membrane was one of the first attempts to construct a photocatalytic membrane [46]. Several properties of the TiO_2/GO/

polysulfone membrane over pristine polysulfone membrane have been identified, including the effective photodegradation of methylene blue under UV (about 60–80% faster) and sunlight (3–4 times faster) beside improved membrane flux. After that many attempts have been carried out to construct and utilized photocatalytic membrane for water and salty water purification [47–51]. In the next-generation of water treatment photocatalytic membranes, the antimicrobial character was also included. In situ implementation of Ag nanoparticles onto the surface of GO/TiO_2 nanocomposite membrane assemblies, allowing for simultaneous filtration, and disinfection [52].

5.2. Air pollutants removal

According to national ambient air quality standards (NAAQS) carbon monoxide (CO), ozone (O_3), particulate matter, nitrogen oxides (NO_x, $x = 1 \text{ or } 2$), sulfur dioxide (SO_2), and lead (Pb) considered harmful to public health and the environment. Unfortunately, gases such as NOx, SO_2, and CO are difficult to oxidize and remove. Hence, the role of photocatalysis as an effective economic alternative to oxidize the aforementioned gases to products, which are harmless to public health.

Recently, novel TiO_2/GO functionalized with a cobalt complex for significant degradation of NO_x and CO has been reported [53]. The cobalt-imidazole functionalized GO incorporating with the TiO_2 result in a notable decrease of the band gap and increased the sensitivity to visible light irradiation. Experimental results revealed a high percentage deterioration of NOx (51%) and CO (46%). This photocatalyst reflects the ability of TiO_2 to act as photocatalyst with the ability of GO to modify its band gap with the exploitation of cobalt to form complex formation with pollutant gases.

5.3. CO_2 reduction

Reduction of carbon dioxide (CO_2) to hydrocarbons represents a perfect example of simultaneous solar energy harvesting. Side-by-side to exploit CO_2, the main cause of global warming, emitted into the atmosphere as a major product of combustion operations. Unfortunately, exploiting CO_2 gas needs high energy. Therefore, the existence of some processes related to the exploitation of solar energy as an energy source represents an opportunity for two birds with one stone, that is, the energy harvesting/storage and environmental issues. Superior advantages of the graphene-based photocatalyst for CO_2 reduction was categorized into six aspects [54]: (i) prevent carrier recombination, (ii) increasing specific surface areas, (iii) strong π-π interaction between graphene and CO_2, (iv) enhancing photocatalyst mechanical and chemical stability, (v) improving nanoparticles (NPs) dispersion, and (vi) enhancing light absorption.

Since GO could act as an active photocatalyst, it was used as a photocatalyst for CO_2 to methanol conversion. The photo-reduction of CO_2 to methanol conversion rate on modified GO achieve six-fold higher than the pure TiO_2 under 300-watt halogen lamp irradiation [55]. The research was not limited to use GO standalone, but there is a growing effort to improve using TiO_2 spread over the surface of the GO. For instance, GO doped oxygen-rich TiO_2 hybrid

($GO\text{-}OTiO_2$) was synthesized through the wet chemical impregnation technique [56]. The photocatalytic performances were evaluated through the photoreduction of CO_2 under the irradiation of low-power energy-saving daylight bulbs. GO extent the reactivity of doped oxygen-rich TiO_2 to 95.8% even after 6 h of light irradiation. This observation firmly established the role of GO as an effective catalyst support. The composite with 5 wt%, GO has a CH_4 yield of 1.718 μmol g^{-1}cat. after 6 h of reaction, that is, 14.0 folds comparison to commercial Degussa P25.

Besides TiO_2, other semiconductors, clusters, nanoparticles, and complexes immobilized onto GO has also been investigated for CO_2 reduction to hydrocarbon. Hexamolybdenum cluster compound was used for the modification of GO for visible light absorption [57]. After 24 h of visible light illumination, the yield of methanol was found to be 1644 and 1294 μmol g^{-1}cat. for $GO/Cs_2Mo_6Br^i_8Br^a_x$ and $GO/(TBA)_2Mo_6Br^i_8Br^a_x$ (TBA = tetrabutylammonium), respectively. These values are much higher than GO alone (439 μmol g^{-1}cat.). Halide perovskite quantum dots ($CsPbBr_3$ QD/GO) was utilized for the photochemical conversion of CO_2 [58]. These materials primarily regarded as optoelectronic materials for light emitting diode (LED) and photovoltaic devices. Compared to the individual $CsPbBr_3$ QDs, the rate of electron consumption improved from 23.7 to 29.8 μmol g^{-1}cat. after the incorporation with the GO. As an example of nanoparticles decorated GO with a series of Cu-nanoparticles were utilized to reduce CO_2 to hydrocarbon fuels under visible light irradiation [59]. Cu-NPs (10 wt%) effectively tune the work function of GO 60 times higher. A ruthenium trinuclear polyazine complex was also immobilized onto GO functionalized with phenanthroline ligands [60]. Using a 20 W white cold LED flood light, in a dimethyl formamide-water mixture sacrificing agent, the yield of methanol was found to be 3977.57 ± 5.60 μmol g^{-1}cat. after 48 h.

5.4. Water splitting

Water splitting with hydrogen evolution based on photocatalytic process represents a renewable energy production with no reliance on fossil fuels and no CO_2 emission. The role of GO in photocatalytic water splitting was perfectly reviewed [61]. GO itself as a photocatalyst steadily catalyzes H_2 generation from 20 vol% aqueous methanol solution and pure water under irradiation with UV or visible light [62]. Concurrently with the photocatalytic reaction, the CB of GO with an excessive overpotential associated with the level for H_2 generation reveals fast electron injection from the excited GO into the solution. On the other hand, the holes in the VB of GO do not interact with the water molecules for O_2 generation but are disabled to the hole scavenger (methanol) alternatively.

The GO band gap decrease during the photocatalytic reaction because of GO reduction. However, the H_2 evolution remained unchanged, indicating that the involved oxygenated sites remain accessible to protons in the liquid phase.

Recently, GO sheets covalently functionalized with (5, 10, 15, 20-tetraphenyl) porphinato manganese(III) (MnTPP) GO-MnTPP and tested for water splitting under UV-vis light irradiation [63]. The dye moiety acted as a sensitizer while GO moiety acted as a supporting matrix, electron mediator, enhancing photoexcited electrons transfer, and suppressing charges

recombination. Under UV-vis irradiation, the GO-MnTPP hybrid demonstrates considerable photocatalytic activity for H_2 evolution.

5.5. Sensing applications

Photoelectrochemical sensors based on materials with photoelectric properties, such as TiO_2 have drawn attention in bioanalysis, medical diagnoses, and pollutant monitoring. A density functional theory (DFT) study was carried out to model the NO_2 interaction with pristine and N-doped TiO_2/GO nanocomposites for a promising NO_2 gas sensor [64]. Another example the construction of a blue-light photoelectrochemical sensor based on nickel tetra-amine phthalocyanine-GO for the detection of erythromycin [65]. The prepared composite was fixed on the surface of the indium tin oxide coated glass electrode. When the light was incident on the surface of the material the electron-hole pairs generation process started with a photocurrent response. The erythromycin suppresses electron/hole recombination resulted in changes in the photocurrent with a linear response for erythromycin concentrations ranging from 0.40 to 120.00 μmol L^{-1}.

6. Future perspectives

Incorporation of GO with different semiconductor, metal nanostructures, and complexes allows the design of many generations of photocatalyst systems. In addition, great opportunities still exist in the exploitation of novel GO base hybrids and composites photocatalyst. Dual function photocatalysis that can perform multitasks simultaneously represents the greatest future trend along with the discovery of new materials. This is not a fantasy; previously a dual-functional photocatalysis was introduced based on a ternary hybrid of TiO_2 modified with GO along with Pt and fluoride for both H_2-producing water treatment and degradation of organic pollutants [66]. The positive effect of GO on the dual photocatalytic activity was observed only when Pt and surface fluoride were co-present.

7. Conclusion

Photocatalysts alone almost showed a very low photocatalytic activity because of the rapid recombination of CB electrons and VB holes. The chemical bonding and associated charge transfer at the interface between the photocatalyst and GO support can be used to fine-tune the electronic and chemical properties of the active sites. GO can act as a common platform for more than one active site to produce enhanced heterostructure for photocatalytic activity.

GO is an excellent supporting material due to its high specific surface area and superior electron mobility. GO plays the role of an electron acceptor that accelerates the interfacial electron-transfer process from photocatalysts materials, which strongly hindering the recombination of charge carriers and thus improving the photocatalytic activity. The spread of the oxygenated functional groups on its surface facilitates the process of planting photoactive spots on its surface.

The band gap of GO is tunable by just varying the oxidation level. Fully oxidized GO act as an electrical insulator and partially oxidized GO can act as a semiconductor. Introducing more oxygen enlarges the band gap, and the VBM gradually changes from the p-orbital of graphene to the 2p orbital of oxygen; the π^* orbital remains as the CBM.

Aluminates, ferrites, niobates, tantalates, titanates, tungstates, and vanadates are examples of the metallates, which are incorporated with GO and revealed an enhanced photocatalytic activity on the degradation of organic dyes under visible light due to charge transfer channel of GO.

The heterojunction between p-type GO and n-type semiconductors functioned as the separator for the photo-generated electron-hole pairs. These semiconductors could be excited by visible light with wavelengths longer than 510 nm for the degradation of methyl orange. In most cases, GO served as an electron sink to facilitate separation and store the separated electrons.

Surface modification by photocatalyst grafting provides a very promising route to the fabrication of high-performance photocatalytic membranes for sustainable water treatment.

Some of the outstanding properties of GO-based photocatalysts in CO_2 reduction processes have been shortlisted: (i) block carrier recombination, (ii) Improving specific surface areas, (iii) strong π–π interaction with CO_2, (iv) enhancing either photocatalyst mechanical and chemical stability, (v) improving nanoparticles dispersion, (vi) intensifying light absorption.

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