An overview: recent development of semiconductor/graphene nanocomposites for photodegradation of phenol and phenolic compounds in aqueous solution

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\textbf{ABSTRACT}

The development of graphene-based nanocomposites is currently the issue of enormous research interest. Recent advancements have exhibited that semiconductor/graphene nanocomposites can be prepared as a promising new category of catalysts for the heterogeneous photocatalytic treatment of wastewaters. Since semiconductor/graphene nanocomposites have been found efficient in degradation of organic pollutants, photodegradation of phenol and phenolic compounds as hazardous contaminants in aqueous solution has been most widely investigated by these aforementioned nanocomposites. In the present review, after introduction on the properties and the different synthesis methods of semiconductor/graphene nanocomposites, we will discuss the application of these nanocomposites, in fields of photodegradation of phenol and phenolic compounds in aqueous solution.

\textbf{1. Introduction}

Clean water is an essential human need. Polluted water and poor sanitation are linked to transmission of diseases. Millions of people die each year from preventable diseases caused by a lack of access to safe drinking water and suitable sanitation. While the world’s population has been tripled in the 20th century, recycling of wastewater effluent is one of the best strategic approach in a sustainable water management. Today people are generating and disposing more wastewater than any other time. Toxic substances from towns and farms as well as factories readily mix with water, causing water contamination. The toxic pollutants, such as phenolic compounds that are hazardous to the environment, damaging to humans and hard to remove by natural means, is associated with industrial development. These kinds of pollutants are mostly found in the industrial effluents [1]. There are many common methods employed to remove pollutants from water including filtration, chemical precipitation, ion-exchange adsorption, membrane systems and electrodeposition. However, the aforementioned strategies may not be very beneficial, due to the expensive equipment involved in these methods, slow and non-destructive to a great number of persistent organic contaminants [2,3]. Among the numerous methods, heterogeneous photocatalysis method is one of the most efficient strategies of water decontamination due to its potential to degrade organic pollutants and produce some products including \(
\text{CO}_2\) and \(\text{H}_2\) [4,5]. Heterogeneous photocatalysis involves the utilization of a semiconductor catalysts like \(\text{TiO}_2\), \(\text{Ag}_x\text{PO}_{4y}\), \(\text{CdS}\), \(\text{SnS}_2\), \(\text{CaFe}_2\text{O}_4\), \(\text{Fe}_3\text{O}_4\), \(\text{CdS}\), which illuminated with light (suitable wavelength) in order to form highly active species such as \(\text{OH}^\cdot\), \(\text{O}_2^\cdot\) for degradation of organic contaminants. Heterogeneous photocatalysis as a green strategy has many advantages including low operating costs, ambient operating conditions, and complete degradation of organic contaminants without producing secondary contaminants. Consequently, this method has a lot of applications in wastewater treatment [6–8]. It should be noted that, the narrow excitation wavelength, inadequate quantum efficiency, poor adsorption capacity, high recombination rate of the photoinduced electron–hole pairs as well as deactivation of the semiconductor as photocatalyst limit the application of the aforementioned method. Up to now, many efforts have been made to improve the photocatalytic performance of semiconductors, such as metallic doping and nonmetallic doping, dye sensitization, co-catalysts, but commercially viable photocatalyst still remains an important challenge [9,10]. In the past three decades and with advancements in nanotechnology, conjugated carbon nanomaterials, especially fullerenes, activated carbon, carbon nanotubes and graphite because of their outstanding mechanical, thermal, electrical, and chemical properties have been used for designing next-generation photocatalyst systems with increased activity [11,12]. There has been expositive growth in the
number of studies on the applications of graphene and its derivatives in heterogeneous photocatalysis strategy. Graphene has emerged as a two-dimensional (2D) sheet of sp$^2$-hybridized carbon atoms and has a great number of unique properties such as high electron mobility at room temperature, thermal conductivity at room temperature, high specific surface area, superior mechanical properties with Young’s modulus of 1100 GPa and perfect optical transmittance (97.7%) [13–15]. These outstanding properties make graphene an ideal electron-transfer bridge, electronic sink and a 2D support matrix for photocatalyst carrier or promoter [16–20]. Based on the aforementioned notes, there has been an enhancing research interest in the recent times, seeking to couple graphene with semiconductors to develop semiconductor/graphene nanocomposites with significant photocatalytic degradation of contaminants [9,21]. The conjugation of graphene with semiconductor materials results in photocatalysts with enhanced specific surface area, sufficient quantity, and quality of adsorption sites, improved charge separation, decreased recombination rate of the photoinduced electron–hole pairs [16]. Moreover, recent studies have been carried out using the less expensive and more readily available GO or rGO counterpart due to the defects and heteroatom-containing functionalities introduced into the graphene basal plane or edges by oxidation or reduction remarkably change the physical and chemical properties of neat graphene. For instance, the sheet resistance values of GO are about 1000 Ω sq$^{-1}$ or higher, though the rGO conductivity is about 1000 S m$^{-1}$. Conversely, the presence of functional groups and defects provide potential advantages such as significant dispersibility in solvents and contribute to the catalytic activity of graphene-based catalysts [22,23].

This review is an attempt to provide a comprehensive update of the key advancements in the development of semiconductor/graphene nanocomposites for photodegradation of phenolic compounds in wastewater. The goal of the present review does not only integrate results from the works reported in the literature, but also provide insights into the various methods for the synthesis of semiconductor/graphene nanocomposites and their photodegradation performance for removal of phenolic compounds.

2. Phenol and phenolic compounds as organic pollutants in wastewater

Phenol and phenolic compounds such as nitrophenols and chlorophenols which detect in water and wastewater are toxic in nature even at low concentrations and treated as major water contaminants as per various countries’ regulations. Phenol and its derivatives (Figure 1) are the first compounds included in the United States Environmental Protection Agency (US EPA) list of priority contaminates [24,25]. In fact, these hazardous water-soluble compounds are a major health risk because of their genotoxicity. For instance, nitrophenols and chlorophenols are even more toxic than phenol itself. In Table 1, the uses and toxicity of phenols are integrated [26,27]. The phenolic compounds are ceaselessly released to the environment through industrial and domestic activities. Since all phenolic compounds are aromatic compounds with one or more hydroxyl groups attached to the aromatic ring, are commonly found in wastewater discharged from different industries like petroleum refineries, plastics, chemical synthesis, dyes, coke plants, pulp and paper, detergents, textiles, pharmaceutics, pesticides, and herbicides synthesis. On the other hand, phenol along with its nitrophenol and chlorophenol derivatives are significantly soluble in water (Table 2) [28,29]. It should be noted that these hazardous compounds can also arise from natural sources in the aquatic environment (at low concentration), like lignin transformation, algal secretion, hydrolyzable tannins, and flavanoids, and humidification processes [30–33]. Phenolic compounds can be removed via several methods like biological and physicochemical processes. A comparative study of various phenol degradation methods is presented in the next section. It should be mentioned the following researchers are focused on AOPs for the degradation of phenols. AOPs provide much faster rate of degradation via the participation of hydroxyl radicals. Heterogeneous photocatalysis process is one of the favorite methods among the AOPs which needs three components including semiconductor photocatalyst, light source (solar, visible or UV) and hole acceptor or electron donor.

In the photodegradation of organic contaminants 'OH is the primary oxidant and this oxidant is produced from two pathways including: i) The O$_2$ present in water is reduced to 'O$_2^-$, which then reacts with H$^+$ to form 'OH, followed by rapid decomposition to 'OH.
Table 1. Uses and regulatory limits of phenol and phenolic compounds [24,26].

| Phenol and its derivatives | Uses | Toxicity | Human health for the consumption of water and organism (maximum pollutant amounts) |
|----------------------------|------|----------|---------------------------------------------------------------------------------|
| Phenol                     | -Food industry for packaging | -Phenol and its vapors are corrosive effect on the central nervous system and heart, kidneys, eyes, the skin, mucous membrane and the respiratory tract. | 4 mg L\(^{-1}\) |
|                            | -Detergent Manufacturing    | -it causes lung edema, dermatitis, or even second and third-degree burns. | |
|                            | -Pharmaceutical industry     | -It is also a reproductive toxin causing increased risk of abortion and low birth weight indicating retarded development in utero | |
|                            | -Pesticide manufacturing     | -The noxious influence of chlorophenols and their derivatives on the ecobiota lead to acute toxicity, histopathological changes, mutagenicity, and cancer. | 2-Chlorophenol (0.03 mg L\(^{-1}\)), 3-methyl-4-chlorophenol (0.5 mg L\(^{-1}\)), 2,4-Dichlorophenol (0.01 mg L\(^{-1}\)), pentachlorophenol (0.03 μg L\(^{-1}\)), 2,4,6-Trichlorophenol (1.5 μg L\(^{-1}\)) |
|                            | -Cosmetic industry           | -The transformation of chlorophenols in may bind and damage DNA or gene products. | 2,4-Dinitrophenol (0.01 mg L\(^{-1}\)) |
|                            | -Chemical industry           | -Nitrophenols can reduce the ability of the blood to carry oxygen to tissues and organs. | |
|                            | -Rubber industry             | -They also have harmful effect on the kidney and muscles. | |
| Chlorophenols              | -Disinfectant in homes, farms, hospitals | -As the precursor for the preparation of phenetidine, acetophenetidine, indicators and raw materials for fungicides | |
|                            | -Antiseptics and pesticide production | | |
|                            | -herbicides                  | -As an intermediate for the production of dyestuffs, pigments and rubber chemicals, and fungicides | |
|                            |                               | -As an acid-base indicator and as a reagent for glucose | |
| Nitrophenols               | -Plastic manufacturing       | | |
|                            |                               | | |
|                            |                               | | |

Table 2. Solubility of phenol and its derivatives in water [28,29].

| Phenol and its derivatives | Solubility (g per 100 g) |
|----------------------------|-------------------------|
| Phenol                     | 9.48                    |
| 2-Chlorophenol             | 2.04                    |
| 2-Nitrophenol              | 0.21                    |
| 3-Chlorophenol             | 2.25                    |
| 3-Nitrophenol              | 2.19                    |
| 4-Chlorophenol             | 2.77                    |
| 4-Nitrophenol              | 1.34                    |

ii) The oxidation of OH\(^{-}\). The possible degradation mechanism for phenol upon light is depicted in **Scheme 1**. In fact, phenol and phenolic compounds degradation went through the formation of dihydroxybenzene (catechol or resorcinol), pent 2-enedioic acid, and oxalic acid. In a parallel reaction path, benzoquinone and maleic acid were formed during the degradation [34].

A great number of research has mentioned that phenol can be destroyed to carbon dioxide and water [35,36].

**Scheme 1.** Probable degradation mechanism for phenol
Moreover, some of the intermediate products formed during photocatalytic degradation of phenol. The most commonly used way to discover intermediates is extraction via organic solvent, after esterification or acetylation, followed by analysis through gas chromatography or gas chromatography/mass spectrometry. The possible byproducts of the phenol degradation are hydroquinone, resorcinol, catechol, pyrogalol, 1,4-benzoquinone, 1,2,4-benzenetriol, salicylic acid, 2-propylphenol, 2-hydroxy-1,4-benzoquinone, 2,2-dihydroxybiphenyl, 2-hydroxybenzophenone, hydroxybenzoic acid, 2-hydroxybenzophenone, 4,4'-dihydroxybiphenyl, 2-propylphenol, hydroxybenzoic aldehyde, muconic acid, muconic aldehyde, maleic acid, 3-hydroxypropyl acid and hydroxylacetic acid. Scheme 2 illustrates the main phenol degradation intermediates, which these intermediates undergo more photocatalytic oxidation generate polar intermediates such as carboxylic acids and aldehydes and finally CO₂ and H₂O [37–39].

Grabowska et al. prepared new tungsten-containing TiO₂ powders by sol–gel method and by surface impregnation method. The photocatalytic activity was investigated through photocatalytic degradation of phenol in the aqueous solution under visible light irradiation. The photodegradation pathway was investigated via detection of phenol degradation byproducts, generated after irradiation in the presence of W-TiO₂ photocatalyst. The reported byproducts of phenol degradation were Catechol and Muconic aldehyde [40].

Tao et al. investigated photocatalytic degradation of phenol in the presence of nano-ZnO as immobilized photocatalysts. Phenol in water was first extracted through the fiber, that was subsequently inserted into an aqueous system with nano-ZnO photocatalysts exposed to an irradiation source (ultraviolet A (UVA) lamps). After various illumination times (5–80 min), four main intermediates of photodegradation produced on the fiber were detected via chromatography/mass spectrometry including hydroquinone, catechol, benzoquinone, and acetic acid [41].

Wang et al. reported a facile, one-step synthesis of GO/Ag₃PO₄ and the photocatalytic activity of the composites studied by the degradation of RhB and
Bisphenol A under visible light irradiation. The possible degradation path was suggested via liquid chromatography mass spectrometry analysis. It could be vividly seen that Bisphenol A (m/z 227) eluted at a retention time of 5.83 min and reduced quickly in the reaction. Only one intermediate at m/z 151 was detected through the liquid chromatography mass spectrometry analysis and identified as methyl 4-hydroxybenzoate. According to the intermediates detected, the photogenerated holes and \( \text{O}_2^\cdot \) reacted directly with Bisphenol A molecules adsorbed on the surface of catalyst in order to generate 4-isopropenylphenol and then the 4-isopropenylphenol was further degraded to methyl 4-hydroxybenzoate [42].

### 3. Treatment of organic pollutants by heterogeneous photocatalysis and the role of graphene in enhancing the photocatalytic performance of heterogeneous photocatalysis

Heterogeneous photocatalysis describes as the acceleration of sequence of reactions in the presence of a catalyst. Recently, heterogeneous photocatalysis has focused on the use of semiconductors as photocatalysts to removal of contaminants from aqueous solutions. When a semiconductor is irradiated with photons which light energy is equal to or greater than their band gap energy, there is absorption of the photons and formation within the bulk of electron/ hole pairs, that separate into free photoinduced electrons in the CB and photoinduced holes in the VB. The photoinduced holes oxidize water molecules or the hydroxyl groups to form \( \text{^\cdot} \text{OH} \) radicals while the photoinduced electrons reduce the dissolved oxygen to produce \( \text{O}_2^\cdot \), which then reacts with \( \text{H}^+ \) to generate \( \text{^\cdot} \text{OOH} \), followed by decomposition to \( \text{^\cdot} \text{OH} \) radicals (Figure 2) [43–45]. It should be mentioned that \( \text{^\cdot} \text{OH} \) radical is the primary oxidant in the photocatalytic oxidation of contaminates such as phenolic compounds. \( \text{^\cdot} \text{OH} \) radicals (\( E^0 = 2.80 \text{ V vs. NHE} \)) has a higher oxidation potential than other ordinary oxidizers like \( \text{H}_2\text{O}_2 \) (\( E^0 = 1.77 \text{ V} \)) and \( \text{O}_3 \) (\( E^0 = 2.07 \text{ V} \)) also, the repeated attack of organic contaminants by \( \text{^\cdot} \text{OH} \) radicals finally leads to complete oxidation [46–51]. The basic photocatalytic processes are represented by the following chain reactions [52]:

\[
\text{photocatalyst} + h\nu \rightarrow \text{photocatalyst} (e^- + h^+) \quad (1)
\]

\[
\text{photocatalyst} (h^+) + \text{H}_2\text{O} \rightarrow \text{^\cdot} \text{OH} + \text{H}^+ \quad (2)
\]

\[
\text{photocatalyst} (e^-) + \text{O}_2 \rightarrow \text{^\cdot} \text{O}_2^- \quad (3)
\]

\[
\text{^\cdot} \text{O}_2^- + \text{H}^+ \rightarrow \text{^\cdot} \text{OOH} \quad (4)
\]

\[
\text{^\cdot} \text{OOH} + \text{H}^+ + \text{photocatalyst} (e^-) \rightarrow \text{H}_2\text{O}_2 \quad (5)
\]

\[
\text{H}_2\text{O}_2 + \text{photocatalyst} (e^-) \rightarrow \text{^\cdot} \text{OH} + \text{OH}^- \quad (6)
\]

\[
\text{Pollutant} + h\nu \rightarrow \text{Oxidation products} \quad (7)
\]

\[
\text{Pollutant} + e^- \rightarrow \text{Reduction products} \quad (8)
\]

\[
\text{Pollutant} + \text{^\cdot} \text{OH} \rightarrow \text{Degradation products} \quad (9)
\]

The absorption of photons to generate electron/hole pairs is the key to an effective photocatalytic reaction. Lots of semiconductors have wide band gaps, so they can be excited under UV illumination. Since the visible light accounts for 46% and UV light only accounts for 5% of the total energy from the sun, it is perfect to utilize visible solar energy because of the large amount that reaches the Earth’s surface [53]. Another profound issue that must be considered is the recombination rate of electron/hole pairs. This factor has significant effect on the photocatalytic performance of semiconductors. It is very necessary to decrease the recombination rate of electron/hole pairs. Moreover, heterogenous photocatalysis also requests for the adsorption of the contaminants on the surface of photocatalyst as an essential step. Consequently, appropriate concentrating the target contaminants around the surface of semiconductor can be highly

![Figure 2. Schematic of reactions occurring via photocatalysis to form \( \text{^\cdot} \text{OH} \) in order to react with pollutants [43–45].](image-url)
efficient in improving the photocatalytic reaction due to the contaminants can then react readily with \( \cdot OH \) radicals, and also serve as scavengers for electrons and holes [54,55].

The sheets of GO exhibit remarkable performance in photodegradation of organic pollutants. Numerous studies on semiconductor/graphene nanocomposites have indicated that GO sheets can act as 2D soft matter with multiple functions. Due to the \( p \)-conjugated basal plane and high surface area, reduced graphene oxide or partially reduced GO has been used as an electron sink for metal-containing photocatalysts to decrease recombination rate of photon-generated charge carries and facilitates charge transport for photodegradation process. Moreover, the unpaired \( \pi \) electrons on GO can bond with the metal atoms of semiconductors with wide band gap such as ZnO in order to extend the light absorption range of these semiconductors. On the other hand, GO sheets due to the presence of hydrophilic oxygen groups on the basal planes and edges are outstanding surfactant to separate and disperse nanoparticle-semic conductors or dye molecules to improve photocatalytic degradation efficiency of semiconductors. Also, sheets of GO can function as a solid-state mediator via storing the photoinduced electrons from the \( n \)-type semiconductor and further transporting the photoinduced electrons to the \( p \)-type semiconductor. It should be mentioned that the sheets of GO are \( p \)-type and sometimes generate \( p \)-\( n \) junctions (with other \( n \)-type semiconductors), instead of being electron acceptor. Furthermore, the electron storage and transport capabilities of GO make it an efficient mediator to separate photoinduced \( e^-/h^+ \) pairs and improve photocatalytic degradation of photocatalysts [56].

Wang et al. prepared the \( Ag_2CO_3/rGO \) composite by a facile chemical precipitation method. The photocatalytic performance and stability of the \( Ag_2CO_3/rGO \) composite were investigated by photodegradation of RhB under visible light illumination. The prepared \( Ag_2CO_3/rGO \) composite exhibited much higher photocatalytic activity than that of neat \( Ag_2CO_3 \) powder because of the multiple effects of rGO such as decreasing the crystal size of \( Ag_2CO_3 \), enhancing light absorption and facilitating for electron transfer. In fact, rGO inhibited the growth of \( Ag_2CO_3 \) crystals and enhanced the specific surface area of \( Ag_2CO_3 \) photocatalyst, that is conducive to more RhB-adsorption. Simultaneously, the rGO accelerated the reduction of \( Ag^+ \) species into metallic \( Ag \) nanoparticles. The surface plasmon response effect of \( Ag \) nanoparticles improved the utilization of visible light. So, the perfect electron-transport performance of rGO facilitated the separation of photoinduced \( e^-/h^+ \) pairs and improved the photocatalytic activity of pure \( Ag_2CO_3 \) powder [57].

Chen et al. reported the preparation of \( GO/TiO_2 \) composites. The authors showed that the prepared samples by GO have band gap energies narrower than 2.43 eV. When \( GO \) formed a \( p \)-type semiconductor, a \( p/n \) heterojunction could be observed. Visible light-driven photocatalytic performance of \( GO/TiO_2 \) composites in degradation of MO showed that the prepared composite has higher photocatalytic degradation efficiency than pure \( TiO_2 \) nanoparticles [58].

Wang et al. reported a facile method for the synthesis of RGO-anatase \( TiO_2 \) nanocomposite. Based on the obtained results, the integration of RGO with anatase \( TiO_2 \) significantly increase the photovoltaic response and significantly prolong its mean life time of electron-hole pairs compared with that of anatase \( TiO_2 \) [59].

Sajjad et al. synthesized nanocomposite of \( GO/WO_3 \) in various ratios to make the efficient visible light heterojunctions. The authors investigated the role of \( GO \) content in the greater absorptivity and photocatalytic degradation of MO under visible light irradiation. According to the obtained results, the highest visible light photocatalytic activity is due to the formation of heterojunction in which \( WO_3 \) is deposited on smooth surface of \( GO \), narrow band gap, and formation of W-O-C linkages. The aforementioned factors are responsible for effective visible light penetration [60].

Zhong et al. synthesized a ternary \( Ag/BiOI/GO \) composite photocatalyst by a facile chemical method. The BiOI modification was performed via noble metal surface sedimentation and nonmetal doping. Compared with \( BiOI \), \( Ag/BiOI \), and \( GO/BiOI \), the synthesized \( Ag/BiOI/GO \) composite showed the highest photocatalytic activity, with a RhB photodegradation rate of up to 99.12% within 120 min. It is reported that the increased photocatalytic capability could be related to the presence of Ag and GO. Because of the surface plasmon resonance effect of Ag, photogenerated electrons were transferred to particles of Ag via formation of Schottky barriers between the Ag and BiOI and thus increasing charge separation and delaying recombination of photoinduced \( e^-/h^+ \) pairs. Moreover, GO remarkably impacts photocatalysis because of its unique electronic storage characteristics. Perfect conductivity between BiOI and GO enables rapid \( e^- \) transfer, that decrease recombination rate of \( e^-/h^+ \) pairs and thereby prolongs the charge carriers’ life-spans [61].

Xu et al. reported preparation of \( Z \)-scheme \( Ag_2CrO_4-GO \) composite photocatalyst by a simple precipitation method. Comparing with the pristine \( Ag_2CrO_4 \) powders, the as-prepared \( Ag_2CrO_4-GO \) composites exhibited significantly increased photocatalytic activity on the dyes photodegradation of dyes and phenol under visible light illumination. Furthermore, the photocorrosion of \( Ag_2CrO_4 \) was effectively inhibited because of the presence of GO as electron transfer medium and acceptor. It should be mentioned that the photocatalytic reaction in the presence of \( Ag_2CrO_4-GO \) photocatalyst followed
a Z-scheme mechanism. Because of the narrow band gaps of $\text{Ag}_2\text{CrO}_4$ and GO, both can be simply excited to yield photoinduced $e^-/h^+$ pairs under visible-light illumination. Since both the CB and VB positions of $\text{Ag}_2\text{CrO}_4$ are lower than those of GO, the photoinduced $e^-$ in the CB of $\text{Ag}_2\text{CrO}_4$ tend to transfer and recombine with the photoinduced $h^+$ in the VB of GO. Also, the photoinduced $h^+$ left behind in the VB of $\text{Ag}_2\text{CrO}_4$ can directly oxidize MB. At the same time, the remained photoinduced electrons in the CB of GO can reduce the adsorbed $\text{O}_2$ to $\cdot\text{O}_2^-$, that is one of the main oxidative species for degradation of MB. However, compared to the $\cdot\text{OH}/\text{H}_2\text{O}$ potential, the VB energy levels of $\text{Ag}_2\text{CrO}_4$ and GO are not positive enough to drive the oxidation process of $\text{H}_2\text{O}$ to form $\cdot\text{OH}$ because of their insufficient oxidation ability, that is confirmed via the photoluminescence technique using coumarin as a probe molecule to detect $\cdot\text{OH}$. According to the obtained results, no significant $\cdot\text{OH}$ could be detected in the photocatalytic reaction here. Consequently, this photocatalytic reaction followed a typical Z-scheme mechanism, that enables a rapid separation and transfer of the photoinduced $e^-/h^+$ pairs and a strong oxidation and reduction ability for effective photodegradation of organic pollutants. Moreover, the rapid transfer of photoinduced electrons from $\text{Ag}_2\text{CrO}_4$ to the sheets of GO

**Figure 3.** Schematic diagram depicting the $e^-/h^+$ pair separation and energy band structure in the p-n heterojunction [65–67].

**Figure 4.** Schematic diagram depicting the $e^-/h^+$ pair separation and energy band structure in the non p-n heterojunction [63,64].
before Ag$^+$ is reduced to Ag$^0$ prevents the photocorrosion of Ag$_2$CrO$_4$ and improves stability of the prepared composite [62]

4. The categories of semiconductor heterojunction photocatalysts

Recently, significant efforts have been placed on the synthesis of heterojunctions for promoting the photocatalytic performance. There are four normal categories of heterojunction photocatalysts, including: the semiconductor/semiconductor heterojunction, the semiconductor/metal heterojunction, the semiconductor/carbon group heterojunction (carbon group: activated carbon, carbon nanotubes and graphene), the multicomponent heterojunction.

4.1. The semiconductor/semiconductor heterojunctions

In overall, the semiconductor/semiconductor heterojunctions can be divided into two various types including: i) p–n semiconductor heterojunction (Figure 3), ii) non-p–n heterojunction systems (Figure 4). The p–n heterojunction involves a p-type semiconductor with an n-type semiconductor, and it has been proved that the generation of p–n heterojunctions are efficient for promoting the photocatalytic performance of composite catalysts. When the p- and n-type semiconductors are in contact (before the illumination of light), create an internal electric field in the region closed to the p–n interface because of the electron/hole diffusion tendency of the composite semiconductors with unequal Fermi levels [63–67]. when the p–n heterojunction is illuminated by a light, the electron/hole pairs will be formed in the semiconductors and because of the presence of an internal electric field, the photinduced electrons and holes will transfer to the CB of the n-type semiconductor and the VB of the p-type semiconductor, respectively. The p–n type of heterostructure has many advantages including: (1) a more effective charge separation, (2) a longer lifetime of the charge carriers, (3) a rapid charge transfer to the catalyst, and (4) a separation of locally incompatible reduction and oxidation reactions in nanospace.

For instance, Pirhashemi et al. reported the preparation of binary ZnO/MnWO$_4$ nanocomposites with p–n heterojunction by a facil ultrasonic-calcination route. The photocatalytic performance of the synthesized samples was investigated by degradations of RhB, MB, MO and fuchsine pollutants under visible-light irradiation. The ZnO/MnWO$_4$ nanocomposites showed better photocatalytic performance than pure ZnO and pure MNWO$_4$. The Photocatalytic performance of ZnO/MnWO$_4$ nanocomposite is 22.5, 17.7, 26.8, and 23.9 times higher than that of the pure ZnO nanoparticles in photodegradations of RhB, MB, MO and fuchsine dyes, respectively. This improved photocatalytic activity was related to the generation of p–n heterojunction between ZnO and MnWO$_4$ with high charge carrier separation efficiency and high visible-light absorption ability. The Fermi level of MnWO$_4$ as a p-type semiconductor is close to its VB while Fermi level of ZnO as n-type semiconductor is close to its CB. When p-type MnWO$_4$ contacted with n-type ZnO to generate a p–n heterojunction, the Fermi energy levels of MnWO$_4$ and ZnO and tend to ascend and descend, respectively to reach an equalized Fermi energy level and the charges diffusion near the interface creates inner electric field, directed from ZnO to MnWO$_4$. This inner electric field creates opportunity for spatial separation of the photogenerated e$^−$/h$^+$ pairs on MnWO$_4$, because of its narrow band gap. So, the photinduced electrons in the CB of MnWO$_4$ are transferred to ZnO, suppressing recombination of the photogenerated e$^−$/h$^+$ pairs. It should be mentioned that due to the wide band gap of nanoparticles of ZnO, these nanoparticles cannot be excited via visible light. So, the migrated electrons from the CB of MnWO$_4$ to that of ZnO are spatially separated from the holes in the VB of MnWO$_4$, leading to effectively separation of the charge carriers. Therefore, the main reason for the improved performance was related to the formation of p–n heterojunctions between ZnO and MnWO$_4$ semiconductors [68].

Wu et al. synthesized a novel p–n heterojunction of Bi$_2$Sn$_2$O$_7$–Ag$_2$CrO$_4$ composite. According to the reported results, the Bi$_2$Sn$_2$O$_7$–Ag$_2$CrO$_4$ composite has the highest degradation efficiency of 97.5% for RhB in 120 min visible light irradiation, that was remarkably higher than that of 76.7% of Ag$_2$CrO$_4$ and 11.8% of Bi$_2$Sn$_2$O$_7$, respectively. The improved photocatalytic performance could be ascribed to the generation of the p–n heterojunction at the interface of p-Bi$_2$Sn$_2$O$_7$ and n-Ag$_2$CrO$_4$ [69].

Figure 5. Schematic of the schottky barrier [73,74,156].
Yang et al. reported that under simulated solar light 4-NP can be effectively degraded in the presence of Cu2O/TiO2 p-n junction network. This network exhibited much higher degradation rate (1.97 µg/min cm²) than the unmodified TiO2 (0.85 µg/min cm²). The increased photocatalytic activity was related to the extended absorption in the visible resulting from the Cu2O nanowire networks and the efficient separation of photoinduced carriers driven by the photogenerated potential difference formed at the Cu2O/TiO2 p-n junction interface [70].

Moreover, there is another type of heterojunction systems which named non-p–n heterojunction system. In the non-p–n heterojunction systems, first semiconductors and second semiconductor with matching band potentials are tightly bonded to form the effective heterostructure. When the CB level of second semiconductor is lower than CB of first semiconductor, photoinduced electrons in the CB of first semiconductor can be migrated to the CB of second semiconductor under visible light illumination. If the VB level of second semiconductor is lower than the VB of first semiconductor, holes in the VB of second semiconductor can be moved to the VB of first semiconductor. Consequently, the separation and migration of photoinduced carriers can be improved by the internal field, so less of a barrier exists. Based on above process, a great number of electrons on the surface of the second semiconductor and holes on the surface of first semiconductor can participate in photoredox reactions to degrade organic pollution such as phenolic compounds, so the photocatalytic reaction can be increased.

For instance, Wang et al. reported a simple X-assisted (X = Cl, Br, I) one-pot hydrothermal reaction to prepare a series of BiOX/Bi2WO6 heterojunction. All BiOX could improve the photocatalytic performance of Bi2WO6, but the BiOBr was the optimum for the maximum improvement of Bi2WO6. Under visible light irradiation, simultaneous excitation of both Bi2WO6 and BiOBr led to electrons migrate from Bi2WO6 to BiOBr and holes migrate from BiOBr to Bi2WO6 that enhanced charge separation efficiency and decreased the recombination rate of electrons and holes. The oxidation of benzyl alcohol was investigated in the presence of the prepared samples. Totally, the band matching of the composites determined their photocatalytic activity difference, which was also consistent with the photocurrent test results. Vividly, the staggered band match was more beneficial than the sandwiched band match for the photogenerated charge separation in the heterojunction structure. This demonstrated that BiOBr was the optimum for the maximum improvement of the photocatalytic activity of Bi2WO6 under visible light irradiation among BiOX (Cl, Br, I) [71].

Huang et al. reported that energy-levels well-matched Mg0.7Cu0.3WO4/Bi2WO6 heterojunctions staggered conduction bands and valence bands have been constructed through semiconductor band gap engineering based on solid solution design and prepared via a simple hydrothermal method. The prepared Mg0.7Cu0.3WO4 and Bi2WO6 samples. The fabrication of well-matched overlapping band structures can result in efficient-photoinduced charge transfer between Mg0.7Cu0.3WO4 and Bi2WO6, enhancing the visible light driven photocatalytic reactivity [72].

4.2. The semiconductor/metal heterojunctions

The semiconductor/metal heterojunction is another useful strategy to create a space-charge separation region which named the Schottky barrier. At the interface of the two materials, electrons flow from the higher Fermi level of one material to the lower Fermi level of another material to align the Fermi energy levels. Generally, the heterostructures of n-type semiconductor/metal has been investigated. The suitable situation is that the work function of the metal is higher than that of the n-type semiconductor and electrons flow from the semiconductor into the metal in order to align the Fermi energy levels (Figure 5). Due to this fact that the metal has excess negative charges and the n-type semiconductor has excess positive charges, the Schottky barrier can be formed. It should be stressed that Schottky barrier can act as an effective electron trap and it can prevent e−/h+ recombination. Recently, a large number of semiconductor/metal heterojunction photocatalysts have been successfully synthesized by various research groups [44,73].

For example, Prof. Antonietti’s group showed the latest progress in the fabricated of semiconductor/metal heterojunctions, such as N-doped carbon–metal and C3N4/metal heterojunctions [74].

Bi et al. reported a simple way to prepare of Ag/Ag3PO4 heterostructures. The photocatalytic performance of this heterostructure showed much higher catalytic activities than pure Ag3PO4 or Ag nanowires for degradation of organic dyes under visible light irradiation. This indicated that metal-semiconductor heterostructures can be an efficient way to improve photocatalytic activity [75].

Meng et al. synthesized a ternary TiO2−MnOx−Pt hybrid photocatalyst by hydrothermal and photodeposition method. The increased activity of TiO2−MnOx−Pt photocatalyst can be related to three different junctions amalgamated in a sole composite for synergistic activity enhancement. Namely, TiO2 generated a surface heterojunction, that separated the photogenerated electrons and holes onto different facets as the formation sites for the p-n junction and semiconductor/metal junction, respectively [76].
4.3. The semiconductor/carbon heterojunctions

4.3.1. Semiconductor/activated carbon heterojunctions

Activated carbon can be used as a support for semiconductor materials in photodegradation processes because of its high specific surface area. The enhance of the surface area leads to the improvement of the photocatalytic performance. So, it can be concluded that combining semiconductors with the activated carbon yields an enhance in adsorbed amounts of contaminants and increases their photocatalytic activity.

Xing et al. prepared TiO$_2$/activated carbon photocatalyst by a sol-gel method. The photocatalytic activity of this composite was investigated through the degradation of RhB under UV light irradiation. The results indicated that TiO$_2$ particles deposited homogeneously on the surface of activated carbon. The high removal rate of RhB of TiO$_2$/activated composite was related to the significant adsorption effect in the dark and high-efficiency photocatalytic degradation under UV light illumination. In dark condition, the removal process depends strongly on the adsorption performance activated carbon as substrate, while under UV light illumination, the RhB removal process requires the contaminant to be adsorbed on the TiO$_2$/activated composites surface prior to immediate photocatalytic degradation. Consequently, the efficiency of photodegradation process can be affected by the adsorption performance of substrate activated carbon and the photocatalytic activity of TiO$_2$ particles [77].

Muthirulan et al. reported the preparation of a simple method for removal of color from printing wastewater and textile dyeing via ZnO as photocatalyst supported with porous-activated carbon. The photodegradation studies were performed for water soluble toxic alizarin cyanin green dye in aqueous suspension along with activated carbon as co-adsorbent. It was seen that photocatalytic degradation by ZnO/activated carbon composite was a more efficient and faster mode of removing dye from aqueous solutions than pristine ZnO particles. According to the obtained results, the decolorization of alizarin cyanin green dye is due to photocatalytic degradation process not by pure adsorption and the improvement of photocatalytic degradation efficiency is due to synergistic or cooperative effect [78].

4.3.2. Semiconductor/CNT heterojunctions

The CNTs with a one-dimensional tubular structure have excellent physical and chemical properties, such as high strength and modulus, outstanding electrical and thermal conductivity, very good chemical stability as well as unique optical properties. Stronger adsorption on photocatalyst for the molecules of contaminants is obtained via the incorporation of the CNTs, because of their high-quality active sites and large specific surface area. Moreover, the CNTs can act as efficient electron transfer unit due to their high electrical conductivity and high electron storage capacity. The CNTs can facilitate the rapid transmission of electrons and the presence of the CNTs in the composite can decrease the recombination rate of photoinduced e$^-$/h$^+$ pairs, thus increasing the photocatalytic efficiency [79,80].

Madadi Mahani et al. successfully synthesized CNT/Ag$_3$PO$_4$ hybrid. The photocatalytic activity of this hybrid was investigated by degradation of RhB as a model contaminant. The obtained results exhibited that CNT/Ag$_3$PO$_4$ hybrid displayed much higher photocatalytic activity than the pristine Ag$_3$PO$_4$ nanoparticles. During photocatalytic degradation process, the Ag$_3$PO$_4$ can be excited to produce photoinduced charge carriers and photogenerated electrons from VB of Ag$_3$PO$_4$ are transferred to the CB of Ag$_3$PO$_4$, leaving the holes in the VB. In hybrid of the CNT/Ag$_3$

![Figure 6](image-url). Schematic illustrations of electrons and holes carrier transfer for (a) semiconductor and (b) semiconductor/graphene composite [7,8,21].
PO₄, the photogenerated electrons are trapped by CNT. The CNT can be improved photocatalytic performance and stability because of the fact that the presence of CNT remarkably improves the separation of photoinduced charge carriers. Consequently, e⁻/h⁺ pairs could be helpfully separated so that the photocatalytic activity of the catalyst would be increased. Due to the narrow band gap of CNT/Ag₂PO₄ hybrid, the optical absorption of this hybrid in the visible light region can be significantly increased. Interestingly, it was found that the CNTs are not only efficient sensitizers, but also highly active co-catalysts in hybrids [81].

Huang et al. prepared TiO₂/CNTs composite via hydrothermal method and phenol and Cr(VI) were selected as target compounds. Based on the obtained, the photocatalytic activity of the prepared composite is higher than that of pure TiO₂. In fact, CNTs can provide a larger specific surface and then produce more active sites, exhibiting adsorption effect. Also, CNTs can stabilize the charge separation via trapping the electrons and then enhance the ‘OH amount, exhibiting electron trap effect [82].

### 4.3.3. Semiconductor/graphene heterojunctions

Graphene is a single layer of graphite with unique properties. It can absorb light over a broad range of wavelengths and it has high specific area. In addition, graphene can decrease photogenerated electrons and holes recombination by acting as electron acceptor and electron transporter. Consequently, the development of semiconductor/graphene composites is a valuable approach to improve performance of semiconductors in heterogeneous photocatalysis. The presence of graphene in the composites promotes the charge separation, delays the electron/hole recombination and provides high surface/interface for heterogeneous reactions that results in an improved photocatalytic performance. As depicted in Figure 6, electron/hole pairs are formed within the semiconductor under light irradiation, the photoinduced electrons tend to transfer to the sheets of graphene and then trapped by dissolved oxygen, decreasing the recombination rate of hole/electron pairs. Meanwhile, the holes leaving from the VB of the semiconductor can either react with adsorbed water or surface hydroxyl to produce hydroxyl radicals or directly oxidize different organic compounds. It should be mentioned that in some composites, the electronic interactions and charge equilibration between graphene and the semiconductor lead to a shift in the Fermi level and reduce the potential of CB of the semiconductor, so the negative shift in the Fermi level of semiconductor/graphene and the high migration efficiency of photogenerated electrons can restrain the charge recombination efficiently, resulting in the improved photocatalytic performance [7,8,21,83].

#### 4.3.3.1. Synthesis of semiconductor/graphene nanocomposites

Up to now, a great number of semiconductors such as metal oxides (e.g., TiO₂ [84], SnO₂ [85], WO₃ [86], ZnO [87], Nb₂O₅ [88], Fe₂O₃ [89]), metal sulfides (e.g., CdS [7], In₂S₃ [90], SnS₂ [21], Sb₂S₃ [91]), metallates (e.g., BiVO₄ [92], CoFe₂O₄ [93], BiFeO₃ [21], MgFe₂O₄ [8], Bi₂WO₆ [94]) and other semiconductor materials (e.g., Zn(CH₃COO)₂ [95]) have been loaded on graphene-based templates. There are many techniques for preparing these kinds of composite photocatalysts. Lots of the procedures are similar to those utilized for other nanocomposite systems. In overall, all of these procedures can be divided into two fundamental categories: in-situ crystallization and ex situ hybridization.

#### 4.3.4. In situ crystallization

In-situ crystallization is a well-known strategy for preparation of semiconductor/graphene materials. In-situ crystallization is the producing of nanocrystallites in the presence of graphene-based materials such as GO, followed by their growth into nanomaterials on the surface of GO nanosheets and latter reduction of GO to form graphene-based composite. For instance, ions of Ti⁴⁺ or Sn⁴⁺ were added into the dispersion solution of GO and converted to TiO₂ or SnO₂ nanoparticles (at low temperatures). In fact, in this process GO was reduced by TiCl₄ or SnCl₂. The growth of nanocrystals of TiO₂ and SnO₂ with different morphologies on the rGO sheets was related to the various reduction abilities and hydrolysis rates of Ti⁺³ and Sn⁺³, respectively [96].

Due to the in situ nucleation of nanoparticles, homogeneous distribution of nanocrystals occurs on the surface of nanosheets. It should be noticed that the oxygen functional groups on GO can act as nucleating sites to control the size, crystallinity of the in situ grown nanoparticles and morphology. Moreover, the direct contact of semiconductors with sheets of graphene increases the rate of electron transport [97,98].

**Solution mixing**: This technique has been widely used and involves the mixing of colloidal suspension of graphene-based materials such as GO platelets with the certain amount of semiconductor materials under ultrasonic agitation or vigorous stirring. During the mixing, the aforementioned precursors are transformed into products, that distribute themselves on the sheets’ surface and interconnect each sheet when the solvent is evaporated to produce the composite. On the other hand, graphene-based nanocomposites can be prepared by the reduction of GO, employing reducing agents such as sodium borohydride, amines, or ascorbic acid [99].

For example, Paek et al. prepared the sol of SnO₂ via hydrolysis of SnCl₄ with NaOH and after that the as-prepared dispersion of graphene was added to the SnO₂ sol in ethylene glycol as solvent to prepare the composite of SnO₂/graphene [100].
Mukherji et al. synthesized nitrogen-doped Sr$_2$Ta$_2$O$_7$ coupled with sheets of graphene by blending the dispersion of GO and Sr$_2$Ta$_2$O$_7$-N$_x$, followed by reduction of GO under xenon lamp illumination [101]. Zhu et al. employing the system of water/oil to form the composite of GO/Ag/AgX (X = Br, Cl). In the aforementioned work, the GO aqueous solutions and AgNO$_3$ was added to chloroform solution of CTAB or CTAC under stirring at room temperature. Graphene’s large network (sp$^2$ hybridized carbon) can form strong π-π bonds with other graphite-like materials. For example, Sun et al. prepared graphene/graphitic carbon nitride composite via a combined solution mixing–chemical reduction method. In fact, graphitic carbon nitride was deposited on the GO sheets’ surface to produce a layered composite via polymerizing melamine molecules which adsorbed on surface of GO because of the π – π interaction of aromatic structures between graphitic carbon nitride and GO [102].

**Hydrothermal/solvothermal process:** This method is one of the traditional methods for crystal growth of semiconductors. It should be noted here that the hydrothermal/solvothermal process is an efficient method for the preparing of semiconductor/graphene composites. During this process, nanoparticles of semiconductor or their precursors are loaded on the sheets of GO. The aforementioned process involves the using of single or heterogeneous phase reactions in aqueous solution at elevated pressure and temperature to crystallize metal-based nanostructures directly. The solvothermal method involves a similar reaction in the presence of various organic and inorganic solvents. For this reactions (hydrothermal/solvothermal reactions), an autoclave is needed [103,104]. For instance, Fu et al. prepared a composite of ZnFe$_2$O$_4$–graphene as photocatalyst via a one-step hydrothermal method. The precursors of Fe(NO$_3$)$_3$·9H$_2$O and Zn(NO$_3$)$_2$ was used to produce of ZnFe$_2$O$_4$, and GO was used as a source of graphene sheets. During the hydrothermal process, GO was reduced to rGO and at the same time nanoparticles of ZnFe$_2$O$_4$ were formed on the sheets of graphene [105].

Bagherzadeh et al. synthesized a composite of CdS–NiFe$_2$O$_4$ with GO as photocatalyst by simple hydrothermal steps. The photocatalytic performance of nano-composite showed excellent performance in photodegradation of MB and its activity was improved compared with the activity of a mechanical mixture of three components in the prepared composite [7].

Similarly, Zhang et al. fabricated the graphene–TiO$_2$ nanocomposite by hydrothermal process of GO sheets and Degussa P25 TiO$_2$ in an ethanol–water solvent [106].

Very recently, Wen Pu et al. prepared N-doped graphene/Fe$_3$O$_4$ nanocomposite by a facile hydrothermal method [107].

Consequently, using the hydrothermal/solvothermal methods for synthesizing of semiconductor/graphene nanocomposites has become increasingly common compared with other methods. This issue has several reasons including low energy requirement, high reactivity, nonpolluting set-up, high yield of nanocomposites at low cost, simple control of the solvent, and mild reaction conditions [108].

**Sol–gel method:** The sol–gel process is a beneficial chemical approach for preparation of semiconductor/graphene composites. Although the sol-gel process can be conducted under mild conditions including the atmospheric pressure and low temperature, however, it always requires further heat treatment to remove the organic compounds and enable the crystallization of the semiconductors. This method involves the phase transition of a system from a sol (colloidal liquid) into a solid gel by a sequence of hydrolysis and polycondensation reactions. Most of the time, the precursor materials utilized in the forming of the sol are metal alkoxides, metal chlorides, or organometallic compounds [109,110]. For instance, Davoodnia et al. reported the microwave-assisted sol-gel synthesis of nanoparticles of MgO and their catalytic activity in the fabricate of Hantzsch 1, 4-dihydropyridines [111]. Farhangi et al. synthesized Fe-doped TiO$_2$ on the surface of functionalized graphene sheets through a sol-gel strategy in the green solvent. During this process, the nanosheets of graphene play a role of template for nanowire growth via surface – COOH functionalities [112]. Botta et al. investigate the photocatalytic activity of neat and Fe-containing ZrO$_2$ nanoparticles in transformation of substrates nitrite, Cr (VI) and EDTA and compared with that of TiO$_2$ (Degussa P-25) through the sol-gel process [113]. Ghorbani et al. reported hierarchical porous nanostructured ZnO and ZnO/rGO composite by sol–gel method [114]. Rostami et al. prepared a ternary nanocomposite of TiO$_2$–graphene–ZnFe$_2$O$_4$–Tb$_2$O$_4$ by sol-gel process. During this process, GO was reduced to rGO and anatase TiO$_2$ and cubic spinel ZnFe$_2$O$_4$ were grown on the surfaces of rGO nanosheets at the same time [115].

**Combustion synthesis:** This is another main approach for the in situ synthesizing of semiconductor/graphene composite. Compared with the other methods of preparation semiconductor/graphene composites, the combustion synthesis has some advantages including low external energy consumption, complete conversion of the reactants to products, high-temperatures, short reaction times, self-sustaining instantaneous reaction, fast heating rates, and low-cost equipment. Since high temperatures expel the volatile impurities, fine particles are obtained. In the combustion synthesis, stoichiometric amounts of the semiconductor precursors and graphene-based materials are blended together and an organic fuel such as urea or hydrazides is added. After
that, the obtained mixture is dehydrated and ignited via an external source of energy. The exothermicity of the combustion process provides the needed energy for the synthesis reaction to transpire (upon ignition). The hot combustion waves self-sustaining instantaneous reaction at extremely high velocities through the heterogeneous mixture of reactants, producing the wanted product [116,117]. Gao et al. synthesized GO/TiO₂ composite with increased photocatalytic performance by a one-step combustion method employing titanyl nitrate and urea as the oxidizer and fuel, respectively. During the process, the precursors (GO, fuel and oxidizer) were maintained at various combustion temperatures (300–450°C) for limited time to ignite the combustion reaction [118]. Zhang et al. prepared NiFe₂O₄/rGO composite by a one-pot combustion method. During the combustion synthesis process, GO was reduced rather than severely oxidized and the growth of NiFe₂O₄ was restricted after the combination with rGO. The nanoparticles of NiFe₂O₄ were loaded on the surface of rGO sheets [119].

Microwave-assisted deposition: Microwave synthesis has been characterized as an uniform, energy-efficient, scalable approach and fasted to synthesis semiconductor/graphene composites. The fast microwave heating prepares homogenous reaction environment and leads to good control of size distribution, shape, and aggregation of the product materials. Up to now, microwave irradiation has been identified as an efficient tool to gain carbon-based composites with size and morphology control and uniform dispersion, because the microwave energy allows rapid heating and very rapid rate of crystallization to prepare the nanocrystalline products. During the microwave-assisted synthesis process, it is probable to control the growth of the desirable crystallographic plane through changing the concentrations of various organic surfactants and reaction time. Consequently, various semicon-ductor/graphene nanocomposites with controlled shape and size and shape can be prepared with the help of ecofriendly microwave-assisted method [120–122]. Yang et al. synthesized nanocomposite of graphene-metal oxides (Fe₂O₃ and MnO₂) by solid-state microwave illumination and build asymmetric super capacitor [123]. Hu et al. prepared a composite of graphene/ZnS by microwave-assisted synthesis in aqueous medium. During the microwave irradiation process, GO and Zn(CH₃COO)₂·2H₂O were reduced with thioaceta-mide at the same time [124]. Similarly, Liu et al. synthesized Fe₂O₃/rGO composite by a facile microwave-assisted reduction of graphite oxide in Fe₂O₃ precursor solution using a microwave system and studied as anode material for sodium ion batteries [125]. It is worthy to note here that, it is probable to control and program the steps of synthesis.

Electrochemical deposition: Electrochemical deposition is an efficient approach to synthesize certain types of semiconductor/graphene nanocomposites. Ren et al. reported the dispersed multilayer structures of graphene in a nickel plating solution through employing a surfactant with stirring method. The composites of nickel/graphene were generated on target substrate. In this process nanosheets of graphene were completely dispersed in the nanoparticles of nickel and the oxygen radicals (present in the graphene) were reduced during the electrodeposition process [126]. Purna et al. prepared ZnO bi-pods on rGO films. The nanoparticles of ZnO were directly grown on the rGO films via single-step electrodeposition method. Electrochemical deposition is a simple, fast and clean way to prepare semiconductor/graphene composites. Yin et al. deposited nanorods of ZnO on spin-coated rGO thin films on quartz, with oxygen-saturated aqueous media of ZnCl₂ and KCl (as electrolyte) [127]. Similarly, Du et al. reported an electrochemical deposition approach to synthesize the composite of the graphene–ZrO₂ on a glass carbon electrode [128].

Photo-assisted reduction: The method of photo-assisted has been recognized as a promising strategy for preparing of semiconductor/graphene composites. Photochemical reduction via illuminating a graphene precursor in the presence of metal salts creates a proper way to prepare semiconductor/graphene composites. The photo-assisted synthesis method has lots of advantages such as high spatial resolution and reaction controllability [129]. For instance, Cui et al. synthesized a heterostructure photocatalyst of Ag₃PO₄/reduced graphene oxide/Ag nanocrystals (Ag₃PO₄/rGO/Ag) by a facile photo-assisted reduction approach. The prepared nanocomposite consists of chemical bonding between rGO and Ag₃PO₄ nanoparticles and dispersive plasmonic nanocrystals of Ag on the rGO sheets [130].

4.3.5. Ex situ hybridization

Ex-situ hybridization involves the blending of commercially available or pre-prepared nanocrystals with graphene dispersions. The inorganic nanoparticles attach to the nanosheets of graphene by binding with oxygen functional moieties of GO/rGO [131]. One advantage of this method is its overcoming any incompatibilities between the formation of nanocomposites and nanomaterials syntheses. Also, this method allows co-assembly of nanoparticles with distinctively various shapes, sizes, compositions, and properties on GO/rGO sheets. It should be mentioned that the ex-situ hybridization strategy suffers from non-uniform coverage of the nanoparticles on the GO/rGO sheets’ surface and low density [99].

For instance, Morawski et al. synthesized TiO₂–rGO photocatalyst via mechanically mixing TiO₂ nanoparticles with desired amount of rGO in 1-butyl alcohol and consecutive ultrasonication [132]. Gao et al. prepared GO–CdS nanocomposites via mixing nanoparticles of
CdS with aqueous suspension of GO sheets. GO in the composite can be further reduced by thermal or chemical methods [133]. Before mixing, surface modification of the nanoparticles or nanosheets can be performed to enhance the loading rate of the inorganic nanoparticles on the nanosheets of graphene-based materials. Yong Liu et al. synthesized an aqueous dispersion of graphene via sonication a mixture of graphene raw materials in the presence of polyvinylpyrrolidone (as surfactant) and a suspension of TiO2 via dispersing powder of TiO2 in deionized water with ultrasonicication. During this process, composite of graphene-TiO2 was prepared through simple mechanical blending and sonication using anhydrous ethanol to improve the wettability of the dispersion [134].

4.3.5.1. Semiconductor/graphene nanocomposites for photocatalytic degradation of phenolic compounds. As mentioned, semiconductor/graphene composite photocatalysts have attracted lots of attention for degradation of organic pollutants such as phenol and phenolic compounds. The semiconductor/graphene nanocomposites have many advantages over pure semiconductors. For example, the unique electronic properties resulting from the sp2 hybridized carbon atoms suggest a picosecond ultrafast electron transfer process from the excited semiconductors to the sheets of graphene. The controllable size of the semiconductors and decreased agglomeration of the graphene sheets improve efficiency of the photocatalytic performance. The high transparency of the graphene sheets due to their one or several atoms thickness, increases the utilization of the exciting light. Therefore, chemical characteristics and unique morphological of graphene-based nanocomposites such as high surface area, reactive surface site, tunable structure, high electron conductivity, high mechanical strength, high optical transparency as well as good recyclability allow these nanocomposites to become outstanding choice for photocatalysis. Since neat graphene has low functional groups and it won’t dissolve in wood or organic solvents, GO has attracted considerable attention in the field of photocatalysis. High electron extraction ability and suitable energy level permits the GO/rGO to extend the light absorption process during photodegradation of phenol and phenolic compounds in the presence of GO/rGO-semiconductor nanocomposites. In addition, GO/rGO decreases recombination rate of e- /h+ pairs via capturing the photoinduced electrons to further facilitate the phenol and phenolic compounds photodegradation process [135–138].

Malekshoar et al. synthesized graphene-based titanium dioxide (TiO2/graphene) and zinc oxide composites (ZnO/graphene) by a hydrothermal method. Photocatalytic performance of the prepared composites under visible light was investigated by photodegradation of phenol as a hazardous compound. The reported results show a 30% improvement on the photodegradation performance by the TiO2/graphene composite and ZnO/graphene compared with pure TiO2 and ZnO. It indicates the synergistic effect of graphene suppressing charge recombination and extending the range of light absorption range [139]. He et al. prepared a 3D dimensional BiOI/GO composite via a simple self-assembly method. The as-synthesized BiOI/GO composite exhibited a higher photocatalytic activity than that of neat BiOI nanoparticles toward the photodegradation of phenol under visible light illumination, that could be related to the more efficient separation of photoinduced electron/hole pairs [140]. Chakraborty et al. reported the photocatalytic performance of rGO/CdS composite toward the photodegradation of 4-NP under visible light irradiation. The composite of rGO/CdS prepared via one pot single-step solvothermal method, which the reduction of GO, prepare and attachment of CdS onto the sheets of rGO were done at the same time. According to the obtained results, the photocatalytic activity of rGO/CdS composite is 2.6 times higher in comparison to nanoparticles of CdS. In the composite of rGO/CdS, the photogenerated electrons transfer from CdS nanorod to the sheets of rGO, which decreases the recombination rate of photoinduced electron/hole pairs in the CdS. These well-separated charges improved the photocatalytic performance of the rGO/CdS composite [141]. Naknkhun et al. synthesized a composite of graphene/TiO2 by sol-gel method, which had better photocatalytic activity toward phenol degradation under visible light irradiation compared to pure TiO2 nanoparticles [142]. Xue et al. used a hydrothermal synthesis and in-situ reduction method for preparing the BiOBr, BiOBr/Graphene, and Au/BiOBr/Graphene composites. The photocatalytic activity of Au/BiOBr/Graphene toward phenol degradation under visible light irradiation was investigated. According to the observations, the Au/BiOBr/Graphene composite shows superior photocatalytic activity in the degradation of aqueous phenol, in comparison with BiOBr/Graphene composite and the composite of BiOBr/Graphene composite shows better performance toward the degradation of aqueous phenol in comparison with nanoparticles of BiOBr [143]. Le et al. successfully synthesized the CuFe2O4/GO composite by co-precipitation in-situ using CuCl2·2H2O and FeCl3·6H2O as the sources of copper and iron on GO and followed by thermal reduction. The nanocomposite of CuFe2O4/GO was employed to test the photodegradation of phenol from aqueous solution. After 90 minutes of reaction, the conversion was obtained 90%, which indicated
highly photocatalytic activity of this catalyst. The outstanding performance of the aforementioned catalyst can be related to high catalytic surface area because of the small-sized CuFe$_2$O$_4$ and sheets of GO sheets as well as perfect synergistic coupling of Cu/Fe species and presence of GO sheets that holds the organic species via π–π interactions [144]. Liu et al. fabricated a new GO/Ag$_3$PO$_4$ composite as a visible light-induced photocatalyst by an ion-exchange approach of CH$_3$COOAg and Na$_2$HPO$_4$ in the presence of sheets of GO sheets. The photocatalytic activity of the prepared composite was tested by the degradation of organic dye (AO7) and phenol under visible-light illumination. The results exhibited that composite of GO/Ag$_3$PO$_4$ has remarkably higher photocatalytic activities compared with bare Ag$_3$PO$_4$. In fact, the GO sheets could facilitate charge transfer and suppress the recombination of electron/hole pairs of the GO-based composites. So, GO could work as good electron acceptor and Ag$_3$PO$_4$ as the electron donor. When the composite of GO/Ag$_3$PO$_4$ was irradiated by visible light, the photoinduced electrons could be transferred to the sheets of GO, therefore inhibiting the charge recombination and improving the photocatalytic performance. The effective electron transferring from semiconductor of Ag$_3$PO$_4$ to sheets of GO sheets also maintains the stability of the GO/Ag$_3$PO$_4$ composite via holding electrons away from the Ag$_3$PO$_4$ nanoparticles. On the other hand, the holes on valence band of Ag$_3$PO$_4$ could oxidize pollutants, while the electrons on GO could adsorb surface O$_2$ to generate different reactive oxygen species [0].

Paradhan et al. reported the fabrication of hematite nanorod-graphene composite (α-Fe$_2$O$_3$ nanorod/rGO) through a template-free hydrothermal route. The nanorods of α-Fe$_2$O$_3$ were completely decorated on the surface of the graphene sheets that help in electron transfer from α-Fe$_2$O$_3$ to graphene. The aforementioned process can retard the recombination rate and leading to the improvement in photocatalytic performance. This improvement is attributed to the synergism between α-Fe$_2$O$_3$ nanorods and rGO sheets, surface area, interaction between nanorods and nanosheets of graphene, and light-harvesting properties of the prepared composites [145]. Liu et al. fabricated Bi$_2$O$_3$rGO composite with visible light response via a facile solvothermal approach. The photocatalytic activity of the Bi$_2$O$_3$rGO composite was investigated by the photodegradation of RhB and phenol under visible illumination. The obtained results indicated that the nanoplates of Bi$_2$O$_3$rGO dispersed uniformly on surface of rGO. The photocatalytic activity of Bi$_2$O$_3$/rGO in photodegradation of RhB and phenol was 2.13 and 2.29 times that of Bi$_2$O$_3$ nanoplates, respectively [146]. Gawande et al. employed a simple microwave assisted hydrothermal method for synthesizing the nanocomposite of graphene/BiPO$_4$. The experimental results were promising and exhibited increased photocatalytic activity than BiPO$_4$ for phenol degradation [147].

4.4. The multicomponent heterojunctions for photocatalytic degradation of phenol and phenolic compounds

In spite of all the aforementioned approach, there are still some weakness like the limited region of visible light photo-response. In order to overcome these drawbacks, systems of multicomponent heterojunction have been developed. In a common photocatalytic process, the photoinduced electrons and holes transfer with irregular patterns to the photocatalyst’s surface to react with the adsorbed reactants. Moreover, they suffer from the recombination on the photocatalyst’s surface or in the bulk. Often in the multicomponent heterojunction systems, both semiconductors can be excited by light and have various ranges of photoabsorption, the conjunction of their photoabsorption can broaden the range of light photo-response. The photoinduced electrons in the CB of the first semiconductor can migrate to the CB of the second semiconductor and the photo-induced holes in the VB of the second semiconductor can move to VB of the first semiconductor. Aforementioned process can improve the separation of photoinduced electron/hole pairs. The presence of carbon-based materials such as graphene sheets can speed charge transfer ability, which increases the charge separation efficiency, and inhibit the recombination of the photoinduced electron/hole pairs. In fact, the photoinduced electrons in the CB of the first semiconductor migrate to the graphene sheets because of the marvelous electron conductivity. Since the graphene sheets are outstanding electron acceptors, the electrons are quickly transferred to the graphene sheets and then the electrons migrate to the second semiconductor.

Consequently, graphene has been widely used as an electron acceptor and electron storage center to decrease recombination rate of e-/h$^+$ pairs for the photocatalysts due to its high electron storage capacity and perfect electron conductivity. It should be mentioned that the Fermi level of graphene is lower than the CB of a great number of semiconductors, so the electrons in the CB of the semiconductors can be easily transferred from the semiconductors to the graphene, which increases the separation of photogenerated charge carriers.

For instance, Pu et al. reported preparation of porous-protonated graphitic carbon nitride from bulk g-C$_3$N$_4$ by acid-cutting and hydrothermal process. Based on the obtained results, in the 2D/2D g-C$_3$N$_4$/rGO, the electrons can be easily transferred from g-C$_3$N$_4$ to rGO, because of the lower Fermi level of rGO (~0.08 eV vs
NHE) relative to the CB of g-C3N4 (−0.842 eV vs NHE), so prevented the charge recombination. The enriched electron density on the rGO favors the photocatalytic hydrogen evolution from water [148].

Moreover, graphene can act not only as the electron acceptor and electron storage but also as the electron transport bridge between the semiconductors. For example, Yuan et al. prepared two dimensional 2D ternary MoS2-graphene-ZnIn2S4 composite as highly-effective photocatalyst for solar hydrogen-producing. For the ternary MoS2-graphene-ZnIn2S4 composite, both the MoS2 and the ZnIn2S4 are connected to the graphene. The ZnIn2S4 graphene and MoS2 act as the light-harvesting semiconductor, electron transport bridge and hydrogen evolution reaction catalyst, respectively. In this composite, the CB of ZnIn2S4 is more negative than the graphene/graphene− (G/G−) redox potential, so electrons generated from the CB of ZnIn2S4 can be transferred easily to graphene because of the thermodynamic driving force. Further, the G/G− redox potential is more negative than the CB of MoS2 nanosheets, that is useful for the electron transfer from the electron-rich graphene− to the CB of MoS2. Consequently, with the efficient electron transport bridge and the large number of active sites on the MoS2, the H2 evolution rate from MoS2-graphene-ZnIn2S4 composite was 22.8 times higher than that of pristine ZnIn2S4 under visible light irradiation [149].

On the other hand, graphene sheets can delay aggregation of nanoparticles and increase specific surface area of the prepared composite. Consequently, the systems of multicomponent heterojunction can effectively and simultaneously generate holes with a powerful oxidation power in the VB of the first semiconductor and electrons with a powerful reduction power in the CB of the second semiconductor, resulting in significantly improved photocatalytic performance, compared with the single semiconductor or semiconductor heterojunctions mentioned in the previous sections [150,151].

Singh et al. reported synthesis of AgBr/BiOBr composite loaded on the sheets of graphene employing the facile precipitation method. The photocatalyst of AgBr/BiOBr/graphene was efficiently used for the photodegradation of phenol from water. The phenol was completely degraded into CO2 and H2O within 6 h. The experimental results indicated that integration of AgBr/BiOBr with graphene caused an enhance in photocatalytic activity because of the decreased recombination of photoinduced electron/hole pair and electron sink behavior of graphene for photoinduced electrons of BiOBr. Also the AgBr/BiOBr/graphene photocatalyst showed outstanding stability and recyclability after ten cycles [152].

Bagherzadeh et al. synthesis new magnetically separable rGO/CaFe2O4/Ag3PO4 and rGO/MgFe2O4/Ag3PO4 photocatalysts by the hydrothermal and ion-exchange deposition method. The photocatalytic activity of the prepared catalysts was investigated toward the photodegradation of MB, MO and 4-CP in aqueous solution under visible light irradiation. The optimized photocatalyst, i.e. rGO/CaFe2O4/Ag3PO4 composite not only exhibited the highest photocatalytic activity for the degradation of MB, MO, and 4-CP upon visible light irradiation but also showed significant reusability and stability. The impressive separation of electron/hole pairs and the presence of rGO sheets which act as a high-speed charge transfer were responsible for enhancing photocatalytic activity over the optimized photocatalyst [8].

Rakibuddin et al. prepared graphene encapsulated ZnO/Co3O4 (Graphene/ZnO/Co3O4) core-shell composite by a facile self-assembly approach. The mutual electrostatic interaction force drives the nanostructure of ZnO/Co3O4 to be completely wrapped with flexible ultrathin shells of graphene shells. The synthesized composite showed excellent visible light photocatalytic ability toward dechlorination of 2,4-DCP in aqueous phase and the 2,4-DCP was completely degraded into CO2 and H2O in the presence of Graphene/ZnO/Co3O4 after 5 h. The higher photocatalytic performance of the aforementioned composite can be attributed to the synergistic effect of ZnO, Co3O4 and graphene. Also, high contact surface between metal oxides core and graphene shell, which acts as a continuous path for fast electron transport to suggest more number of reactive species can be the main reason for the enhanced photocatalytic activity of the prepared composite [153].

Hayati et al. reported using multi-step method including hydrothermal, solvothermal, and sol−gel methods for fabricating the ZnO/TiO2 anchored on rGO ternary nanocomposite. The photocatalytic performance of the prepared catalyst was evaluated by degradation of phenol in aqueous solutions. According to the obtained results, degradation of phenol was completed at 160 min under visible light illumination [154].

Peng et al. prepared a new composite material consisting of Ag3PO4 sub-microcrystals grown on a layered MoS2 and graphene composite as an active photocatalyst for the photodegradation of toxic organic contaminants. This photocatalyst was synthesized by a facile two-step hydrothermal process and was an efficient catalyst for the photodegradation of 2,4-dichlorophenol under visible light and simulated solar light. Also, the prepared photocatalyst was a highly active for the photodegradation of chlorophenol and nitrophenol. This outstanding photocatalytic activity comes from the synergetic effects of MoS2 and graphene as cocatalysts in the composite. In fact, nanosheets of MoS2/graphene served as electron collectors for the interfacial electron migrate from Ag3PO4 to electron acceptors in the solution and thus increased the separation of the
Table 3. Photocatalytic degradation of phenol and phenolic compounds in the presence of semiconductor/graphene nanocomposites.

| Photoactive nanocomposite | Synthesis Techniques | Pollutant | Initial Pollutant Conc. | Catalyst Conc. | Light source | Power and light intensity | Irradiation time | Apparent reaction rate constant | Degradation (%) | Ref. |
|---------------------------|----------------------|-----------|-------------------------|----------------|--------------|--------------------------|-----------------|-------------------------------|----------------|-----|
| TiO₂-graphene             | Hydrothermal         | Phenol    | 40 ppm                  | 1 g/L          | Simulated solar light | 1000 W Xe arc lamp (AM 1.5 G Filter) | 180 min | 0.0069 min⁻¹ | - | 140 |
| ZnO-graphene              | Hydrothermal         | Phenol    | 40 ppm                  | 1 g/L          | Simulated solar light | 1000 W Xe arc lamp (AM 1.5 G Filter) | 180 min | 0.0221 min⁻¹ | - | 140 |
| BiO₁₋₋GO                 | Self-assembly        | Phenol    | 100 mg/L                | 5 g/L          | Visible                | 350 W Xeon lamp (cutoff filter: λ > 420 nm) | 150 min | - | - | 141 |
| RGO-CdS                   | Solvothermal         | 4-Nitro phenol | -                      | -              | Simulated solar light | Ortel 67,005 Newport- | 25 min | 0.078 min⁻¹ | - | 142 |
| Graphene-TiO₂             | Sol-gel              | Phenol    | 20 ppm                  | 1000 ppm       | Simulated solar light | 300 W xenon lamp | 180 min | 3.92 × 10⁻³ min⁻¹ | - | 143 |
| Au/BiOBr/graphene         | Hydrothermal         | Phenol    | 10 mg/L                 | 1 g/L          | Visible                | 300 W xenon lamp (cutoff filter: λ > 400 nm) | 180 min | - | 64% | 144 |
| GO–Ag₃PO₄                 | Ion-exchang deposition| Phenol | 10 ppm                  | 50 mg/L        | Visible                | 300 W Xe arc lamp (400 nm > λ ≥ 630 nm) | 30 min | 0.038 min⁻¹ | - | 146 |
| α-Fe₂O₃,GO/GO-30          | Hydrothermal         | Phenol    | 10 ppm                  | 1 g/L          | Visible                | 300 W Xe lamp | 120 min | - | 67% | 147 |
| Bi/GO                     | Solvothermal         | Phenol    | 10 mg/L                 | 0.6 g/L        | Visible                | 500 W Xe lamp (cutoff filter: λ > 420 nm) | 150 min | 0.6208 h⁻¹ | 78.3% | 148 |
| Graphene/BiPO₄            | Microwave assisted hydrothermal | Phenol | 100 ppm                 | 0.25 g/L       | Visible                | 300 W Xe lamp | 120 min | - | - | 149 |
| AgBr/BiOBr/graphene       | Precipitation        | Phenol    | 7 × 10⁻⁴ mol/dm³        | 0.5 g/L        | Visible                | 35 W LED lamp | 120 min | 0.089 min⁻¹ | 98% | 154 |
| ZnO/TiO₂/GO               | Hydrothermal/Solvothermal and Sol-gel | Phenol | 60 ppm                  | 0.6 g/L        | Visible                | Three 270.7 Cd lamps | 160 min | 0.0124 min⁻¹ | 100% | 156 |
| Graphene/ZnO-Co₃O₄        | Self-assembly        | 2,4 dichloro phenol | 20 mg/L                | 1 g/L          | Visible                | 300 W Phillips visible lamp (UV-cut off filter) | 150 min | 3.3 × 10⁻² min⁻¹ | 91% | 155 |
| RGO/CaFe₂O₄/Ag₃PO₄        | Hydrothermal and ion-exchange deposition | 4-Chloro phenol | 25 mg/L                | 2 g/L          | Visible                | 250-W mercury lamp (cutoff filter: λ ≥ 240 nm) | 160 min | 0.0149 min⁻¹ | 90% | 8 |
| RGO/MgFe₂O₄/Ag₃PO₄        | Hydrothermal and ion-exchange deposition | 4-Chloro phenol | 25 mg/L                | 2 g/L          | Visible                | 250-W mercury lamp (cutoff filter: λ ≥ 240 nm) | 160 min | 0.0128 min⁻¹ | 86% | 8 |
| Ag₃PO₄/MgO/6S/gene       | Hydrothermal         | 2,4-Dichlorophenol & 4-Nitro Phenol & 2-Chloro phenol | 20 mg/L                | 0.4 g/L        | Solar light | 500 W xenon lamp (cutoff filter: λ > 420 nm) | 60 min | - | 100% & 50% | 157 |
electron/hole pairs and made the holes more available for organic oxidation. Moreover, the graphene and MoS$_2$ provided more active sites for adsorption and allowed for the activation of dissolved O$_2$ for organic degradation in water [155]. Table 3 summarizes the photodegradation data of phenol and phenolic compounds in aqueous solution by various semiconductor/graphene nanocomposites.

5. Conclusion

In the present review, an effort has been made to integrate the recent progresses on the methods of synthesis and application of semiconductor/graphene nanocomposites for photodegradation of phenol and phenolic compounds in aqueous solution. Unquestionably, semiconductor/graphene nanocomposites hold major potential for photodegradation of contaminants such as phenolic compounds and offer considerable advantages over the currently available commercial semiconductor photocatalysts. The presence of two or more semiconductors into the prepared composites can cause a more effective charge separation, a longer lifetime of the charge carriers, a rapid charge transfers to the catalyst, and a separation of locally incompatible reduction and oxidation reactions in nanospace. Also, the incorporation of graphene materials into different composite of semiconductors can remarkably promote their photocatalytic activity toward photodegradation of pollutants due to the superior electron conductivity, extended range of light absorption range, enhanced specific surface area and high adsorption capacity. In the photodegradation of organic contaminants, ‘OH which is generated from two pathways including: 1) The O$_2$ present in water is reduced to form ‘O$_2$ ‘, which then reacts with H$^+$ to form ‘OOH, followed by rapid decomposition to ‘OH. 2) The oxidation of ‘OH, is an important oxidant.

Disclosure statement

No potential conflict of interest was reported by the authors.

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