Recent Advances in Semiconductor–Graphene and Semiconductor–Ferroelectric/Ferromagnetic Nanoheterostructures for Efficient Hydrogen Generation and Environmental Remediation

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ABSTRACT: Semiconductor heterostructures have attracted intensive research attention during the past few years owing to their great potential for energy and environmental remediation related applications. Effective optical absorption and efficient separation of photogenerated charge carriers are among the key factors for achieving high efficiency in a photocatalytic process. This mini-review summarizes state-of-the-art activities in designing nanosemiconductor heterostructures using multifunctional semiconductors for solar-to-hydrogen conversion and degradation of organic pollutants. Various novel design strategies such as semiconductor/graphene heterojunctions including graphene as a semimetal and photosensitizer, semiconductor/ferromagnetic, and semiconductor/ferroelectric nanoheterostructures for enhancing the performance of photocatalytic processes have been discussed. Finally, key challenges and future prospects for designing more efficient photocatalytic materials are briefly outlined.

1. INTRODUCTION

The worldwide growth of the population and industries has led to an increase in environmental pollution and energy consumption which has raised serious concerns for sustainable development of society in the near future. Our natural water resources have been affected severely due to the disposal of a large amount of wastewater containing toxic organic dyes from many industrial processes such as in the textile, plastic, leather good, cosmetics, and electroplating industries. Also, burning conventional energy sources such as coal, methane, and petroleum releases a variety of green-house gases such as CO₂, CO, and N₂O, which further pose a serious threat to the environment and eventually to human health. Thus, there is an urgent need for efficient strategies for reducing environmental pollution and developing clean and environmentally friendly energy sources. Semiconductor photocatalysis using abundant solar energy is a promising approach to deal with the energy crisis and worsening environmental issues through the generation of hydrogen and detoxification of organic pollutants, respectively. Hydrogen is considered as a potential renewable energy source for the future due to its high energy density and near-zero-emission operation which also provide high-quality energy services in a wide range of applications. The basic requirements for the generation of hydrogen and detoxification of organic pollutants using semiconductor materials are nearly the same, except for the mechanisms involved in both the processes, which will be discussed further in a later section of this mini-review.

Over the past few years, significant research efforts have been devoted to improving the photocatalytic efficiencies of semiconductor materials. An efficient photocatalytic process requires semiconductor materials with wide optical absorption range, efficient charge carrier separation, and excellent chemical...
stability in aqueous environments. At the beginning, a wide bandgap semiconductor such as TiO₂, as the representative photocatalytic material, has been studied extensively. However, due to its limited optical absorption, the need to use narrow bandgap semiconductors to enhance the effective optical absorption range of solar energy was eventually realized. Besides, the continuous development of visible-light-active semiconductor materials, it is also of significant importance to enhance their chemical stability and reduce the recombination rate of photogenerated charge carriers. Recently, a variety of functional semiconductors such as ferroelectric, ferromagnetic, and graphene photosensitizers have been used to address the above-mentioned issues, and using ferroelectric materials, an internal electric field can be produced which helps in separating out the photogenerated charge carriers. Similarly, research progress in using ferromagnetic semiconductors demonstrated improvement in the photocatalytic activity in the presence of external magnetic fields. However, it was realized that simultaneously achieving high efficiency and stability using a single semiconductor photocatalyst is impossible due to limited absorption of a solar spectrum, low carrier diffusion length, and higher recombination rate. Therefore, multicomponent semiconductor heterostructure systems have been developed in order to overcome the limitations of single-component semiconductor photocatalysts. Combining two or more semiconductors with different functionalities can greatly enhance the efficiency as well as stability of the photocatalytic materials. Recently, interesting reviews on the development of photocatalysts using organic semiconductor/semiconductor heterostructures, facet-dependent and interfacial plane-related photocatalytic heterostructures, heterostructured semiconductor nanowires, and graphitic carbon nitride based metal sulfide heterojunction have been published.

In this mini-review, we present a succinct and critical survey of recent advances in semiconductor heterostructures and their catalytic application prospects utilizing semiconducting heterostructures of multifunctional semiconductors including graphene as a photosensitizer and ferroelectric and ferromagnetic nanostructures. Finally, we conclude with a comprehensive discussion on the key challenges and promising future pathways for making more efficient photocatalytic materials.

2. PRINCIPLE OF SEMICONDUCTOR PHOTOCATALYSIS

The mechanism for semiconductor photocatalysis is mainly comprised of five steps: (I) absorption, (II) excitation, (III) migration, (IV) surface reaction with electron donors and acceptors, and (V) recombination. Step I consists of an effective absorption of solar energy by semiconductor material corresponding to its bandgap \( E_g \); step II consists of excitation of electrons from the valence band (VB) to the conduction band (CB), thereby generating electron–hole pairs in the semiconductors; and step III comprises the recombination process in which the excited carriers due to their very short lifetime come to the original states. Step III also runs in parallel to step IV where the charge carriers in the excited states migrate to the surface of the semiconductors. Only the successfully migrated electrons and holes to the surface are involved in driving the reduction and oxidation reactions, i.e., Step V. However, Step V can have different reaction mechanisms depending upon the type of application for which the photocatalytic process is used. In the case of photodecomposition of organic pollutants, the holes in the VB participate in oxidizing the water molecules (H₂O) to generate hydroxyl radicals (OH·), which are strong oxidizing agents and can oxidize most of the organic pollutants.

Figure 1. Schematic diagrams showing (a) the basic principle of a semiconductor photocatalytic process, (b) reactions involved in the photocatalytic degradation of organic pollutants, and (c) reaction mechanism involved in the photocatalytic water splitting for generation of H₂ and O₂.
and O₂. However, due to some kinetic losses, the energy required for the water splitting is ≥1.6 eV. In general, for both applications, the semiconducting materials with bandgap in the visible-light region are preferred so that the maximum part of the solar spectra can be utilized for the photocatalytic activity.

3. SEMICONDUCTOR HETEROSTRUCTURE SYSTEMS

Depending upon the energy band positions of the semiconductor components forming the heterostructure, it can be categorized into three types: Type I, Type II, and Type III heterostructures which are schematically shown in Figure 2(a). Out of these three types, the Type III band edge alignment is not very suitable for photocatalytic applications and thus not explored much. Although both Type I and Type II schemes have been used for photocatalytic applications, among these two types, Type II band edge alignment is the most preferred and widely used for achieving a high efficiency photocatalytic process.

3.1. Type I Semiconductor Heterostructure Systems.

Figure 2(a) schematically describes the relative position of the band edges in the construction of a Type I heterostructure system. The energy band positions of the two combining semiconductor materials are such that the conduction (CB) and valence band (VB) positions of one of the semiconductors lie in between the energy band positions of the second semiconductor. The separation of the photogenerated charge carriers in these types of heterostructure systems depends upon the difference in the migration rate of photogenerated electrons and holes at the interface. Thus, the positions of the band edges of the combining semiconductors play an important role in determining the enhancement in the photocatalytic activity. Fang et al. reported the synthesis of the Bi₂S₃/CdS heterostructure using the wet chemistry approach. Figure 2(b) shows the TEM picture of the CdS/ZnO/RGO nanocomposite which exhibits higher photochemical activity for the photodegradation of methyl red under UV light irradiation due to the improved charge carrier transport. Figure 2(c) compares the photodegradation rate of methyl red with various catalysts (CdS NPs, Bi₂S₃ NW, TiO₂ (P25), Bi₂S₃ + CdS NP, and Bi₂S₃/CdS heterostructure) under UV light.

Figure 2.

(a) Different types of semiconductor heterostructure with their band edge positions, (b) TEM image of the Bi₂S₃/CdS heterostructure, (c) comparison of the photodegradation rate of methyl red (MR) with various catalysts (CdS NPs, Bi₂S₃ NW, TiO₂ (P25), Bi₂S₃ + CdS NP, and Bi₂S₃/CdS heterostructure) under UV light, (d) TEM image of CdS/ZnO/RGO nanocomposites, and (e) photodegradation rate constant of MB dye using different photocatalysts CdS, ZnO, CdS/ZnO, and CdS/ZnO/RGO. Reprinted with permission from ref 11. Copyright 2011, American Chemical Society. Reprinted with permission from ref 14. Copyright 2015, Elsevier.
separation process [Figure 2(c)]. The band edge potentials of Bi$_2$S$_3$/CdS favor the transfer of photogenerated electrons and holes in CdS to Bi$_2$S$_3$; however, the migration rate for the two types of charge carriers (i.e., electrons and holes) is different, and this results in the enhancement in the performance of the semiconductor heterostructure photocatalysis.

In addition to the nanocomposite heterojunction, core/shell type heterostructure systems have also shown better potential to manipulate the charge transfer process at the interface. Depending upon the band edge potentials of the semiconductors used for the construction of the core/shell heterostructure, the migration of the photogenerated electron−hole pairs can be achieved either toward the core semiconductor or toward the shell semiconductor. Thibert et al.$^{12}$ reported a 10-fold increment in the photocatalytic activity toward H$_2$ evolution using a Type I CdS/CdSe core/shell nanostructure as compared to the CdSe nanostructure alone. The enhancement in the photocatalytic activity has been attributed to the passivation of surface-deep trap states in the CdSe core due to the coating of the CdS shell around it, which resulted in sufficient redox potential of electrons in the core for the reduction of water. The electrons in the core semiconductor also participate in the photocatalysis reaction at the surface after tunneling through the CdS shell.

3.2. Type II Semiconductor Heterostructure Systems. Among different strategies to enhance the efficiency of semiconductor photocatalysis, the design of Type II heterostructure systems has been paid maximum attention. In the Type II heterostructure system, the conduction and valence band positions of one of the semiconductors lie above the conduction and valence bands of the second semiconductor [Figure 2(a)], which provide an optimum pathway for improving the

Figure 3. (a) Left: the π* and π band dispersion of pristine graphene in the Brillouin zone. Right: zoom-in of the linear energy bands at the Dirac point and the position of Fermi level for n- and p-type doping.$^{16}$ (b) Schematic band diagram of the graphene/semiconductor Schottky junction for photocatalytic H$_2$ evolution.$^{20}$ (c) Hydrogen production efficiency of xRGO-NiPO catalysts under visible-light illumination.$^{20}$ (d) Schematic energy band diagram of the CdS/CoFe$_2$O$_4$/RGO ternary heterostructure.$^{15}$ (e) Rate constants for the degradation of MB dye using CdS, CFO, CdS/CFO, and CdS/CFO/RGO nanostructures under visible-light irradiation.$^{15}$ Reprinted with permission from ref 16. Copyright 2010 American Chemical Society. Reprinted with permission from ref 20. Copyright 2019 American Chemical Society. Reprinted with permission from ref 15. Copyright 2015, Royal Society of Chemistry.
separation of the photogenerated charge carriers and can efficiently enhance the photocatalytic activities. A variety of material combinations for the design of the Type II heterostructure are explored in the literature. Recently, 2D materials have been extensively studied for the electrocatalytic or photocatalytic activities due to their layered structures. The electrical and optical properties of a 2D material can be tuned by controlling the number of layers. The synthesis of a CdS/ZnO/RGO ternary nanohybrid for efficient photocatalytic degradation of methylene blue dye has been demonstrated. Figure 2(d) shows the TEM picture of trio nanohybrids. The CdS/ZnO core/shell nanostructure after coupling with reduced graphene oxide (RGO) exhibited much enhanced degradation of methylene blue dye as compared to its bare counterparts such as CdS/ZnO, ZnO, or CdS, which is due to the formation of a Type II heterostructure, resulting in efficient transfer of photogenerated electrons from CdS to ZnO and further to reduced graphene oxide (RGO) exhibited much enhanced degradation of methylene blue dye. In a Schottky junction, graphene is used as a conducting nanoplatform for facilitating charge transfer for improving hydrogen production and environmental remediation activities. On the other hand, a tunable bandgap can also be induced in graphene by chemical doping, thereby converting it into a semiconductor. To date, various semiconductor/graphene heterojunctions including Schottky junctions and Type II heterojunctions using semiconductors and graphene have been constructed for photocatalytic applications. Some recent studies also make use of the optical properties of RGO to effectively absorb the solar spectrum for enhancing the photocatalytic activities.

Zhang et al. proposed the use of graphene in fabricating semiconductor/graphene heterojunctions using P25 titania for the degradation of MB dye. In a Schottky junction, graphene is coupled to semiconductors with higher work functions, and consequently, an upward band bending arises at the contact interface due to the alignment of Fermi energy levels. Recently, Samal et al. constructed a Schottky junction of RGO–NiPO and demonstrated enhanced H2 production with an admirable rate of 9000 μmol h/g. Further, to improve interfacial charge transport of Schottky heterojunctions, using 2D graphene sheets with 2D semiconductors was also reported. For the efficient charge transfer process, the contact area between the semiconductor and graphene sheets is also an important parameter. In order to demonstrate this effect, Bera et al. synthesized CdS nanostructures with different dimensionalities, i.e., zero-dimensional nanoparticle, one-dimensional nanorods, and two-dimensional CdS nanosheets, and coupled these nanostructures with reduced graphene oxide sheets. The RGO coupled CdS nanosheets exhibit 4 times higher conductivity than the CdS nanoparticle/RGO composite and 3.4 times higher than the CdS nanorod/RGO nanocomposite. The observed enhancement is attributed to the increase in the interfacial contact area between the CdS and RGO using sheet-like structures of CdS. The interfacial contact between graphenes and semiconductors is also found to depend upon the number of graphene layers used in the formation of nanocomposites with semiconductors.

Almeida et al. designed a ternary nanocomposite comprised of TiO2, Cu2O, and RGO and showed higher photoresponse of ternary TiO2/Cu2O/RGO nanocomposites as compared to TiO2/RGO and Cu2O/RGO nanocomposites. The photo-sensitization role of RGO was initially proposed by Du et al. by the ab initio calculations and demonstrated that the electrons in the upper valence band of RGO can be directly excited to the conduction band of TiO2 under visible-light excitation. The simulated results were also supported with experimental observation of appreciable visible-light response in the photocurrent density measurements of the RGO–TiO2 nanocomposite. The chemically modified reduced graphene oxide (RGO) can be directly used as a semiconductor for photocatalytic applications. Singh et al. also reported a visible-light responsive Type II ternary heterostructure system using CdS/CoFe2O4/RGO for photocatalytic degradation of methylene blue dye. Under visible-light irradiation, the electrons from the conduction band of CdS are transferred to the conduction band of CoFe2O4, and holes are transferred from the valence band of CoFe2O4 to the valence band of CdS. Also, due to the visible-light response of RGO and its Fermi level position, the photoexcited electrons in RGO are transferred to the conduction band of CoFe2O4 thereby increasing the electron concentration in the CoFe2O4 which improved efficient separation of the electron–hole pairs and resulted in the enhancement in the photocatalytic activity.

For effective utilization of the optical properties of RGO toward high efficiency of the photocatalytic materials, the understanding of the interfacial interaction between the graphene and semiconductor is critical and needs to be addressed.

5. SEMICONDUCTOR/FERROELECTRIC/FERROMAGNETIC HETEROSTRUCTURES

The use of ferroelectric materials as semiconductor photocatalysts has recently attracted a lot of attention and is considered as a new pathway for efficient solar water splitting and degradation of organic pollutants. The spontaneous electrical polarization in ferroelectrics can generate an internal electric field which helps in the efficient separation of photogenerated charge carriers as well as the modulation of band alignment at the semiconductor/liquid interface, resulting in an enhanced photocatalysis efficiency. Ji et al. demonstrated the effect of ferroelectric polarization on photocatalytic water splitting using epitaxial BiFeO3 thin films. A saturated photocurrent of ~10 μA·cm−2 at 0.64 V vs Ag/AgCl and an ~0.016 V shift in the photocurrent onset were attained after electrical polarization. Thereafter, tremendous research efforts have been devoted, especially, to solar water splitting using a variety of ferroelectric films such as Na0.5Bi0.5TaO3, PZT.
and BaTiO$_3$, either as photoanodes or photocathodes. In order to improve the charge transport properties, ferroelectric materials at the nanoscale with different morphologies were also fabricated. Li et al. fabricated vertically aligned epitaxial KNbO$_3$ nanowire arrays on a Nb-doped SrTiO$_3$ substrate, and by switching the polarization state the photocurrents were tuned from 0.7 $\mu$A·cm$^{-2}$ to 11.5 $\mu$A·cm$^{-2}$ at 0 V vs Ag/AgCl [Figure 4(a)]. However, chemically grown nanostructures exhibit various structural defects resulting in higher recombination losses. Singh et al. reported the growth of an oriented, highly crystalline nanoporous structure of Ag,Nb-codoped SrTiO$_3$(Ag/Nb:STO) with ferroelectric properties using pulsed laser deposition. These vertically aligned nanoporous structures exhibited enhanced surface area and directional charge transport, resulting in enhanced PEC properties using ferroelectric polarization. By manipulating the external electrical bias, ~3-fold enhancement in the photocurrent from 40 to 130 $\mu$A·cm$^{-2}$ was obtained. Concurrently, the flat-band potential was found to decrease from $-0.55$ to $-1.13$ V, revealing a giant ferroelectric tuning of the band alignment at the semiconductor surface, and results in the enhanced charge transfer.

Large band gaps and high dielectric constants possessed by most of the ferroelectric materials resulted in small photocurrents. In order to overcome the disadvantages of poor light absorption, ferroelectric materials were coupled with plasmonic nanostructures. Wang et al. demonstrated surface plasmonic...
effect induced enhancement in the PEC properties of PbZr0.2Ti0.8O3 thin films anchored with Ag nanoparticles. Further, Cheng et al.33 constructed a Si-pnn+/ITO/Au/BiFeO3 (BFO) hybrid photocathode catalyzed by MoS2/Pt using visible-light active semiconductors for efficient transfer of photogenerated electrons from Si to the electrode surface. In the Au/BFO33 system, the local surface plasmonic resonance effect of Au/Ag nanoparticles and the depolarization electric field of BFO were found to enhance the PEC activity of the photocathode, and also the tunability in the PEC performance was demonstrated.

Ferroelectric/semiconductor heterostructure systems which synergize the advantages of both ferroelectric and semiconductor materials are demonstrated to be a potential approach in achieving higher photocurrents.33 The effect of ferroelectric polarization on the electronic properties and band alignment at the ferroelectric/semiconductor interface was studied by Jang et al.34 using the PbTiO3/TiO2 heterostructure. By using the macroscopic average approach, it was found that the negative polar surface at the interface favored the transfer of holes from PbTiO3 to TiO2, while the positive polar interface favored the transfer of electrons from PbTiO3 to TiO2. Accordingly, a polarization-dependent photocatalytic performance for the degradation of organic pollutants and hydrogen evolution reaction was demonstrated. Cheng et al.35 fabricated a Si-pn+/ITO/PZT photocathode for hydrogen generation. An enhancement in the photocurrent from −100 μA cm−2 to 1.2 mA cm−2 (at 0 V vs RHE) was demonstrated due to the depolarization electric field generated in the PZT film which helped in driving the photogenerated charge carriers from the Si-pn+ junction to PZT. Xie et al.36 demonstrated that by using ferroelectric BiFeO3 as a passivation layer for the BiVO4 photoanode an efficient and stable solar water oxidation performance can be realized. Furthermore, due to the ferroelectric properties of BiFeO3, the PEC performance of the composite photoanode can be manipulated based on the direction of self-polarization in BiFeO3. The charge recombination rate was found to be decreased from 17 s−1 to 0.6 s−1. A polarization-dependent photocatalytic performance was also demonstrated combining multiple photocatalysts in a Z-scheme system. An enhanced transfer of the charge carriers was attained by inserting a ferroelectric material (i.e., BiFeO3) with downward band bending between BiVO4 and CuInS2 photocatalysts. Consequently, a 2-fold enhancement in the photocurrent and ~16-fold enhancement in the photocatalytic degradation rate of 4-nitrophenol were reported.37

In order to effectively collect the photoexcited charge carriers generated in the semiconductors, nanoscale ferroelectric/semiconductor heterostructure systems were fabricated. For the core/shell nanostructures of TiO2/BaTiO3, spontaneous electrical polarization in the ferroelectric layer significantly improved the charge separation efficiency, leading to ~67% enhancement in the photocurrents, respectively38 (Figure 4(c) and (d)). A few efforts in designing flexible ferroelectric/semiconductor photodevices were also made for the commercial viability of PEC technology. Singh et al.39 fabricated a large area flexible PVDF/Cu/PVDF-NaNbO3 photoelectrode with ferroelectric properties and demonstrated an enhanced photocurrent of ~1.3 mA cm−2 with electric field polarization (Figure 4(e)). Using a similar concept of ferroelectric materials, few researchers have also used ferromagnetic materials to modify the charge transport properties of semiconductors using external magnetic fields. Singh et al.40 fabricated the CoFe2O4 photoanode and demonstrated enhanced photoelectrochemical properties under low external magnetic fields [Figure 4(g)], which has been attributed to a magnetophotonic effect. However, further efforts in understanding the exact mechanism for the enhanced PEC properties are required.

6. CONCLUSIONS AND FUTURE PERSPECTIVES

In this mini-review, a comprehensive overview of the current achievements in preparing nanojunction photocatalysts using multifunctional semiconductors such as graphene, ferroelectric, and ferromagnetic materials, and their design strategies including fundamental aspects in constructing various semiconductor heterostructure systems for photocatalytic H2 evolution and degradation of organic pollutants are discussed. Graphene-based heterostructures including Schottky junctions and Type II heterostructures are also thoroughly highlighted and discussed. Inclusion of ferroelectric and ferromagnetic in nanoheterostructures provides the opportunity to achieve higher charge transfer efficiency through electrical/magnetic tunneling. Extensive research progress has been achieved in the formation of semiconductor heterostructures; however, for practical applications and commercialization of heterostructure photocatalysts, further research efforts are required in designing more efficient and stable heterostructure photocatalysts. For future research directions in this exciting and highly rewarding field, the following aspects can be highlighted.

(i) Good interfacial contact between different combining layers in multicomponent heterostructure systems is very much required. Thus, further progress in preparing heterojunction photocatalysts with interfacial engineering for achieving suitable band alignment and efficient charge transport properties and also exploring new visible-light-active photocatalyst materials with proper band alignment can be a promising strategy.

(ii) Fabricating heterostructure photocatalysts using multifunctional semiconductors such as ferroelectric and ferromagnetic materials is a promising strategy for achieving high efficiency. However, systematic studies using advanced spectroscopic techniques are required to understand the migration pathways of the photogenerated charge carriers. Further, theoretical calculations and modeling methods are required for a deep understanding of the charge migration kinetics at the interface.

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