Boosting Photocatalytic Activity Using Reduced Graphene Oxide (RGO)/Semiconductor Nanocomposites: Issues and Future Scope

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ABSTRACT: Semiconductor nanoparticles are promising materials for light-driven processes such as solar-fuel generation, photocatalytic pollutant remediation, and solar-to-electricity conversion. Effective application of these materials alongside light can assist in reducing the dependence on fossil-fuel driven processes and aid in resolving critical environmental issues. However, severe recombination of the photogenerated charge-carriers is a persistent bottleneck in several semiconductors, particularly those that contain multiple cations. This issue typically manifests in the form of reduced lifetime of the photoexcited electrons-holes leading to a decrease in the quantum efficiency of various light-driven applications. On the other hand, semiconducting oxides or sulfides, coupled with reduced graphene oxide (RGO), have drawn a considerable interest recently, partly because of the RGO enhancing charge separation and transportation through its honeycomb sp² network structure. High electron mobility, conductivity, surface area, and cost-effectiveness are the hallmark of the RGO. This Mini-Review focuses on (1) examining the approach to the integration of RGO with semiconductors to produce binary nanocomposites; (2) insights into the microstructure interface, which plays a critical role in leveraging charge transport; (3) key examples of RGO composites with oxide and sulfide semiconductors with photocatalysis as application; and (4) strategies that have to be pursued to fully leverage the benefit of RGO in RGO/semiconductors to attain high photocatalytic activity for a sustainable future. This Mini-Review focuses on areas requiring additional exploration to fully understand the interfacial science of RGO and semiconductor, for clarity regarding the interfacial stability between RGO and the semiconductor, electronic coupling at the heterojunction, and morphological properties of the nanocomposites. We believe that this Mini-Review will assist with streamlining new directions toward the fabrication of RGO/semiconductor nanocomposites with higher photocatalytic activity for solar-driven multifunctional applications.

1. INTRODUCTION

Semiconductor nanoparticles are used in various light-driven applications, including pollutant remediation, aromatic nitro reduction, and water-splitting reactions.¹ These materials also find applications in quantum-dot (QD) sensitized, dye-sensitized, and perovskite solar-cells, where n-type broad band gap single metal oxides are used as an electron transport layer (ETL).² Apart from single metal oxides, multivalent oxides such as strontium tantalite-Sr₂Ta₂O₇, strontium titanate-SrTiO₃, bismuth titanate-Bi₂Ti₂O₇, and bismuth vanadate-Bi(VO₄)₃ are also noted to be highly promising as photocatalysts in the area of solar-driven clean fuel production, where the band gap can be tuned significantly to absorb visible light.³

The fundamental process that occurs in a semiconductor (described in Scheme 1), after photoillumination (1), is the exciton [electron (e⁻)-hole (h⁺)] generation (2). These photogenerated electron–hole pairs break into free charge-carriers and migrate to the photocatalyst surface (3A and 3B), and participate in “red-ox” reactions (as shown in the Scheme 1 as (5), hole mediated oxidation; and (6), electron mediated reduction). Recombination of the charge carriers (either surface or bulk; as shown as 4 in Scheme 1) is a competitive process that occurs after the photogeneration. The potential energy of the valence/conduction band is the most stringent criterion that drives the choice of a photocatalyst in a specific “red-ox” reaction. The recombination step (4) of the electron (e⁻)–hole
(h+) pairs restrict semiconductor material from performing to its full capacity in redox reactions, thereby limiting the efficiency. If the lifetimes of the photogenerated electron (e⁻)–hole (h+) pairs of the semiconductors are enhanced, then it would be far more attractive for several photocatalytic reactions. In addition, the stability of a photocatalyst is also an essential criterion for long-term operation.

The charge recombination of the oxides after photo-illumination can be reduced through noble metal addition [platinum (Pt), silver (Ag), and gold (Au)], but this increases the cost of the catalyst in addition to their well-known toxicity. A possible green approach and cost-effective way to enhance the lifetime of the electron (e⁻)–hole (h+) pairs is to couple oxide nanoparticles with carbon, which can in principle function similar to metal nanoparticles.

Various types of conductive carbon-based nanomaterials are available such as carbon nanotubes (CNT; band-gap: 0.5 eV, surface functional groups: none), fullerences (band-gap: 1.77 eV, surface functional groups: none), graphene (band-gap: 0 eV, surface functional groups: none), reduced graphene oxide (band-gap: 2–0.02 eV, surface functional groups: epoxy, hydroxyl (−OH), aldehyde (−CHO), carboxylic acid (−COOH)), carbon quantum dots (band-gap: 2.47 eV, surface functional groups: −OH, −COOH, amine (−NH₂)), carbon sponge (band-gap: 0.5–0.7 eV, surface functional groups: none), carbon nanofiber (band-gap: 1.07 eV, surface functional groups: none), and graphene quantum dots (band-gap: 1.8–2.4 eV, surface functional groups: epoxy, −OH, −CHO, −COOH). Such materials have been used for photocatalytic reactions, and these are listed in Table 1.

Table 1. Carbon-Based Conductive Materials for photocatalysis applications

| Material Type         | Structural Description | Reference  |
|-----------------------|------------------------|------------|
| carbon nanotubes      | 1D tube                | 5ñ,m       |
| graphene              | 2D sheet               | 5ñ,q       |
| reduced graphene oxide| 2D sheet               | 5ñ,r       |
| graphene quantum dots | 2D sheet (small graphene fragments, <20 nm) | 5ñ,a       |
| fullerenes            | 0D hollow sphere       | 5v         |
| carbon quantum dots   | 0D nanoparticles       | 5w         |
| carbon nanofiber      | 1D cylindrical nanostructures | 5x         |
| carbon sponge         | 3D network             | 5y         |

From these carbon-based nanomaterials, our interest is in RGO because of its relative ease of synthesis, tunable electrical properties, transparency, and ability to integrate with various photoactive surfaces to improve their efficiencies. Furthermore, RGO, having a large surface area, can wrap the semiconductor surface and serve as an "encapsulant". In comparison, CNTs, graphene, carbon nanofiber, carbon sponge, and fullerenes-based nanostructures are expensive additives and need intricate methods/tools to synthesize. The aforementioned features make RGO a desirable candidate for the solar-driven applications. RGO coupled with oxides can promote electron separation, which results in boosting photodriven reactions such as carboxylic acid (methylene glycol) degradation, value-added chemical syntheses (aromatic nitro-group reduction), and solar-fuel (hydrogen) production. There are other related areas in the domain of RGO/semiconductor photocatalysis such as interfacial engineering, dye sensitization, and charge transfer dynamics; however, the purpose of this Mini-Review is to identify future directions involving RGO in these areas.

2. SYNTHESIS OF RGO AND INTEGRATION OF RGO WITH OXIDE SEMICONDUCTORS

Graphene has a 2D sheet-like structure, with sp² carbon atoms arranged in an ordered hexagonal honeycomb pattern, and it demonstrates excellent electrical conductivity (charge-carrier mobility of >15 000 cm² V⁻¹ s⁻¹ at room temperature), high mechanical strength, and gas barrier properties, and additionally, it has a high surface area. Because of these fascinating properties, graphene has been used for the following: (1) to enhance the mechanical properties of polymers, (2) as a catalyst support, (3) to enhance energy conversion efficiency, and (4) for use in sensing applications. It is worthy to mention that RGO has a structural similarity with graphene, except that it contains oxygen-containing functionalities, which modulate its electronic properties. The high work function (4.42 eV) of graphene facilitates the transfer of photogenerated electrons from the conduction bands of most of the semiconductors to the graphene sheets. Because of the extended sp² bonded carbon network, electrons can be effectively transported through the π* orbital of the carbon atoms in the two-dimensional (2D) graphene framework with a large surface area.

The reduced graphene oxide (RGO) is generally produced from graphite by a modified Hummers’ method. In this method, graphite is first oxidized by a chemical process and exfoliated to produce graphene oxide (GO). The oxidation step generally breaks sp² hybridization and introduces oxygen-containing functionalities and thus helps to increase the spacing between the graphite layers, which aids in easy delamination of GO layers. GO contains several oxygen-containing functional groups such as −COOH, −OH, −CHO, and epoxy groups. The reduction of GO produces RGO, which has more defects than "graphene" because of the presence of remaining oxygen-containing functionalities (Scheme 2A), and hence, RGO and "graphene" are not the same. The reduction techniques such as thermal treatment and chemical methods can lead to different carbon to oxygen ratios in the RGO. This oxygen content is a crucial parameter affecting the electrical property of RGO.

The presence of oxygen-containing functionalities in GO facilitates its dispersion in polar solvents. This property allows the synthesis of the RGO-based nanocomposites with various semiconductors through solution processing techniques. The oxygen functionalities can interact with oxide surfaces through van der Waal’s interaction during the solution-based synthesis and promote interfacial interactions prior to composite formation. Semiconductor/RGO composite catalyst assemblies can be prepared by various methods, such as reducing agent (hydrazine)-assisted chemical reduction, hydrothermal reduction (high pressure), photoreduction, self-assembly followed by thermal annealing (under inert or ammonia atmosphere), or chemical reduction method (Scheme 2B). It is worthy to mention that during GO to RGO conversion, while the "chemical reduction method" uses toxic/nonecofriendly chemicals (such as hydrazine), the "thermal annealing" uses high temperature (>300 °C; energy intensive), and the "hydrothermal method" is limited to small-scale synthesis; however, the "photoreduction method" is much greener/eco-friendly and can be used for large-scale synthesis, if "sun-light" itself is used as a light source.
Scheme 2. Schematic of (A) Graphene Oxide (GO) to Reduced Graphene Oxide (RGO) Conversion, (B) Leading Synthesis Techniques for Preparation of Semiconductor/RGO Nanocomposites, (C) Photogenerated Charge Separation at the Interface between Semiconductor and RGO, and (D) The Energetics of Electron Transfer from Conduction Band (CB) of the Semiconductor to the RGO Surface.

\[ V_{\text{loss}} \] indicates the loss in energy of the photogenerated electron in the semiconductor [VB indicates valence band].

Figure 1. Degradation of methylene blue under (a) UV light and (b) visible light (wavelength >400 nm) over (1) neat P25, (2) P25-CNTs (P25-carbon nanotubes), and (3) P25-GR (P25-RGO) photocatalysts and (c) TEM images of RGO loaded -P25-TiO\text{2}. Reprinted with permission from ref 12b. Copyright 2009 American Chemical Society. (d) The rate–constant values of RGO/TiO\text{2} composites (X = 0, 0.5, 1.5, 2.5, and 3.0 wt %), P25-TiO\text{2}, and mechanically mixed (Mixing) samples. (e). TEM (a, b) and HRTEM (c, d) images of 2.5 wt % RGO/TiO\text{2} nanocomposite. Reprinted with permission from ref 14. Copyright 2013 American Chemical Society.
3. SEMICONDUCTOR/RGO COMPOSITES FOR PHOTOCATALYSIS

We have shown representative examples (in section 3.1 and section 3.3) of hierarchical heterostructures of oxide- (0D and 1D) and sulfide-based (0D, 1D, and 2D) semiconductor/RGO nanocomposites and their role in enhancing photocatalytic activity such as pollutant remediation, solar fuel generation, and nitrosametic reduction. RGO has been chosen as one of the benchmark materials toward semiconductor nanoparticle performance improvement as evidenced in many available publications.11 In these composites, RGO assists in separating the photogenerated charge carriers of semiconductors through the catalyst/RGO interface (Scheme 2C) and improves photocatalytic performance. The nature of the interface and defects in the synthesized RGO plays a key role in the photocatalytic activity of the nanocomposites. The energy difference between CB (of the semiconductor) and the RGO is critical as there will be a certain voltage loss (indicated as $V_{\text{loss}}$ in Scheme 2D) during the electron transfer process). Perhaps this loss plays an important role in semiconductor/RGO-mediated photocatalysis.

### 3.1. (Single) Metal Oxide/RGO Composites for Photocatalysis

We define single metal oxides as those containing one cation in the lattice structure of the unit cell: such as TiO$_2$, Fe$_2$O$_3$. Zhang et al. have developed a P25-TiO$_2$/RGO-based nanocomposite by the hydrothermal method.12b The composite catalysts enhanced the rate of methylene blue (MB) degradation under UV and visible irradiation, as compared with neat P25-TiO$_2$ and P25-TiO$_2$/carbon nanotube-based composites (Figure 1a and 1b). Intimate contact between the P25-TiO$_2$ and RGO sheets was observed by the authors from TEM images (Figure 1c). Furthermore, electrochemical impedance analysis showed better separation of electron–hole pairs, leading to better photocatalytic activity. The presence of Ti–O–C bonds (as indicated from FTIR spectroscopy) shows that a strong interaction between the hydroxyl (–OH) groups at the TiO$_2$ surface and carboxylic acid (–COOH) groups of RGO. The formation of Ti–O–C bond also resulted in a red-shift in absorbance in the nanocomposites compared with neat P25-TiO$_2$.

Hydrothermal strategy was followed by Huang et al. to fabricate TiO$_2$/RGO composites.14 In this study, an X-ray photoelectron spectroscopy (XPS) study indicated Ti–C bond formation by the RGO and the TiO$_2$ surface. This chemical bonding enhances the “interfacial charge transfers (IFCT)” from TiO$_2$ to RGO, resulting in a remarkable increase in photocatalytic activity. The enhanced charge separation was also evidenced from electrochemical impedance analysis. The photocatalytic activities of the TiO$_2$/RGO nanocomposites were examined by the oxidation of formaldehyde (HCHO) gas in air. A 2.6 times enhancement in “rate constant” was observed for 2.5 wt % RGO loaded composites (labeled as G2.5-TiO$_2$ in Figure 1d) compared with pristine TiO$_2$ (Figure 1d). It was observed (Figure 1d) that simple mechanical mixing of RGO (at 2.5 wt %) with TiO$_2$ did not enhance the photocatalytic performance compared with hydrothermally treated G2.5-TiO$_2$ nanocomposites. Thus, it is reasonable to conclude that an intimate contact between the TiO$_2$ nanoparticles and RGO (through Ti–C bond) plays a critical role in the improvement in photocatalytic activity. The intimate contact was evidenced from the HR-TEM images as shown in Figure 3e (TEM images a and b) and HR-TEM images (c and d).

The self-assembly method was developed by Lee et al. to wrap RGO on the TiO$_2$ surface.15 The wrapping of RGO sheets over TiO$_2$ was confirmed by the authors through scanning electron microscopy (SEM). TiO$_2$/RGO composite showed a remarkably higher methylene blue (MB) degradation compared with neat anatase TiO$_2$ and Degussa P25 under visible light ($\lambda > 420$ nm). Interestingly, a red-shift in the absorbance as well as a strong absorbance in the visible range in the composites was observed. This phenomenon was attributed to Ti–C bond formation through the unpaired $\pi$-electron of carbon and free titanium (Ti) atom at TiO$_2$ surface, during the hydrothermal method. An important question arises: if such Ti–C bond formation may alter the band bending at the RGO/TiO$_2$ interface, does it facilitate the electronic transportation?

Xiang et al. have synthesized RGO/TiO$_2$ nanosheet composites through a microwave-hydrothermal method by mixing various wt % (1 to 5) of GO with TiO$_2$.31 The photocatalytic hydrogen generation (from methanol/water system) showed a 41% increase in $H_2$ generation rate for 1 wt % RGO loaded TiO$_2$ as compared with neat TiO$_2$. The lower intensity of photoluminescence (PL) for the RGO/TiO$_2$ nanosheet composites compared with pristine TiO$_2$ nanosheets indicated that the composites have a lower recombination rate of electrons and holes under UV-light irradiation. This reflects the fact that the photogenerated electrons will move to the RGO sheet, preventing electron–hole recombination.

Pradhan et al. have integrated 1D $\alpha$-Fe$_2$O$_3$ nanorods over RGO surface through a template-free hydrothermal method.38 The composites with 5 wt % RGO loaded $\alpha$-Fe$_2$O$_3$ nanorod-based composites showed 67% degradation of phenol (under visible light irradiation for 2 h) compared with a pure $\alpha$-Fe$_2$O$_3$ nanorod, which showed 18% degradation. The decrease in PL signal intensity of RGO loaded nanocomposites indicated a better separation of the photogenerated charge carriers compared with 1D $\alpha$-Fe$_2$O$_3$ nanorods.

### 3.2. Multimetal Oxide/RGO Composites for Photocatalysis

We define multimetal oxides as those that contain more than one element in their unit cell structures: such as pyrochlores ($A_2B_5O_{12}$), perovskites ($ABO_3$), and so on. Bismuth titanate (Bi$_2$Ti$_2$O$_7$–BTO; pyrochrome type crystal structure) with an RGO-based composite have been investigated by Gupta et al.16 In this work, electrostatic self-assembly following the thermal annealing method was used to conjugate the BTO with RGO with various weight ratios (0.25, 0.75, 1 to 6 wt %). A red-shift in the absorbance property was observed with an increase in the encapsulated BTO loadings, possibly because of the carbon doping effect, as observed by Lee et al. in a previous study.15

The composite photocatalyst with 1 wt % RGO loading showed a ~3 times increase in hydrogen generation compared with neat Bi$_2$Ti$_2$O$_7$.16 Besides, photoelectrochemical measurements showed a ~130% increase in the photocurrent for the composite photocatalyst compared with neat BTO. The work showed RGO-mediated enhancement in photocatalytic activity because of greater separation of photogenerated charge carriers and their utilization. The inclusion of 3d group elements such as Fe as dopants in the BTO showed red-shifted absorbance. The design of a visible light active photocatalyst with such elements ($Fe^{2+}/Ce^{3+}/Mn^{2+}$) within the Bi$_2$Ti$_2$O$_7$ framework coupled with RGO is expected to be significantly superior in photodriven reactions. We envision that this approach could be further extended toward other families of mixed metal oxide catalysts such as perovskites ($ABO_3$), delafossite, ($A_2O_2$) or sillenite ($A_2BO_6$).16
A RGO/Sr$_2$Ta$_2$O$_7$–$x$N$_x$-based composite photocatalyst was synthesized through photoreduction of GO by Mukherji et al.\textsuperscript{12g} The authors prepared platinum (Pt) deposited RGO/Sr$_2$Ta$_2$O$_7$–$x$N$_x$ by photoreduction of chloroplatinic acid (H$_2$PtCl$_6$). During the photoreduction process, the RGO acted as a support for the Pt deposition, and the photogenerated electrons effectively transported through the RGO sheets to reduce platinum salt to metallic Pt. Figure 2A shows the hydrogen generation profile from 20% methanol solution (using 300 W xenon lamp as a light source) using pristine Sr$_2$Ta$_2$O$_7$–$x$N$_x$ and RGO/Sr$_2$Ta$_2$O$_7$–$x$N$_x$ (at various% of RGO loadings) for a period of 4.5 h, using Pt as a cocatalyst. An approximately 1.5 times increase in hydrogen rate (per hour) was observed for RGO (5%)/Sr$_2$Ta$_2$O$_7$–$x$N$_x$ compared with neat Sr$_2$Ta$_2$O$_7$–$x$N$_x$ (Figure 2B). An intimate contact between the oxide catalyst and the RGO was observed from TEM analysis (Figure 2C,D), which forms the basis for electron transfer and efficient collection at the Pt surface, thus enhancing the photocatalytic hydrogen production (Figure 2E).
3.3. Metal Sulfide/RGO for Photocatalysis. Li et al. demonstrated the synthesis of CdS/RGO composites by a hydrothermal method, which results in a uniform distribution of CdS nanoparticles over the RGO sheet (Figure 3 (1A) and (1B)). The RGO sheet prevented the aggregation of the CdS nanoparticles and having a significant impact on photocatalysis. During photocatalytic hydrogen generation (Figure 3 (1C)), it was observed that an RGO content of 1 wt% of CdS/RGO (labeled as GC1.0) showed a hydrogen production rate of 1.12 mmol h⁻¹, which is ~5 times compared with neat CdS nanoparticles (observed rate: 0.23 mmol h⁻¹; labeled as GC0). The apparent quantum efficiency of 1 wt% RGO loaded CdS was observed to be 22.5% (at 420 nm), while for neat CdS it had 4.6%. The enhanced hydrogen yield was attributed to the following factors: (1) Compared with neat CdS, 1 wt% RGO/CdS provides more active sites attributed to a larger specific surface area provided by RGO, leading to a higher photocatalytic activity. (2) In 1 wt% RGO/CdS composite, RGO accepts the photogenerated electrons generated in the CdS, reducing the recombination with holes. However, beyond 1 wt% of RGO loading, a decrease in photocatalytic activity was observed and attributed to a possible light “shielding effect”.

Lv et al. have demonstrated the synthesis of cadmium sulfide-CdS/RGO by an electrostatic interaction method. During the photocatalytic hydrogen production, CdS/RGO composites showed improved activity compared with CdS and CdS/Pt. However, the yield was reduced in the second cycle. The reason for the reduction was attributed to the reduced interaction between RGO and CdS. Time-resolved fluorescence measurement showed a decrease in excited charge carrier lifetime of CdS/RGO (1.7 ns) compared with neat CdS (3.0 ns). Significant photoluminescence quenching was also observed for CdS/RGO. On the basis of these results, the mechanism proposed was that the RGO acts as an acceptor for photogenerated electrons from the semiconductor (energy level of RGO is located slightly below than the conduction band of the semiconductor, facilitating the electron transfer), and the adsorbed protons (H⁺) on the RGO surface gets reduced to produce H₂ gas. The authors concluded that the (1) semiconductor/RGO interface and (2) the energy position of the RGO also plays a vital role in photocatalysis.

In another work, Chen et al. have shown that the degree of reduction of GO to RGO plays an important role in the photocatalytic activity of RGO/ZnIn₂S₄ nanocomposites. Surprisingly, it was observed that RGO/ZnIn₂S₄ nanocomposites (prepared by hydrothermal route) has a lower photocatalytic H₂ generation rate (10.1 μmol h⁻¹) compared with pure ZnIn₂S₄ (14.1 μmol h⁻¹). However, when the same nanocomposites were further treated with hydrazine and photoirradiation, an increased H₂ generation rate was observed. The hydrazine-treated and photoirradiated nanocomposites showed a hydrogen generation rate of 21.4 and 27.8 μmol h⁻¹, respectively. The oxygen content in RGO was decreased as RGO/ZnIn₂S₄ composites (prepared by hydrothermal method; 30% oxygen bound carbon) were treated with hydrazine (25% oxygen bound carbon) and photoirradiation (13% oxygen bound carbon). This study showed the importance of oxygen-containing functionalities in the RGO/semiconductor photocatalysis.

Meng et al. have coupled p-type “MoS₂” over n-type (nitrogen-doped) “RGO sheets (N-RGO)” to form nanoscale p–n junctions (p-MoS₂/N-RGO) through the hydrothermal method. It was observed that p-MoS₂/N-RGO produces a higher photocatalytic H₂ generation rate (24.8 μM·g⁻¹·h⁻¹) compared with neat MoS₂ nanoparticles (0.1 μM·g⁻¹·h⁻¹) and MoS₂ supported over undoped RGO-MoS₂/RGO (7.4 μM·g⁻¹·h⁻¹). The authors showed that nanoscale p–n junctions are important for enhanced charge separation and higher photocatalytic activity.

A Zn₀.₈Cd₀.₂S/RGO-based nanocomposite has been synthesized by Zhang et al. following a hydrothermal methodology. HRTEM analysis indicated Zn₀.₈Cd₀.₂S are well dispersed in the RGO matrix. RGO loading of 0.25 wt% (GS0.25) showed a photocatalytic hydrogen generation (H₂) rate of 1824 μ·mol h⁻¹ g⁻¹, which is 450% higher compared with the pristine catalyst (Zn₀.₈Cd₀.₂S; GS0). Furthermore, Zn₀.₈Cd₀.₂S/RGO (0.25 wt%) showed a better transient photocurrent response under solar irradiation compared with pristine catalyst. This fact suggests a better charge separation in the composite catalysts at the RGO–catalyst interface. However, beyond 0.25 wt%, a steady decrease in H₂ generation rate was observed, and the following reasons were suggested by the author: (i) the presence of a large fraction of black RGO creates a shielding of the incident light, which prevents the photogeneration of electrons from the Zn₀.₈Cd₀.₂S nanoparticles; and (ii) an excess amount of RGO may cover the active sites of Zn₀.₈Cd₀.₂S, hindering the contact of the sacrificial agents with the catalyst.

Bera et al. have systematically studied 0D-CdS (nanoparticles)/RGO, 1D-CdS (nanowires)/RGO and 2D-CdS (nanosheets)/RGO nanocomposites toward visible-light-assisted photocatalytic degradation of methylene blue. A 4-amino thiophenol (ATP) linker was used to graft the CdS with the RGO surface. The 2D-CdS (nanosheets)/RGO showed higher photocatalytic efficiency (98.2%) compared with 0D-CdS (nanoparticles)/RGO (64.2%) and 1D-CdS (nanowires)/RGO (77%). Besides, the individual nanocomposites showed higher degradation efficiencies compared with the pristine nanosystems.

Lui et al. have developed CdS Nanowires-NWs (1D) Reduced RGO Oxide Nanocomposites through the electrostatic self-assembly method, followed by a hydrothermal reduction process. TEM images indicated the formation of CdS NWs/RGO composites as shown in Figure 3 (2A and 2B). The CdS NWs/RGO nanocomposites showed enhanced photoactivity as compared with pristine CdS nanowires (CdS NWs) toward nitro aniline reduction Figure 3 (3A and 3B).

As discussed in sections 3.1 and 3.2, surface grafting of RGO at the oxide surface, through Ti–O–C bonding, enhances the interfacial interaction and facilitates the charge transport. It is thus important to examine the type of interaction that persists in chalcogenide/RGO-based nanocomposites or when RGO remains adsorbed at the surface of chalcogenide type semiconductors. Furthermore, it is crucial to examine (1) if there is an impact of the number of RGO layers on the photocatalytic activity of semiconductor/RGO composites and (2) the light blockage caused by RGO layer (beyond critical% loading of RGO) at the surface of the photocatalysts. The answer to the above queries would pave the pathway to design novel “RGO/semiconductor composites” for sustainable photocatalysis. More details on the future scope have been discussed in section 5.

4. STABILITY OF SEMICONDUCTOR/RGO COMPOSITES

RGO is a cost-effective and environmentally safer alternative toward the enhancement of photocatalytic activity compared
with expensive noble metals such as platinum (Pt) or gold (Au). However, the stability of nanocomposites is a major issue for critical applications. It should be noted that in semiconductor/RGO composites, RGO can irreversibly degrade under prolonged light irradiation conditions. As discussed in section 3.3, Lv et al. have observed a decrease in the photocatalytic hydrogen generation (λ>380 nm) from CdS/RGO composites after the second cycle. The disruption in the interaction between CdS surface and RGO was the possible reason for the decrease because of extended irradiation and stirring conditions. Selvaraj et al. observed that the current density and photo-voltage drastically reduced when Bi₂Ti₂O₇–BTO/RGO (2 wt % RGO loading) composite thin films were continuously illuminated (UV–visible) for 3 h in a three-electrode setup. Kamat et al. have shown the degradation of RGO by TiO₂ under UV–visible illumination using a xenon lamp (both TiO₂ and RGO were dispersed in oxygen saturated water). The degradation of RGO was probed using UV–visible spectroscopy, which showed a decrease in the absorbance with the time of illumination from oxygen (O₂) saturated water medium. The proposed mechanism was that the photogenerated electrons at the conduction band of TiO₂ react with the dissolved O₂ and promote the generation of a high concentration of hydroxyl radical (OH•; a potential oxidant), which irreversibly degrades RGO through an oxidative pathway. However, when ethanol was used as a hole scavenger, such oxidative damage was not observed, as ethanol reacts with holes (produced in the valence band of TiO₂), preventing OH• generation. Furthermore, under “visible light” irradiation (using UV cutoff filter), such oxidative damages were not observed because visible radiation does not produce OH• radicals. Jia et al. have reported a steady photocatalytic “hydrogen generation yield” even after 30 h of reaction from CdS/RGO-based (N-doped) nanocomposites under visible light irradiation (λ ≥ 420 nm). Zhang et al. have observed that Zn₁Cd₁₋₅S/RGO-based (0.25 wt %) catalysts were stable for >12 h during photocatalytic hydrogen generation (under UV–visible irradiation; nitrogen-N₂ was bubbled for 30 min before the photocatalytic reaction). Thus, because of multiple responses of RGO, a careful examination is essential to determine under what photocatalytic reaction conditions (such as O₂ concentration, UV exposure, pH, and nature of sacrificial oxidizing agent), the stability of the semiconductor/RGO nanocomposites can be improved.

5. FUTURE DIRECTIONS

From this analysis, it is observed that beyond certain “threshold loading” of RGO, the photocatalytic activity decreases. The “threshold loading” depends on the size, surface area of the semiconductor nanoparticle, and the method used for the oxide–RGO integration. While it is clear that RGO helps, a careful control of the microstructure of the overall nanocomposite, integration strategy, and uniformity of RGO distribution over the photocatalyst surface is yet to be fully achieved, particularly for mixed oxides.

First, it is necessary to systematically examine the leading approaches to integrate RGO with mixed metal oxide to achieve better photocatalytic activity. If a large-scale synthesis of “composite catalysts” is required for the technological purpose, better control of the mentioned parameters through tuning the parameters such as temperature, synthetic conditions, pH, and chemical composition would be crucial. A universally acceptable reduction method needs to be optimized (for GO to RGO conversion), which produces RGO with lower oxygen functionalities. Furthermore, during the production of the nanocomposite catalyst system on a commercial scale, control of (1) defect states caused due to oxygen-containing functionality and (2) the dimensions of the RGO sheets would be crucial for achieving enhanced activity.

Second, the tunability of the electronic properties of RGO and its impact on photo(electro)chemical processes is not fully understood. We know (i) the thermal treatment (along with the nature of gas within the heating chamber) can impact the n-/p-characteristics and (ii) oxygen functionalities together influence the electronic property in RGO. Building on this, it is critical to understand what degree of n-/p-characteristics, choices of functional groups (–OH, –COOH, –HCHO), and their ratios must be present on RGO to optimally influence photocatalytic processes. While these aspects impact the work-function (Wₚ) of RGO, however, it is unclear how they can be tuned particularly in mixed metal oxides. For example, understanding Vₐfm during the electron transfer (as discussed in section 3) may allow us to choose the “best fit” method for fabrication of an RGO-based nanocomposite with suitable functional group(s) tailored for a specific semiconductor nanoparticle. Additional study is required to determine if the photogenerated “holes” from the semiconductor surface can migrate over the RGO and can act as a charge recombination center.

Third, many of the investigations on enhancement of photocatalytic activities of semiconducting materials are discussed over short time frame (few hours) and in idealized conditions (temperature, electrolyte composition, pH etc.). The long-term (several hours/days) impact on the interface between RGO and semiconductors needs to be examined more carefully to verify what happens to the RGO–oxide interface: if the whole fraction of RGO continues to be attached to the surface of the catalyst, if it undergoes chemical transformation (stability issues), and/or if there is any evidence of C-doping. Since it has been observed that Ti–C bond formation occurs in TiO₂/RGO composites, further investigation is required to understand how the band bending occurs at the Oxide/RGO junction/ interfaces. The use of “theoretical/simulation” based insights into the interfacial analysis of RGO-oxide composites from the perspective of stability as well as redox chemistry analysis is sparse in the current literature. These modeling-driven experimental studies can be a key component in the understanding of RGO and its impact in oxide-driven photocatalysis.

6. CONCLUSIONS

In this Mini-Review, we highlight the different efforts taken by researchers across the globe including us for enhancing the photo(electro)catalytic activity of widely accepted conventional semiconductor materials by incorporating RGO as a composite forming entity. Recapitulating, to qualify as a good photocatalyst, a composite material should have proper light absorption, excellent carrier mobility, a higher lifetime of carriers, good charge separation, and thereby less recombination. Widely accepted single and mixed metal oxides and metal sulfides lack some of these properties. To overcome such limitations, researchers have explored many ideas, including carefully engineered heterojunctions, by incorporating noble metals or RGO. The latter has attracted much interest because of its cost-effectiveness, sustainable attributes, and clean energy nature, along with its chemical stability and electronic properties. Herein we have commented on some of the works on RGO-based heterojunction photocatalysts, showing significant improvement in the activity compared with their
counterparts without RGO for various applications, highlighting the synthesis methods and the scientific evidence.

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