



ORIGINAL ARTICLE

Graphene/inorganic nanocomposites: Evolving photocatalysts for solar energy conversion for environmental remediation



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Received 18 July 2022; revised 13 August 2022; accepted 6 September 2022

Available online 13 September 2022

KEYWORDS

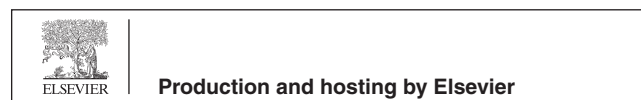
Graphene;
Nanocomposites;
Photocatalysts;
Solar energy;
Environmental remediation

Abstract Current energy crisis and environmental issues, including depletion of fossil fuels, rapid industrialization, and undesired CO₂ emission resulting in global warming has created havoc for the global population and significantly affected the quality of life. In this scenario the environmental problems in the forefront of research priorities. Development of renewable energy resources particularly the efficient conversion of solar light to sustainable energy is crucial in addressing environmental problems. In this regard, the synthesis of semiconductors-based photocatalysts has emerged as an effective tool for different photocatalytic applications and environmental remediation. Among different photocatalyst options available, graphene and graphene derivatives such as, graphene oxide (GO), highly reduced graphene oxide (HRG), and doped graphene (N, S, P, B-HRG) have become rising stars on the horizon of semiconductors-based photocatalytic applications. Graphene is a single layer of graphite consisting of a unique planar structure, high conductivity, greater electron mobility, and significantly very high specific surface area. Besides, the recent advancements in synthetic approaches have led to the cost-effective production of graphene-based materials on a large-scale. Therefore, graphene-based materials have gained considerable recognition for the production of semiconducting photocatalysts involving other semiconducting materials. The graphene-based semiconductors photocatalysts surpasses electron-holes pairs recombination

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rate and lowers the energy band gap by tailoring the valence band (VB) and conduction band (CB) leading to the enhanced photocatalytic performance of hybrid photocatalysts. Herein, we have summarized the latest developments in designing and fabrication of graphene-based semiconducting photocatalysts using a variety of commonly applied methods such as, post-deposition methods, *in-situ* binding methods, hydrothermal and/or solvothermal approaches. In addition, we will discuss the photocatalytic properties of the resulting graphene-based hybrid materials for various environmental remediation processes such as; (i) clean H₂ fuel production, photocatalytic (ii) pollutants degradation, (iii) photo-redox organic transformation and (iv) photo-induced CO₂ reduction. On the whole, by the inclusion of more than 300 references, this review possibly covered in detail the aspects of graphene-based semiconductor photocatalysts for environmental remediation processes. Finally, the review will conclude a short summary and discussion about future perspectives, challenges and new directions in these emerging areas of research.

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1. Introduction:

Over the couple of decades, the threat of environmental degradation has been increasing rapidly than earlier [1]. Currently, major causes of environmental destruction are anthropogenic in nature involving a combination of various factors including industrial revolution, extensive population growth and unplanned consumerism [2]. The environmental destruction is mainly caused by the release of toxic substances in the environment, such as hazardous gases emitted from fossil fuel combustions, industrial wastes, and disposing homemade utilities, processed materials including, garbage, electronic wastes, and plastics. [3,4]. Apart from the conventional produced waste, the greenhouse gases such as SO₂, NO_x, CO, and CO₂ has become a globally significant challenge [5]. Particularly, over-dependence on fossil fuels has significantly contributed to the excessive discharge of CO₂ into the environment [6,7]. This has created acute environmental issues, including global warming, depletion of ozone layer, ocean acidification, rising sea levels and extreme weather. [8,9]. In addition, the disproportionate usage of fossil fuels and excessive deforestation have disturbed the carbon cycle on the earth which further accelerated the environmental degradation and depletion of natural resources including fossil fuel [10,11].

Fossil fuels are non-renewable resources and are not distributed evenly across the globe, the threat to the energy security is significantly enhanced and raises serious concerns about their constant availability and future generations [12,13]. Controlled consumption of fossil fuels should be encouraged to avoid their complete depletion and to reduce the environmental impact [14,15]. Global CO₂ emissions are directly correlated to the fossil fuels based energy production, consumption, their cost and accessibility [16]. For example, high-energy consuming countries (developed and developing countries) will ultimately generate excessive amount of CO₂ in the atmosphere, causing undesirable distress to the environment [17]. The global primary energy consumption more than doubled, from 270.5 EJ in 1978 to 580 EJ in 2018 (cf. Fig. 1) [18].

Therefore, limiting the dependence on fossil fuels and development of alternative renewable energy technologies is required to safeguard and sustainable energy supplies at low costs and to address problems of climate change [19]. Renewable energy sources are either carbon neutral or generate less carbon emissions. Therefore, renewable energy sources are

the guarantee to limit the harm to the environment in comparison to the fossil fuels-based energy production methods [20]. Renewable energy sources include, solar energy, geothermal energy, wind energy, ocean energy, biomass energy and fuel cell technology [21]. Recently, among various renewable energy resources, H₂ based energy sources have gained immense fame as clean energy alternatives to the fossil fuels due to its high energy content and carbon neutrality [22,23]. H₂ is colourless and odourless gas which is relatively less dense than air, however, the gravimetric density of H₂ energy is several times higher (142 MJ kg⁻¹, upper heating value), than the density of fossil fuels [24–26]. Besides, due to zero emission of CO₂, H₂ is considered as the suitable clean energy carrier, which greatly reduces the environmental issues.

Typically, H₂ is produced at large scale by several well-established approaches including hydrocracking of fossil fuels through refinery processes. However, most of these conventional methods often require high energy consumption and emission of carbonaceous materials which largely hamper their applications [27–29]. In this regard, sunlight is considered as a sustainable source of clean energy, which has been exploited in both natural and artificial processes to obtain high-energy resources [30]. As an example, the conversion of water and CO₂ into O₂ and high-energy carbohydrates through natural photosynthetic process and sunlight driven water splitting methods to produce clean H₂ (cf. Fig. -2) [31–34]. Particularly, the H₂ production through water splitting has attracted great attention as it employs sunlight to produce clean H₂ gas using simple technology by producing non-hazardous side-products [35].

Typically, the photocatalytic H₂ evolution occurs on the surface of semiconductor based photocatalyst in which water is directly converted into H₂ and O₂ through electrolysis (cf. Fig. 3) [36,37]. Photocatalyst absorbs the light and convert it to an electrical charges which potentially derive the surface redox reactions [38]. Ideally, the most economic method of generating clean H₂ would be a ‘particulate’ system in which photocatalysts can be directly dispersed in water to obtain H₂ gas [39,40]. Besides, a single photocatalyst which is capable of delivering overall water splitting (OWS) through simultaneous oxidation and reduction of H₂O into H₂ and O₂ is highly desirable [41]. However, only limited number of particulate photocatalysts are capable of achieving OWS which are mostly based on wide bandgap semiconductors including TiO₂, ZnO, SrTiO₃ etc. [42]. In addition, these photocatalysts are only

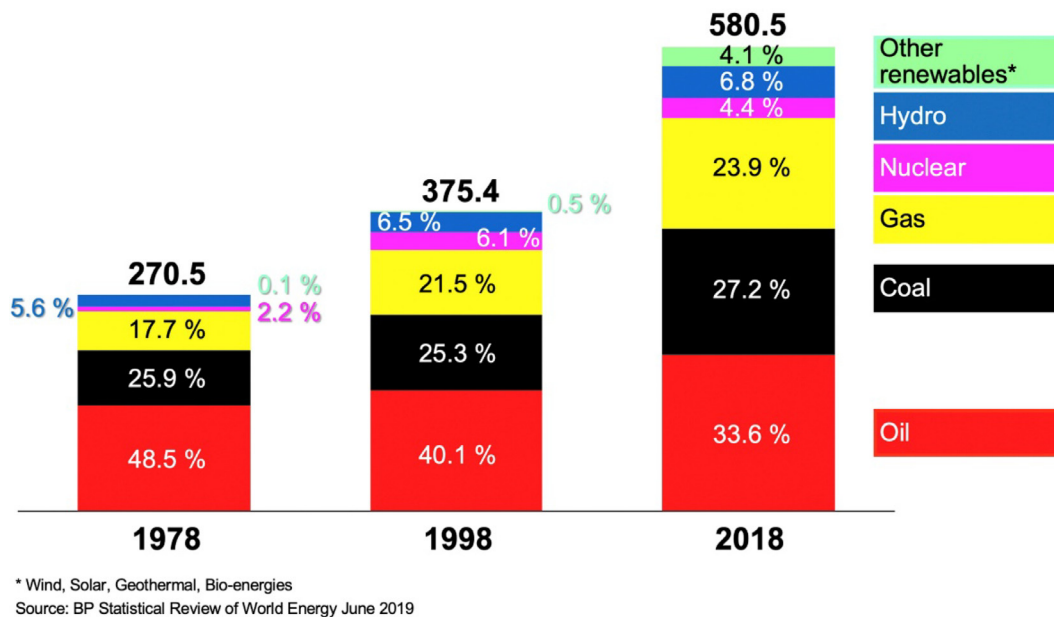


Fig. 1 Overview of global energy consumption from 1978 to 2018. [18].

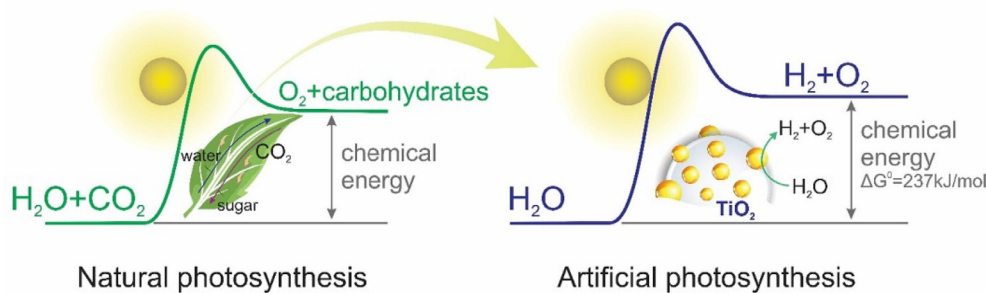


Fig. 2 Sunlight driven natural photosynthesis to produce high energy carbohydrates and photocatalytic water splitting for clean H₂. [32].

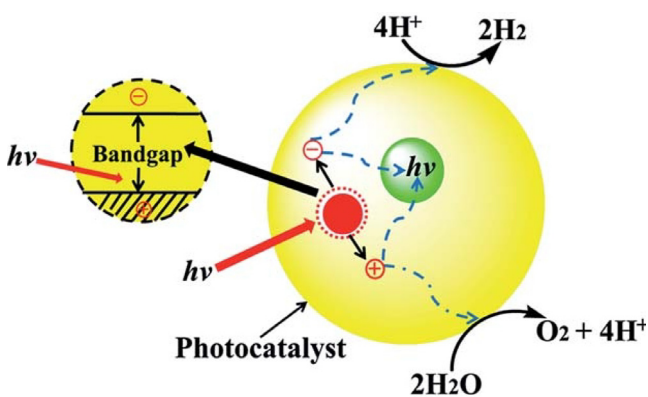


Fig. 3 Schematic illustration of the photocatalytic process of water splitting over a semiconductor photocatalyst [43].

active under UV light which constitute < 5 % of the solar spectrum, which seriously limits their H₂ producing efficiency and commercial applicability. So far, remarkable strides have

been made toward increasing the efficiency of photocatalysts in past several decades, however, scientists are still trying hard to achieve the absorption in the visible portion of solar spectrum to utilize it with full potential.

In addition to the production of clean H₂, semiconductor based photocatalysts have also found large applications in other environmental remediation processes including pollutant degradations[44,45]. Currently, increasing population and rampant industrialization has seriously strained the atmosphere due to the contamination of global water bodies including river and underground water [46]. The water pollution is mainly caused by the mixing of hazardous pollutants into the water, which is harmful to human health and aquatic ecosystems [47]. The pollutants are of various forms, such as physical pollutants like colour, odour, biological pollutants like pathogens and chemical pollutants involving hazardous organic and inorganic chemicals [48,49]. Among these pollutants, hazardous organic compounds are of more concern even in smaller quantity, due to their carcinogenic and mutagenic properties [50]. Additionally, these organic pollutants are not

easy to remove (from the waterbodies) or decompose by the conventional water-treatment processes and thus possess dreadful danger to the humans and aquatic organisms [51].

Particularly, the degradation of refractory organic pollutants, such as organic dyes and other high-molecular-weight organic compounds is challenging due to their resistance towards biological treatment processes [52]. Application of other conventional treatment technologies like precipitation and flocculation are also not fruitful as they require post-treatment to remove the pollutants [53]. Therefore, researchers rely on photocatalytic degradation of pollutants which is an effective in removing both organic and inorganic contaminants simultaneously without forming hazardous side products [54]. Photocatalysts are capable of mineralising recalcitrant organic contaminants and reducing metal ions in water at low cost without producing harmful side products. Apart from this semiconductors based photocatalytic materials have also been extensively utilized in other environmental remediation processes including conventional organic synthesis and CO₂ reduction etc. [55].

Due to this, research on semiconductor based photocatalysts is skyrocketed in recent years and so far, numerous semiconducting photocatalytic nanomaterials have been developed, including metal oxides (TiO₂, V₂O₅), mixed metal oxides (ZnAl₂O₄, Bi₂WO₆), metal sulfides (MoS₂, Bi₂S₃), metal phosphides (Ni₂P, Co₂P), metal selenides (CdSe, MoSe₂), metal halides (such as AgBr), metal-organic frameworks (MOFs) and other 2D layered materials including graphene and carbon nitride (g-C₃N₄). [56–59]. These photocatalysts offer vast benefits in photocatalytic environmental remediation, however, their large-scale applications are often suffered from a variety of limitations [57,60]. For instance, low photon absorption in the visible region, chemical stability under required reaction conditions, high recombination rate for the photo-induced excitons [61]. Therefore, continuous efforts are being made in the field of photocatalysis to enhance the efficiency of these photocatalysts through structural and electronic modifications using advance methods such as, metal deposition, co-doping, dye sensitization, coupled semiconductor, defect-induced photocatalysis, and supported photocatalysis [62–65]. For example, the combination of metal and metal oxide nanoparticles (TiO₂, ZnO, Ag, Au, Pt) has been known to enhance the light absorption efficiency of the resulting photocatalysts due to the localized surface plasmon resonance (LSPR) of metal nanoparticles [66–68]. Amidst several techniques, supported photocatalysis has been proven as an effective strategy for overcoming aforementioned limitation of bare nanomaterials [69–71]. In this regard, inorganic photocatalysts have been often supported on a variety of support materials including polymers, biomaterials, and various carbonaceous materials such as, poly (vinyl chloride) (PVC), poly (methyl methacrylate) (PMMA), and polystyrene (PS), lignin, starch, chitosan, bio-char, activated carbon and various graphene-based materials. The support materials are used to enhance the stability, adsorption capacity and photocatalytic properties of inorganic photocatalysts [72–74].

Among these materials, graphene has gained remarkable attention as support material for inorganic photocatalysts, since most of other supports suffer from lower stability, conductivity or very small surface area. [75,76]. Graphene is a sp²-carbon packed, 2D layered, zero band gap semiconductor with extraordinary physicochemical properties including excel-

lent electrical and optical properties such as, exceptional Young's modulus values (~1.0 TPa), high mobility of charge carriers (greater than 200 000 cm² V⁻¹ s⁻¹ at electron densities of 2×10^{11} cm⁻²), large spring constants (1– 5 Nm⁻¹), excellent thermal conductivity (~5000 Wm⁻¹ K⁻¹), high electrical conductivity (10⁸ A cm⁻²), large theoretically specific surface area (2630 m²/g), and optical transmittance (~97.7 %). Besides, locally conjugated aromatic system and high electrochemical stability have made graphene very popular in photocatalysis as a support and carrier or promoter [77–79]. Other benefits of graphene based photocatalysts involve low cost, ease of availability and processing, lowered chances of aggregation of nanoparticles and possibility of surface modification for enhanced absorption [77,80,81]. Since, the interfacial contact with additional components is maximized due to the large specific surface area of graphene, the chances of the agglomeration of nanoparticles on its surface is minimized significantly [82].

In the recent times graphene/inorganic based light assisted (both UV and visible light) photocatalysts have emerged as effective, environment friendly, and economical materials for variety of environmental remediation processes [83]. Therefore, the combination of graphene with inorganic semiconducting nanomaterials offers a facile strategy to strengthen photocatalytic activities and stabilities of resulting photocatalysts [84]. These hybrid photocatalysts offer enhanced absorptivity, improved light absorption capacity, fast charge carrier migration, reduced rate of recombination, and increased photo-efficiency [85]. This review offers current advancements in the field of graphene-based photocatalytic materials consisting of semiconducting nanomaterials with enhanced photocatalytic activity under UV or visible light. Besides, herein a systematic, updated summary of the current status of the applications of graphene-based photocatalysts in a variety of environmental remediation processes have been highlighted. Such as, nonselective degradation of pollutants, water splitting to clean H₂ fuel, photocatalytic transformations for organic compounds and CO₂ reduction. In addition, recent developments in the preparation of graphene and graphene-based photocatalysts have also been briefly discussed. Furthermore, the current challenges and prospects of tailoring graphene-based hybrid photocatalysts are summarized towards the end of this review.

2. Synthesis

2.1. Preparation of graphene

Reports of the synthesis of graphene have been exploded ever since the successful fabrication of graphene has been reported by Novoselov et al. in 2004 through manual mechanical cleavage of graphite using scotch tape [86,87]. Although, the scotch tape cleavage method became popular, but it only results in producing pile of sheets or few isolated sheets in small amount [88]. On the other hand, sequential oxidation–reduction methods are capable of producing large quantity of defected graphene like materials which is often referred as highly reduced graphene oxide (HRG) [89]. Generally, the synthesis of graphene is broadly classified in two different categories including *bottom-up* and *top-down* methods (cf. Fig. 4) [90,91]. Bottom-up methods are suitable alternative to the mechanical exfolia-

tion of graphite which produce relatively high yield of graphene than the scotch tape method using atoms or molecules of a variety of precursors other than graphite using chemical reactions [92,93]. Some of these methods include epitaxial growth on single-crystal SiC and chemical vapor deposition on metal foil surfaces and unzipping carbon nanotubes. [94,95]. Thus, in the cases where bulk quantity of graphene is required (such as, for the synthesis of graphene nanocomposites), the top-down approaches are more suitable, wherein bulk amount of slightly defected graphene-like sheets can be obtained using reduction of graphite derivatives including graphite oxide (GO) and/or graphene oxide (GRO) [96,97].

GO is typically synthesized by the slight modification of well-established Brodie, Staudenmaier, and Hummers approaches involving the oxidation of graphite powder under the influence of strong mineral acids and oxidants [98,99]. These oxidation processes render a variety of oxygenated groups on the surface of graphite layers including hydroxyl, epoxy, carboxylic acids and other oxygen containing functional groups which facilitate the separation of graphitic layers [100,101]. To convert GO into HRG, the oxygen containing functional groups are removed from the surface of starting material using a variety of reduction techniques such as, chemical, thermal, microwave, hydrothermal, solvothermal and var-

ious other green reduction method [102–104]. For instance, Jiang et al., have reported the preparation of high-quality HRG by a facile microwave reduction method under ambient conditions [105]. The reduction of GO was achieved by strong arc discharge, which is caused by aggregation of electrons at the junction between HRG and GO under microwave irradiation. During this process, O₂ atoms were removed and carbon atoms were rearranged simultaneously in the HRG lattice. Very recently, HRG was prepared using a nontoxic reducing agent from the bio-extract of pomegranate peels (cf. Fig. 5) [106]. The reduction of GO was achieved by the elimination of a substantial contents of oxygenated groups and the partial restoration of sp² carbon structures.

2.2. Preparation of Graphene-Based inorganic Photocatalysts:

The hybridization of semiconducting inorganic nanomaterials on graphene for the synthesis of graphene-based photocatalysts is typically performed by a variety of different methods, among them most prominent methods are *ex-situ* hybridization (post-deposition), *in-situ* crystallization (*in-situ* binding). The former involves combining of separate precursor dispersions including graphene and pre-synthesized nanomaterials, this method is also referred to as solution mixing method.

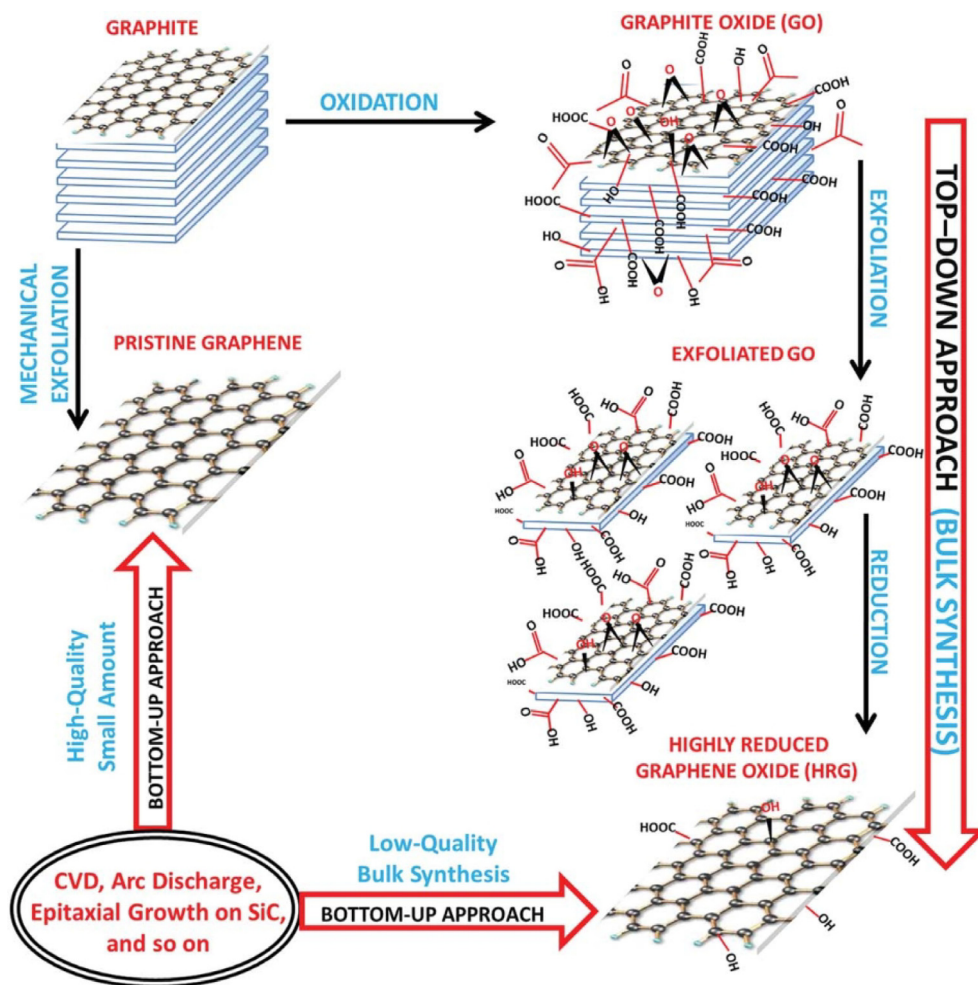


Fig. 4 Schematic illustration of the preparation of graphene by different methods.[90,91].

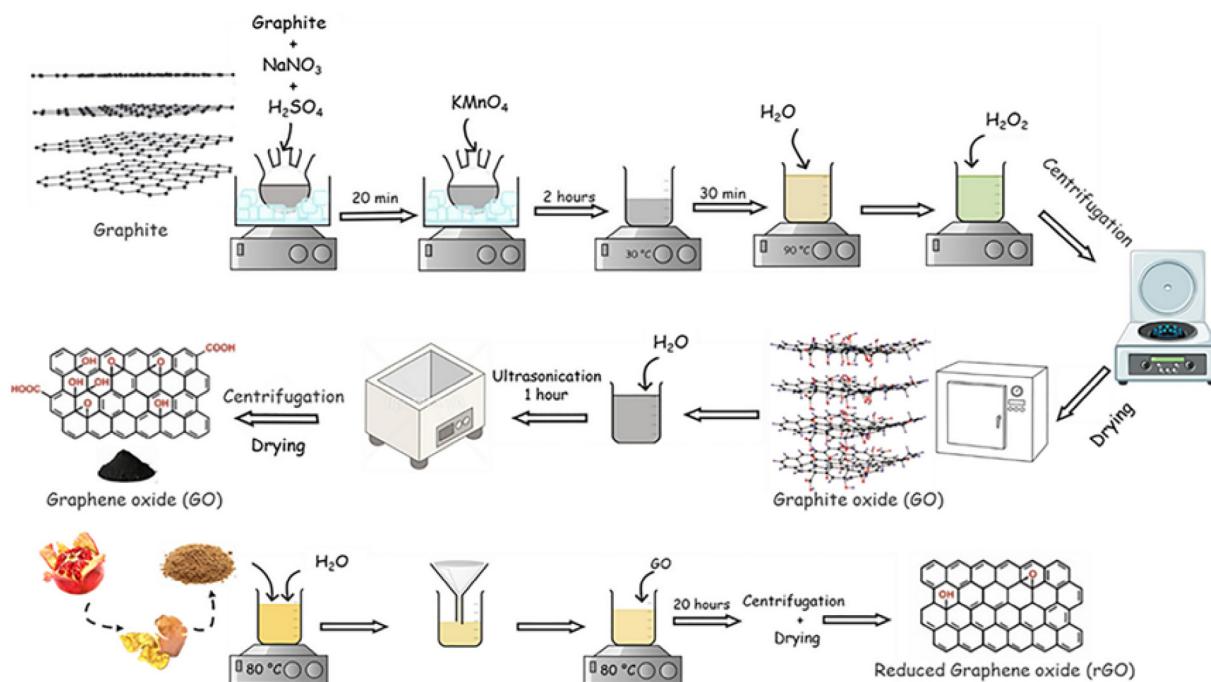


Fig. 5 Reduction of GRO using the bio-extract of pomegranate peels [106].

While, in the latter case, simultaneous reduction of GRO and metal precursor salts is performed using suitable reduction technique [107]. Besides, a variety of other methods involving hydrothermal, solvothermal, microwave and many other techniques have also been applied [108,109]. Using these methods, different kinds of graphene-based semiconducting photocatalysts involving different types of nanoparticles have been prepared. These nanoparticles include, TiO_2 , ZnO , Cu_2O , SnO_2 , ZnS , CdS , CdSe , Bi_2WO_6 and metal chalcogenides. In the following section, we will discuss the latest developments in the preparation of graphene-based photocatalysts using some of these prominent methods [110,111].

2.2.1. Post deposition methods

In the post deposition techniques, two separate solutions containing previously prepared graphene and desired nanoparticles are mixed together to perform the deposition. In many cases, the surface of graphene is often modified to improve the dispersibility and adsorption capability of graphene. The surface of graphene is often functionalized using covalent and non-covalent functionalization techniques [112–114]. The covalent functionalization of graphene surface is typically performed using a variety of ligands containing carboxylic, amine and other functional groups which are known to attract and hold the nanoparticles [115]. Whereas, in the non-covalent functionalization large molecules with conjugated carbon networks, such as pyrene, coronene derivatives are used which possess excellent ability to homogeneously disperse on the surface of graphene using π - π stackings [116]. In some cases, the surfaces of nanoparticles are also functionalized with suitable ligands to improve the chances of homogeneous deposition and uniform coverage of nanomaterials on the surface of graphene. However, the post-deposition techniques often suffer

from low density and non-uniform coverage of nanoparticles onto the graphene sheets.

Post deposition techniques have been widely applied to prepare graphene inorganic semiconductor photocatalysts. Such as, pre-synthesized TiO_2 nanoparticles and GRO dispersion were mixed using ultrasonication, the resulting dispersion was subjected to ultraviolet irradiation to initiate the reduction of GRO and deposition of nanoparticles on the surface of graphene [118]. Chen et al. have prepared different number of graphene, ZnO nanorods based photocatalysts using different weight ratios of graphene [117]. For the synthesis, pre-synthesized dispersions of ZnO nanorods and GRO were mixed ultrasonically (cf. Fig. 6). The mixed solutions were vigorously stirred to achieve firm deposition of ZnO nanorods on the surface of graphene. The resulting dispersion was transferred to autoclave and the reduction of GRO was performed under hydrothermal conditions to obtain graphene- ZnO nanorods based photocatalysts. Recently, Ahmadi et al. have reported the fabrication of strontium titanate (SrTiO_3) and graphene based photocatalyst [119]. In this study, the photocatalyst was prepared using SrTiO_3 nanoparticles and GRO as precursors which were mixed together, followed by stirring under UV light irradiation for 5 h. In this period, the original brown color of solution was turned to black indicating the reduction of GRO to graphene which finally resulted in the formation of graphene- SrTiO_3 photocatalyst. In another study, a Z-scheme heterojunction with enhanced photocatalytic activity was fabricated using a novel oxygen-defective ZnO (O- ZnO)/HRG/UiO-66- NH_2 nanocomposite by a facile solvothermal route [120]. In this study, pre-synthesized oxygen deficient ZnO were used to deposit on the surface of graphene, which is obtained by solvothermal reduction method in the presence of MOF precursors and ZnO nanoparticles (Fig. 7).

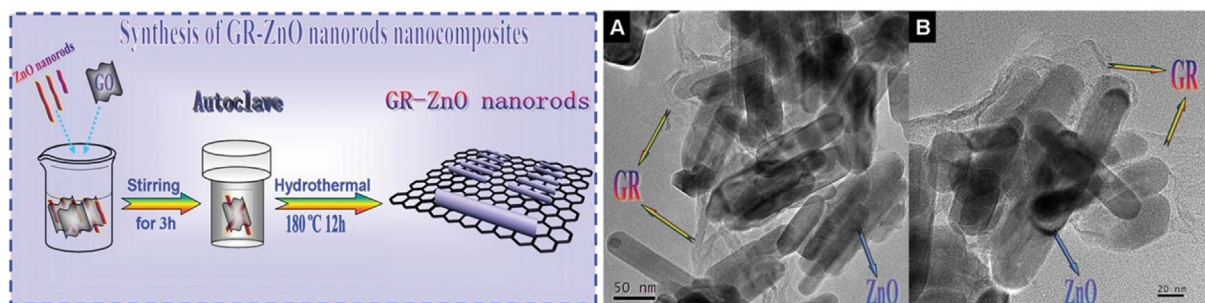


Fig. 6 Schematic representation of the preparation of graphene-ZnO nanorods photocatalyst using hydrothermal post-deposition method. a and b are the HR-TEM images of the resulting photocatalyst [117].

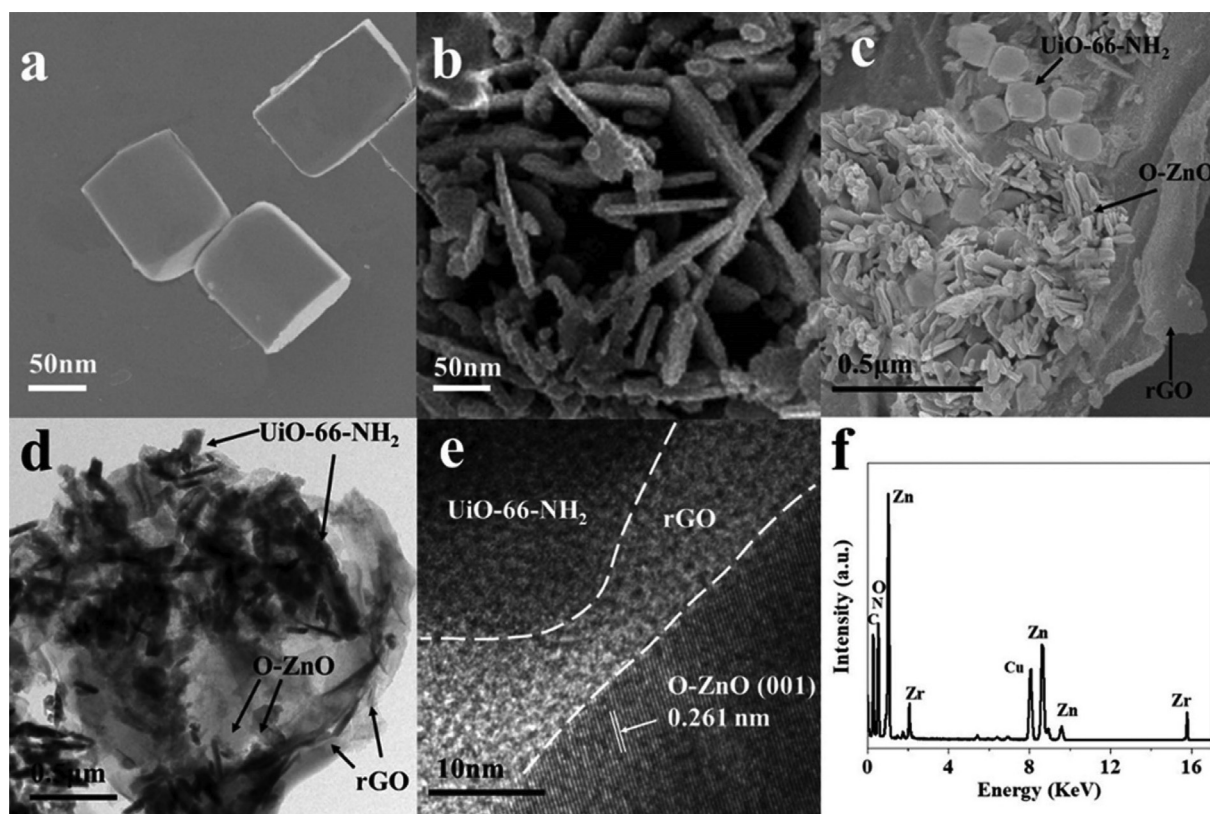


Fig. 7 SEM images of (a) UiO-66-NH₂, (b) O-ZnO, and (c) OZ/R/U; (d) TEM and (e) HRTEM images and (f) EDX spectrum of OZ/R/U. [120].

2.2.2. In-situ binding methods

The *in-situ* binding techniques are the most common methods which are usually applied for the direct deposition of nanoparticles including semiconducting metal oxide nanoparticles on the surface of graphene to produce photocatalysts [121,122]. In this method, widely applied precursor of graphene like GRO or GO and metal salts are mixed together to convert them into corresponding oxide nanoparticles and GO composite. Subsequently, after reduction of GO, which is typically performed using a variety of reductants, graphene based semiconducting photocatalysts are produced [123]. For instance, Zhang et al. have reported the preparation of different photocatalysts based on HRG with tin dioxide (SnO₂) and titanium dioxide (TiO₂) nanoparticles [124]. The *in-situ* growth of metal

oxide nanoparticles was achieved by mixing separate dispersions of GO and metal salts (titanium trichloride (TiCl₃) and tin (II) chloride dihydrate (SnCl₂·2H₂O)) under acidic conditions and stirred for few hours. The composites were obtained by the direct redox reaction between the GO and the reactive cations Sn²⁺ and Ti³⁺, forming HRG-SnO₂ and HRG-TiO₂ composites [125]. Similarly, graphene-ZnO photocatalyst was also obtained in another study, Zn²⁺ ions were deposited onto GO and converted into ZnO nanoparticles by adding NaOH for condensation of zinc hydroxide and NaBH₄ for the reduction of GO at 150 °C. Flower-like anatase HRG-TiO₂ photocatalyst was prepared by the hydrolysis of TiF₄ which was mixed with GO dispersion [126]. In this case, the morphology of the TiO₂ nanoparticles was influenced upon

changing the concentration of GO in the dispersion, at high GO concentration, long-range ordered assemblies of HRG-GO was obtained. Bera et al. have reported a single-pot low-temperature (95 °C) surfactant-free preparation of HRG-SnO₂ composites by changing the GO to tin (II) 2-ethylhexanoate weight ratio [127]. The reaction resulted in the oxidation of Sn²⁺ (of tin precursor) to Sn⁴⁺, forming SnO₂ nanoparticles with the simultaneous reduction of GO to HRG which rendered the deposition of SnO₂ nanoparticles onto the surface of HRG (cf. Fig. 8).

2.2.3. Hydrothermal/-Solvothelmal methods

The hydrothermal/-solvothelmal methods are other commonly applied methods which are used for the preparation of graphene/nanocomposites based photocatalysts [128]. These are one-pot processes which are capable of delivering highly crystalline, homogeneous nanostructures without requiring any post-synthetic annealing or calcination. These reactions are usually performed under closed systems in the presence of solvent or water at a temperature close to their boiling point to create high pressure [129]. Hu et al. have reported the preparation of tungsten trioxide (WO₃) nanorods with HRG nanocomposites by using a single-step *in-situ* hydrothermal method employing sodium tungstate (Na₂WO₄·2H₂O) and GO as precursors [130]. Xiao et al. have reported the synthesis of flower-shaped nanosheets of HRG-Ag₂O/TiO₂ ternary composite using two-step hydrothermal and one-step wet chemical co-precipitation methods [131]. At first, anatase TiO₂ with a nano-flaky flower-like structure was prepared under hydrothermal conditions, which is subsequently used to prepare HRG-TiO₂ nanocomposite under similar condi-

tions (hydrothermal conditions). Later on, graphene-coated Ag₂O/TiO₂ (AT) ternary composite material was formed by a simple wet chemical co-precipitation method. Hydrothermal methods are also efficient in controlling the morphologies of the materials under pressure of the main composition in the reaction [132]. This method was used to fabricate 3D nitrogen (N)-doped graphene aerogel monolith with platinum (Pt) nanocluster [133]. GRO and poly(oxypropylene)diamine were used as precursors, wherein, the concentration of GO and pH influenced the morphologies of the aerogel composite. In another study, hydrothermal conditions were exploited to prepare Fe³⁺-doped TiO₂ nanowires (Fe-NWs), which is subsequently used to fabricate graphene/Fe³⁺-doped TiO₂ nanowire nanocomposites (GR/Fe-NWCs) [134]. GO was reduced to HRG, anatase Fe-doped TiO₂ NWs were simultaneously deposited on the surface of HRG. Similarly, graphene was successfully wrapped around Fe doped TiO₂ sphere to produce G-TiO₂-Fe photocatalyst using hydrothermal method [135]. In addition to aqueous synthesis, a variety of other solvents have also been utilized to prepare graphene based photocatalysts under solvothelmal conditions. For instance, a facile single-step solvothelmal method was employed to prepare graphene/CdS nanocomposites [136]. The fabrication of the composite was performed by the hydrolysis/dissociation of CH₄N₂S in the presence of GO in ethylene diamine (EDA) solution of cadmium acetate dihydrate under solvothelmal conditions at 180 °C. Dong et al. have exploited solvothelmal method for the preparation of graphene/rod-shaped TiO₂ nanocomposite through reduction of colloidal dispersion of graphene oxide in benzyl alcohol. During the synthesis, both the reduction of GO and the growth and depo-

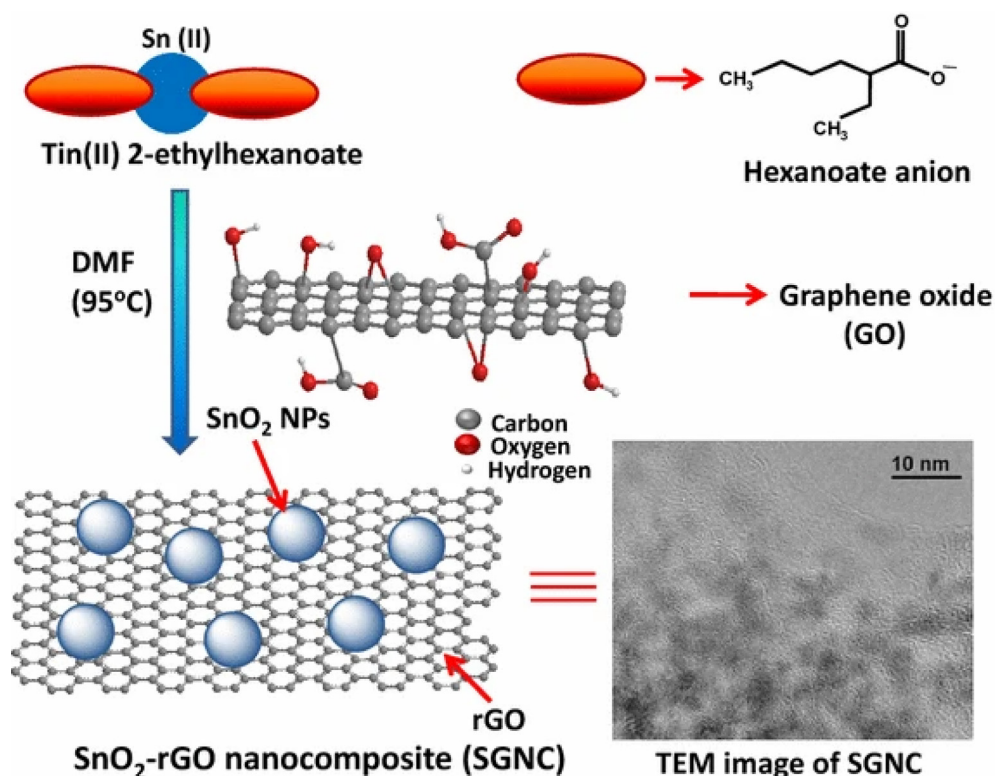


Fig. 8 Schematic illustration of the formation of HRG-SnO₂ nanocomposite [127].

sition of rod-shaped TiO_2 nanocrystals simultaneously occurred on the surface of graphene. Hu et al. have applied solvothermal method for the preparation of novel octahedral shaped CoFe_2O_4 onto HRG to synthesize hybrid and pure CoFe_2O_4 nanoparticles [137]. During the synthesis, HRG influenced the morphology of CoFe_2O_4 nanoparticles which displayed size-dependent changes of shapes from granular (or sheet) to octahedral shapes.

2.2.4. Self-Assembly method

In addition to aforementioned methods, several other techniques have also been applied for the preparation of graphene-nanomaterials based photocatalysts including self-assembly method, electrochemical methods. [81]. The self-assembly is a prominent technique for the fabrication of complex architectures from nano, micro and nanoscale materials, particularly in the preparation of layered materials [139]. Wang et al. has prepared a magnetically separable $\gamma\text{-Fe}_2\text{O}_3/\text{GO}$ composite using low temperature, self-assembly method [140]. In another study, HRG encapsulated LaNiO_3 (LNO-RGO) composites were prepared as crumpled nanoreactors through self-assembly and photocatalytic reduction method [141]. In this case, the interaction between the oxygen vacancies (positive charge) on the LaNiO_3 surface and the oxygenated groups of the GO facilitated the encapsulation, forming a micro-nano multi-level structure (nanoreactor) under ultraviolet irradiation. Wang et al. have produced HRG-ZnO nanorods nanocomposites using a facile two-step self-assembly technique [138]. The composite exhibited uni-

form structure of rod-like morphologies with an average diameter of 30 nm and a length of 1–3 μm with high specific surface area, uniform structure, and good interfacial contact (cf. Fig. 9). The nanocomposite was prepared by electrostatic self-assembly of positively charged ZnO NRs with negatively charged GO, followed by the hydrothermal reduction of GO to HRG.

2.2.5. Electrochemical methods

Electrochemical deposition methods electrochemical deposition of graphene on different supports followed by deposition of inorganic nanoparticles onto graphene. A monolithic, two-side, ternary $\text{Cu}_2\text{O}/\text{graphene}/\text{TiO}_2$ nanotube array based heterostructure was prepared using anodic deposition of TiO_2 nanotube array onto Ti foil (TNA/Ti) as the substrate [142]. Graphene film was electrodeposited on the TNA/Ti and then Cu_2O nanoparticles were deposited onto the graphene sheets by electrochemical method. Furthermore, electrochemical methods were also applied for the preparation of 3D graphene-based photocatalysts, such as the preparation of three-dimensional (3D) porous graphene-based composite materials as reported by the Chen et al. [143]. This was achieved in two consecutive electrochemical steps, such as, the initial electrochemical preparation of 3D graphene (ERGO) porous material, followed by the reduction of concentrated GO dispersion (cf. Fig. 10). In the subsequent step, the second component including semiconducting nanomaterials such as ZnO was electrochemically deposited onto this 3D graphene matrix, which yielded 3D porous graphene-based com-

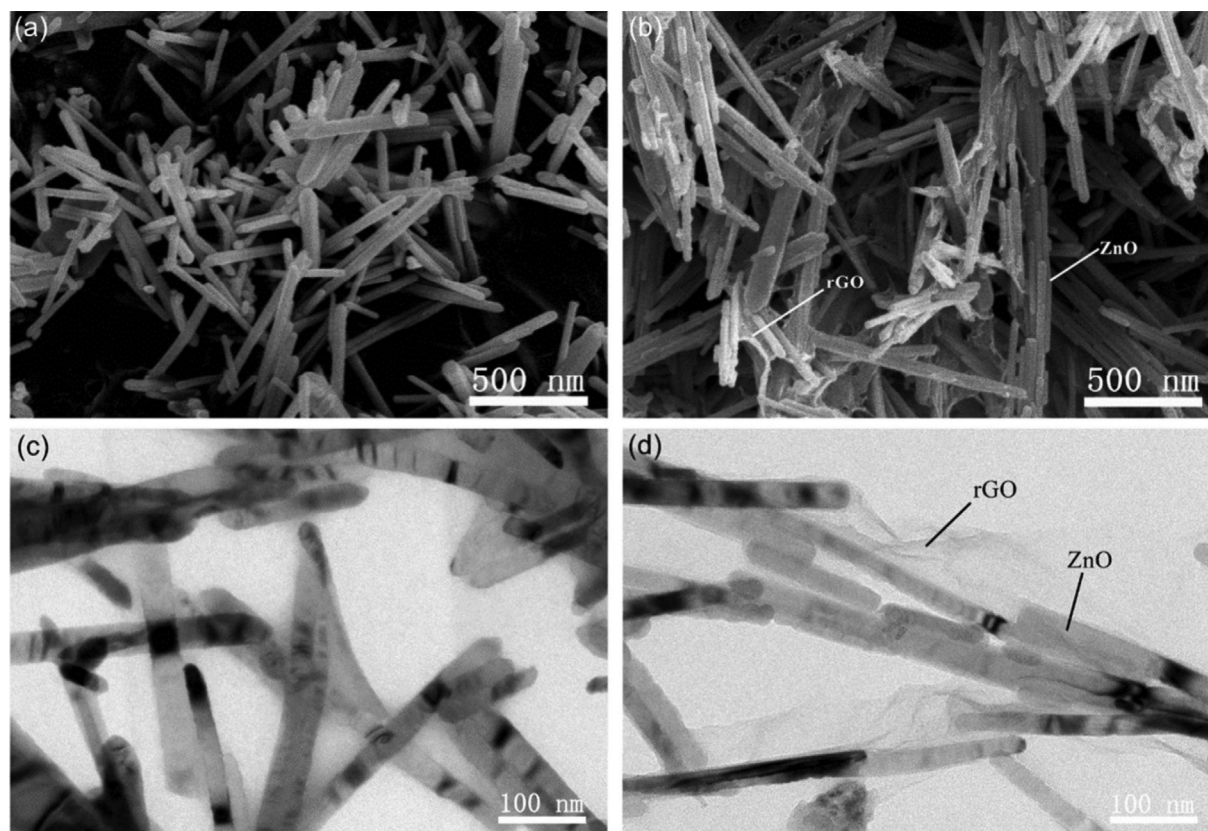


Fig. 9 SEM images of a) ZnO b) 5% HRG-ZnO, TEM images of c) ZnO NRs d) 5% HRG-ZnO. [138].

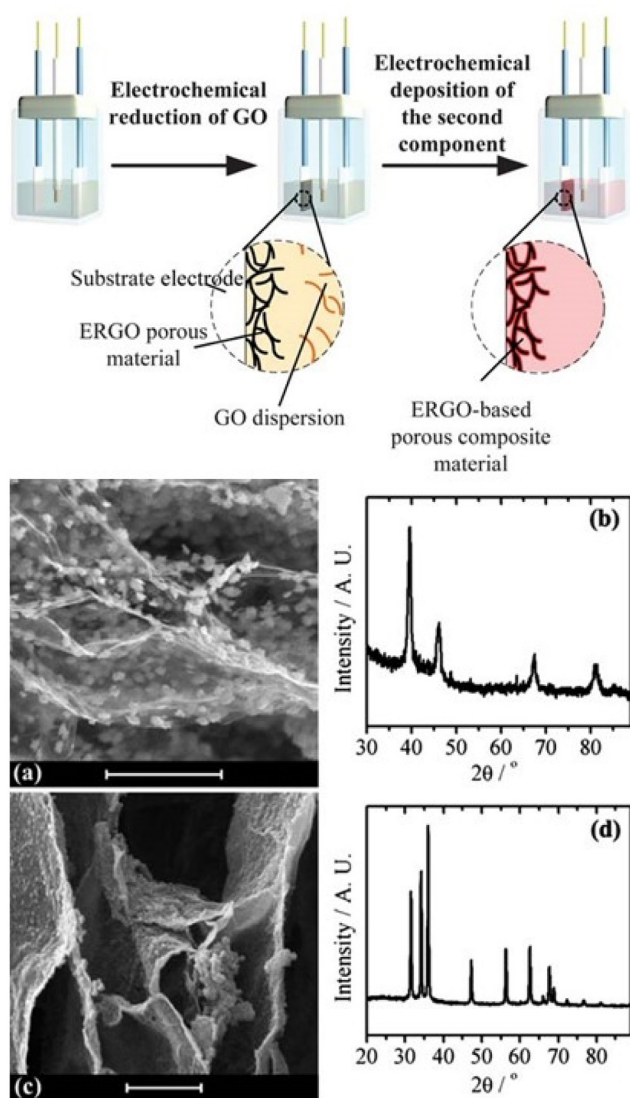


Fig. 10 Schematic illustration of the preparation method for 3D graphene-based composites, (a) and (b) Cross-section SEM image and XRD pattern of the lyophilized ERGO–PtNP composite. (c) and (d) Cross-section SEM image and XRD pattern of the lyophilized ERGO–ZnO composite. Scale bar: 1 mm. [143].

posites. The as-prepared 3D composites exhibited conductive graphene network as the matrix, consisting of homogeneously coated second component, such as noble metal nanoparticles and metal oxide.

3. Environmental applications of graphene based photocatalysts

For the last couple of decades, photocatalytic processes have gained great attention of scientists and technologists due to their excellent abilities in addressing the environmental concerns and energy problems (Table 1) [144,145]. Particularly, heterogeneous photocatalysis have been extensively applied in a wide range of photocatalytic processes including water splitting for hydrogen generation, photocatalytic conversion of CO₂ into hydrocarbon fuels, organic transformation and environmental remediation such as the degradation of organic

pollutants. [146–148]. Typically, the heterogeneous photocatalytic processes involve the conversion of light energy into chemical energy, which occur when a semiconducting material is irradiated by light with photon energies larger than the band gap energy of the semiconductor [149](Fox et al., 1993). The light is partially reflected from the semiconductor surface and partially absorbed in the semiconductor. The absorbed light initiates the excitation of electrons from the valence band (VB) into the conduction band (CB), producing electron–hole pairs, which are responsible for the photocatalytic activity (cf. Fig. 11) [150]. The photogenerated electron-hole pairs dissociate from each other and quickly migrate to catalytically active locations at semiconductor surface where they reduce the electron acceptors or oxidize the donor species. Through the chemical transformations, the abundant solar energy can be effectively stored and utilized [151]. But, usually, the recombination of electron-hole pair takes place and their energy is dissipated as heat before arriving at the semiconductor surface. This is one of the major factor that largely inhibit the efficiency of photocatalytic processes.

The potential of photocatalytic processes of semiconducting materials can only be fully exploited when the following conditions are fulfilled, such as, the generation of electron-hole pair upon the absorption of light across the whole spectrum of light; minimizing the possibility of the recombination of electron-hole pairs; abundance of photocatalytically active sites on the photocatalysts through high surface area. [152]. However, it is often difficult to fulfil all these conditions for photocatalysts at the same time. For instance, even an extensively studied semiconducting photocatalysts like TiO₂, exhibits a large band gap (3.2 eV), therefore, only responsive to the UV light absorption of the solar spectrum which is only 3 to 5 % of whole spectrum [153]. Another widely studied narrow band gap(2.4 eV) semiconductor (CdS) which absorb light under visible light region, suffers from the low separation efficiency of electron–hole pairs and photo-corrosion during irradiation [154]. Therefore, these shortcomings such as the loss of energy of energy during charge transport and recombination significantly affected the photocatalytic processes. In these regards, graphene based semiconducting composites offer great hope in addressing the aforementioned problems in photocatalytic processes [155–157]. Graphene exhibits extraordinary physicochemical properties, due to which, it is largely established as an excellent electron collector and transporter which effectively inhibits recombination of photogenerated electron hole pair [158,159]. In addition, due to the high specific surface area, graphene and graphene based semiconducting photocatalysts significantly enhance the absorption of light intensity and considerably extend the light absorption range of the material for the effective utilization of solar energy [160]. In addition, the combination of graphene and other inorganic semiconductors minimize the chances of aggregation of nanoparticles and restacking of graphene nanosheets leading to the enhance efficiency of resulting composites [161]. So far, several advance characterization techniques such as, photoluminescence (PL) spectroscopy, time-resolved fluorescence spectroscopy, photocurrent response data, electrochemical impedance spectra (EIS) measurement, and electron spin resonance (ESR) spectrum have led to the identification of the efficient photocatalytic properties of graphene [162,163]. Manga et al. have demonstrated ultrafast photocatalytic electron transfer between the TiO₂ and graphene using femtosec-

Table 1 Application of graphene-based metal or metal oxide nanocomposites for most important photocatalytic reactions.					
Catalyst	Source of radiation/ Preparation method	Metal precursor	Reaction	Catalytic performance	Ref.
3 wt% HRG/TNT	100 W UV irradiation/ hydrothermal method	TiO ₂	Removal of MB and MO	100 % decolorization and 77.4 % mineralization	[312]
TiO ₂ /HRG	300 W Xe arc lamp/ sol-gel method	Ti(OnBu) ₄	Removal of MB	0.201 mmol g _{cat} ⁻¹ h ⁻¹	[313]
Ag/Ag@Ag ₃ PO ₄ /HRG	400 W Xe arc lamp/ hetero-growth method	AgNO ₃	Removal of NR, RhB, MB and MO dyes	15 mg/L	[314]
N-doped TiO ₂ /HRG	visible light/ chemical reduction method	Tetrabutyl titanate	Removal of MB	90 % MB removal percentage	[315]
TiO ₂ -GQD	visible light/ ultrasonication process	Tetrabutyl titanate	Degradation of MB	97 % MB removal percentage	[316]
TiO ₂ @HRG	8 W UVC lamp/ hydrothermal procedure	Tetra- <i>n</i> -butyl orthotitanate	degradation of phenol	28 % phenol removal percentage	[317]
HRG-Fe-TiO ₂	UV chamber/ <i>in-situ</i> sonochemical procedure	Titanium isopropoxide, Ferric Nitrate	degradation of crystal violet dye	74.6 % degradation of CV	[318]
HRG-TiO ₂ -Fe	300 W Xe lamp/ hydrothermal method	Titanium isopropoxide, FeCl ₃ ·6H ₂ O	Degradation of MB	–	[135]
ZnO-HRG	300 W Xe lamp/ lyophilization method and thermal treatment process	Zn(OAc) ₂	MB removal	83.3 % MB removal	[319]
HRG-ZnO	300 W, Visible/ solventless method	Zn(OAc) ₂	degradation of MB	74.0 % MB removal percentage	[320]
Ni _{0.4} Co _{0.6} Er _{0.045} Fe _{1.95} O ₄ /HRG	60 W, Visible/ co-precipitation and sonication procedure	Ni(NO ₃) ₂ , Co(NO ₃) ₂ , Er ₂ O ₃ , Fe(NO ₃) ₃	photodegradation of MB	43.1 % MB removal percentage	[321]
TiO ₂ /ZnO/Bi ₂ O ₃ -HRG	solar irradiation/ sol-gel electrospinning method	Zn(OAc) ₂ , Bi(NO ₃) ₃ ·5H ₂ O, Cu(CO ₂ CH ₃) ₂ ·H ₂ O	formaldehyde degradation	degradation rate (k) of 0.1 min ⁻¹	[322]
Ag ₃ PO ₄ /HRG	500 W Xe lamp	AgNO ₃	degradation of bisphenol	100 % bisphenol removal percentage	[323]
AgI-BiOI-HRG	300 W Hg lamp	AgNO ₃ , KI, Bi(NO ₃) ₃ ·5H ₂ O	H ₂ production	168 μmolh ⁻¹ g ⁻¹	[324]
Ag-Bi ₂ WO ₆ -HRG	300 W Hg lamp/ solvothermal method	Bi(NO ₃) ₃ ·5H ₂ O, AgNO ₃	H ₂ production	78 μmolh ⁻¹ g ⁻¹	[325]
NiO/nickel carbide/HRG	400 W Hg lamp/ thermal treatment method	NiCl ₂	H ₂ production	39.4 %	[326]
TiO ₂ /HRG/Pt	9 W lamp	H ₆ PtCl ₆ ·6H ₂ O	H ₂ production	308 μmolg ⁻¹	[327]
Ag-TiO ₂ /HRG	100 mW cm ⁻² irradiation/ microwave assisted hydrothermal method	AgNO ₃	H ₂ production	225 μmolh ⁻¹ g ⁻¹	[328]
AgBr-HRG-TiO ₂	35 W Xe lamp/ reflux method	AgNO ₃ , CTAB	H ₂ production	2025 ppm	[329]
Au/HRG/TiO ₂	300 W Xe lamp	HAuCl ₄	H ₂ production	44 μmolh ⁻¹	[330]
ZrO ₂ -TiO ₂ /HRG	solar irradiation/ hydrothermal method	Titanium(IV) isopropoxide, ZrO(NO ₃) ₂	H ₂ production	7773 μmolh ⁻¹ g _{cat} ⁻¹	[331]
ZIS/HRG	300 W Xe lamp/ microwave-assisted hydrothermal method	ZnCl ₂ ·2H ₂ O, InCl ₃ ·4H ₂ O	H ₂ production	2640.8 μmolh ⁻¹ g ⁻¹	[332]
FG-ZnS	300 W Hg lamp/ chemical vapor deposition method	ZnCl ₂	H ₂ production	H ₂ -production rate 11,600 μmolh ⁻¹ g ⁻¹	[333]
ZnO-ZnS/HRG	300 W Hg lamp	ZnCl ₂	H ₂ production	1070 μmol h ⁻¹ g ⁻¹	[334]
Pd NPs/CS-HRG	<i>in-situ</i> reduction	PdCl ₂ ·4H ₂ O	H ₂ production	42.5 mol _{H₂} mol _{Pd} ⁻¹ min ⁻¹ TOF value	[335]
CdS-HRG-MoS ₂	300 W Xe lamp/ hydrothermal method	Cd(Ac) ₂ ·2H ₂ O, Na ₂ MoO ₄ ·2H ₂ O	H ₂ production	7.1 μmolg ⁻¹ h ⁻¹	[336]
BiVO ₄ QDS/HRG	300 W Xe lamp/ hydrothermal method	Bi(NO ₃) ₃ ·5H ₂ O, NH ₄ VO ₃	CO ₂ reduction	–	[307]
NiO/Ni-HRG	300 W Xe lamp/ reduction method	NiCl ₂	CO ₂ reduction	642 μmolg _{Ni} ⁻¹ h ⁻¹	[308]
GO/CH ₃ NH ₃ PbBr ₃	300 W Xe lamp/ ligand-assisted precipitation method	PbBr ₂ , CH ₃ NH ₃ Br	CO ₂ reduction	1.05 μmolcm ⁻² h ⁻¹	[337]

(continued on next page)

Table 1 (continued)

Catalyst	Source of radiation/ Preparation method	Metal precursor	Reaction	Catalytic performance	Ref.
HRG/TiO ₂	500 W Hg lamp/ reflux and vacuum thermal treatment method	titanium dioxide	CO ₂ reduction	30.30 μmolg ⁻¹ h ⁻¹	[296]
HRG/TiO ₂ (NT)	200 W UV-A lamp/ electrochemical anodization technique	Ti foil	CO ₂ reduction	760 μMolg ⁻¹	[338]
WSe ₂ -HRG-TiO ₂	500 W UV/visible light/ ultrasonic process	C ₁₆ H ₃₆ O ₄ Ti, selenium powder, and WO ₃	CO ₂ reduction	6.3262 μmolg ⁻¹ h ⁻¹	[300]
ZnO-HRG	300 W Xe lamp/ hydrothermal procedure	Zn(NO ₃) ₂	CO ₂ reduction	263.17 μmol/g _{cat}	[339]

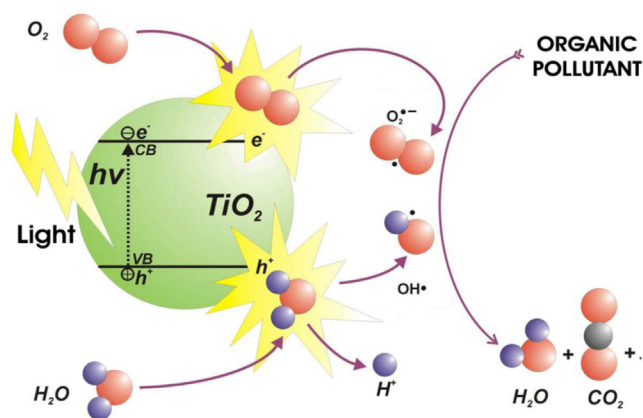


Fig. 11 Schematic representation of semiconductor excitation by band gap illumination leading to the creation of “electrons” in the conduction band and “holes” in the valence band [150].

ond transient absorption spectroscopy [164]. Nyquist plots obtained by the EIS measurement revealed the charge transfer resistance in solid-state interface layer and the charge transfer resistance at the contact interface between electrode and electrolyte solution [165]. The ESR studies confirmed the generation of the radical species including hydroxyl and superoxide radicals in the graphene based semiconducting photocatalysts [166]. Hu et al. has demonstrated the photocatalytic mechanism of graphene-titanate nanotubes (TNTs) photocatalyst, and proposed the electron transport model of the hybrid under visible-light illumination. The electron transport from graphene to TNTs is confirmed using scanning tunnelling microscope, electron paramagnetic resonance and photoluminescence spectra [167].

3.1. Photoelectrochemical H₂ evolution reaction (HER) for green H₂ fuel

Photoelectrochemical (PEC) water splitting is an effective method for the production of green H₂ using a sustainable resources like water, sunlight and specialized semiconducting materials-based photocatalyst [169]. The photoelectrocatalyst accelerates the process of water splitting into H₂ and O₂ using light as a source of energy [170]. Similar to

the solar cells which convert sunlight into electrical energy, photoelectrochemical cells (PEC) transform solar energy into solar fuel like green H₂. The semiconductor-based photocatalytic water splitting involves two conceptual options including a system consisting of two separate devices each for light harvesting and electrolyzation of water (PV-coupled electrolysis) [168]. Whereas, the other is an integrated system which combines both the components of light harvesting and catalytic water splitting interface in the same material (photoelectrochemistry) (Fig. 12a). Currently, photovoltaics are the most efficient solar energy transformation devices, however, their technical advancement is still low because the photo-absorbing material is in physical contact with the electrolyte, limiting the durability of the device. [171]. PEC water splitting offers great potential for the sustainable, green and low-cost H₂. It utilizes the naturally abundant precursors such as water and solar light. However, the photocatalyst capable of harvesting in the visible portion, with suitable bandgap and band edge positions and able to separate the carriers is the key for the commercialization of this technology.

In the quest of finding efficient and cost effective photocatalysts, scientists have explored a variety of different materials including semiconducting metal oxides, metal chalcogenides and organic semiconducting layered materials [172]. However, semiconducting graphene-based photocatalysts have been regarded as promising materials for the photoelectrochemical conversion of solar energy into green H₂ [173]. Particularly, graphene derivatives like graphene oxide, highly reduced graphene oxide consisting of a variety of oxygenated functional groups in combination with semiconducting inorganic nanoparticles exhibited great potential as photoelectrocatalyst for H₂ and O₂ evolution from water [174]. Especially, high electron mobility and surface area of graphene render it as an effective electron acceptor to improve the photoinduced charge transfer and restrict the reverse reaction by the separation of evolution sites of H₂ and O₂ and therefore, enhancing the H₂ production properties [70]. As an example, TiO₂-5 wt% graphene photocatalyst has exhibited two times more H₂ evolution (H₂: 4.5 μmol/h) properties when compared with the pristine TiO₂ under sunlight illumination. This enhancement is attributed to the reduction of electron-hole recombination due to the presence of graphene [175]. To reduce the electron-hole recombination, a low-defect reduced hydroxylated graphene (RGOH) was used as a carrier material to prepare TiO₂/RGOH [176]. The hybrid photocat-

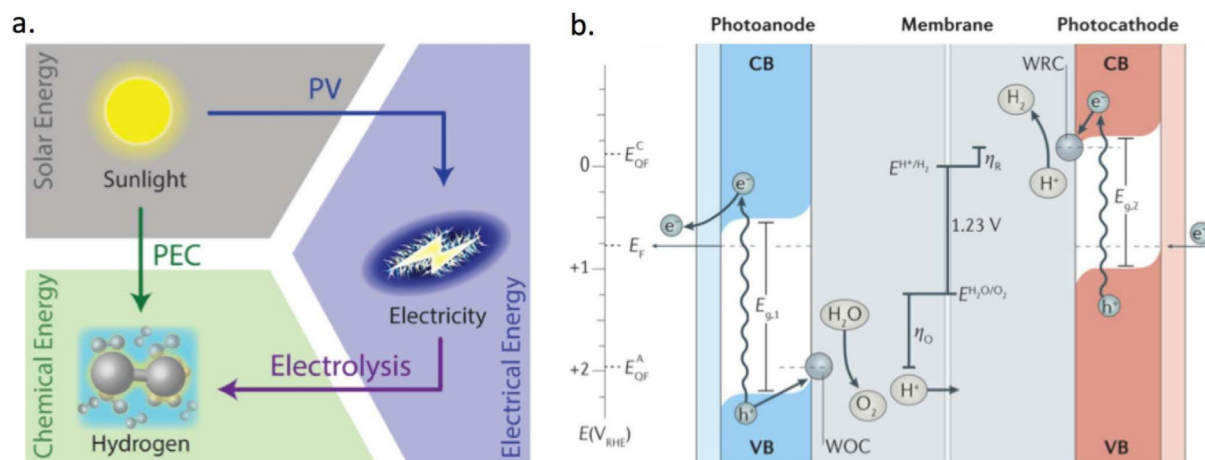


Fig. 12 Two conceptual options for the generation of solar hydrogen: PV-coupled electrolysis, and direct photoelectrochemical (PEC) water splitting. b) Working principle of a tandem PEC cell for water splitting using a photoanode with bandgap energy $E_{g,1}$, and a photocathode with $E_{g,2}$ (where $E_{g,1} > E_{g,2}$) [168].

alyst demonstrated high electrical conductivity, which enhanced the separation and migration efficiency of photogenerated electron-holes. Besides, the possible existence of Ti—O—C bond in the hybrid, facilitated the transfer of photogenerated electrons through this bond to the RGOH flakes and prevented rapid recombination of photogenerated electron-holes. In other study, for enhancing the light capturing properties, avoiding electron-hole recombination, and accelerating charge transfer carbon-doped TiO₂ was fabricated which is deposited onto HRG (C-TiO₂/HRG). The resulting nanocomposite exhibited enhanced photocatalytic activity and longevity [177]. The C-TiO₂/HRG exhibited a band gap of 2.2 ± 0.2 eV and crystallite sizes of 0.9–2 nm in diameter. Other results revealed that, under solar light irradiation C-TiO₂/HRG yielded incredibly high H₂ production rates of 1.50 ± 0.2 mmol g⁻¹ h⁻¹, which is greater than the pristine precursor without graphene and other semiconducting photocatalysts. To explore the electro-photocatalytic H₂ mechanism of HRG with doubly doped graphene-based catalyst, Wang et al. fabricated Pt/TiO₂/HRG photocatalysts [178]. The 2 wt% HRG doped HRG/Pt-TiO₂ hybrid photocatalyst demonstrated superior solar-driven H₂ production rate ($1075.68 \mu\text{mol h}^{-1} \text{g}^{-1}$), which was 81 times higher than bare TiO₂ and 5 times in comparison to the Pt/TiO₂ based photocatalyst. This study revealed that the presence of Ti—O—C bonds in the hybrid, shifted the valence band edge from + 2.2 eV to + 1.83 eV, while the photoelectrochemical tests indicated the enhanced electron density of hybrid which is almost double than TiO₂ (cf. Fig. 13).

Apart from TiO₂, other metal oxides in combination with graphene-based materials have been extensively utilized for PEC water splitting [179]. In this regard, ZnO and graphene-based materials nanocomposites have been prepared. Compare to TiO₂, ZnO possesses 10 to 100 times higher electron mobility and a lower rate of carrier recombination. In addition, it can be easily prepared in variety of morphologies using simple synthetic methods [180]. Hierarchical porous ZnO and ZnO/HRG nanocomposite based photoanodes were prepared by sol-gel method using triethylenetetramine as a stabilizer [181]. The resultant photocatalyst demonstrated enhanced current density (1.02 mA cm^{-2} at 1.5 V vs Ag/AgCl) in 1 wt% HRG,

up to 12 times higher compared to the bare ZnO (0.09 mA cm^{-2} at 1.5 V vs Ag/AgCl). This was due to the positive role HRG electron separation/transportation. Copper (I) oxide (Cu₂O) is another metal oxide which is cheap and abundantly available p-type semiconductor with a direct (forbidden) band gap of 2.17 eV and optical band gap of 2.62 eV. This semiconductor is highly desirable for PEC H₂O splitting under visible light ($\lambda \leq 600 \text{ nm}$) irradiation [182]. Hierarchical Cu₂O nanospheres with a pompon dahlia-like morphology and graphene hybrids were fabricated by electrostatic self-assembly [183]. Introduction of small amount of graphene enhanced the apparent quantum efficiency (AQE) at 475 nm of hierarchical Cu₂O for H₂ production. The values increased from 2.23 % to 3.35 %, giving an increase of evolution rate from $234 \mu\text{mol. g}^{-1} \text{h}^{-1}$ to $352 \mu\text{mol. g}^{-1} \text{h}^{-1}$ respectively. Similarly, doping of other metal oxides with graphene has shown excellent H₂ generation activity, such as, in the case of WO₃ nanostructures, the photocatalytic activity for the H₂ production was increased upon increasing the doping contents of graphene upto 7 wt%. [184](Tahir et al., 2018). In another study, HRG mixed with vanadium oxide (V₂O₅/HRG) photocatalyst demonstrated the enhanced PEC H₂O splitting properties [185]. The photocatalyst exhibited reduced bandgap, which increased the visible light absorption capacity and reduced recombination rate of photogenerated charge carriers in comparison to pristine V₂O₅. This resulted in ~3-fold enrichment in the photocatalytic activity, while the PEC performance enhanced ~3.5 times higher compared to V₂O₅ photoanode. Other oxides like BiVO₄, BiFeO₃, were also applied. For instance, the preparation of BiVO₄-HRG nanocomposite using visible-light-assisted approach as demonstrated by Soltani et al. exhibited the highest photocurrent density ($554.4 \mu\text{A cm}^{-2}$ at 1.2 V vs Ag/AgCl), compared to pristine BiVO₄ ($111.7 \mu\text{A cm}^{-2}$) in PEC H₂O splitting experiments [186]. The photocatalyst also exhibited the high charge carrier density, with an extended lifetime and improved electrical conductivity. In another study, Bi_{1-x}Sm_xFeO₃ (BSFO) nanoparticles were deposited onto HRG using two-step ultrasonication method [187]. The BSFO-HRG nanocomposite based photoanode showed high photocurrent density and solar to hydrogen conversion effi-

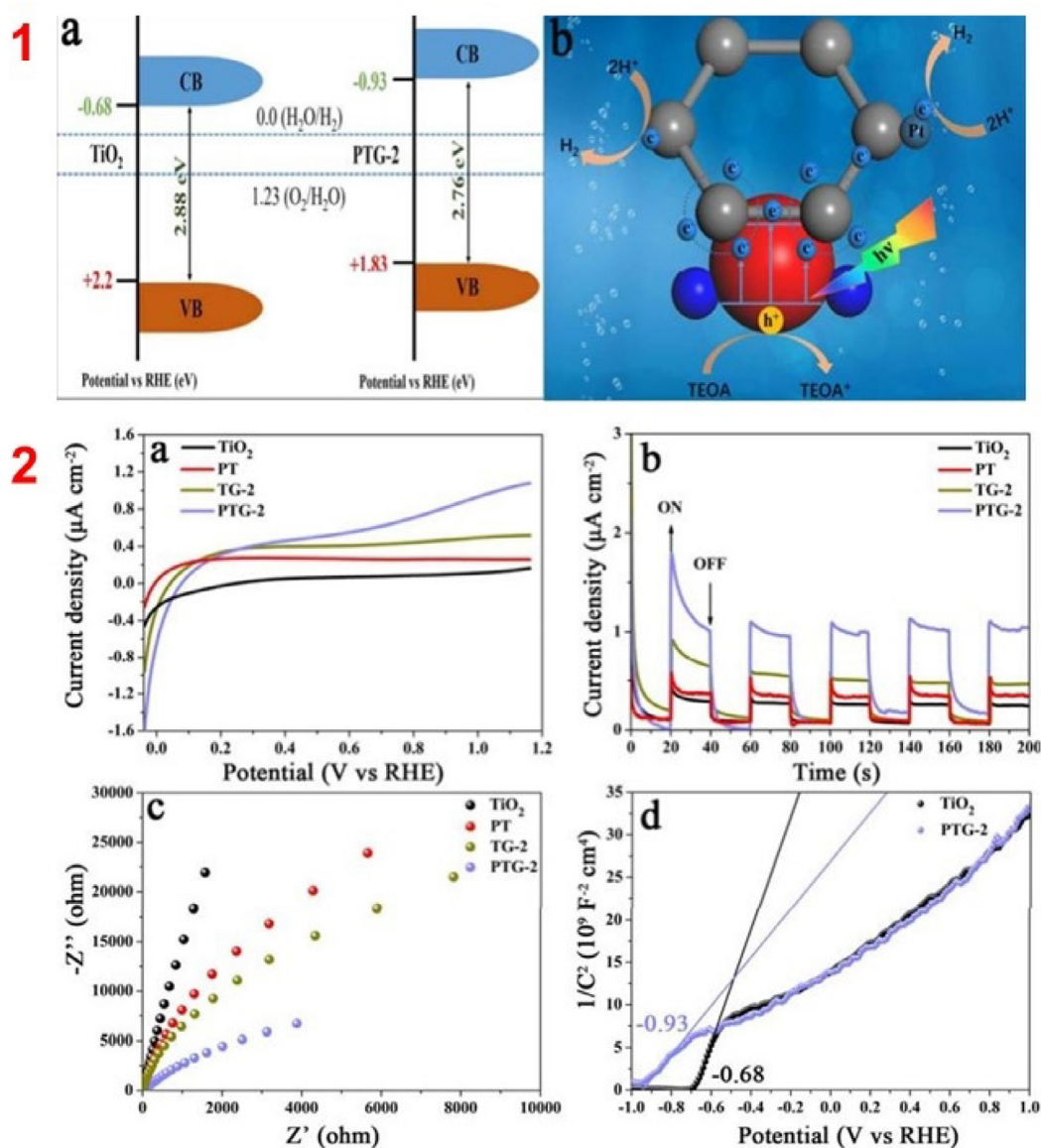


Fig. 13 (1a) Calculated bandgap diagrams. 1b Proposed mechanism for photocatalytic H₂ production on PTG. PEC performances and characterizations of different samples: (2a) J-V curves. (2b) Transient photocurrent response curves. (2c) Electrochemical impedance spectra. (2d) Mott-Schottky plots. [178].

ciency (2.40 mA/cm² at 0.5 V vs saturated calomel electrode) and 2.45 % efficiency.

CdS is a narrow bandgap (~2.4 eV) semiconducting material which is capable of absorbing light in the visible portion of solar spectrum and the reduction and oxidation potential of H₂O remain in the band gap limit of CdS [188]. However, fast recombination rate of electron-hole pairs and aggregation of nanoparticles inhibits the photocatalytic activity of CdS [189]. To address these problems, Peng et al. fabricated GO-CdS-Pt nanocomposites with varying amounts of Pt using a combination of the reduction process and the two-phase method [190]. The hybrid photocatalysts has successfully suppressed the recombination of electron-hole pairs and extended the lifetime of charge carriers by an effective charge transfer route. Besides, graphene helped in inhibiting the aggregation of nanoparticles leading to the high specific surface area of

the material which was easy to separate using centrifugation. The nanocomposite demonstrated excellent H₂ evolution rate of 123 mL h⁻¹ g⁻¹ with strong photostability. These values are 2.5 times higher than that of GO-CdS and 10.3 times higher than the pristine CdS. In another study, the H₂O splitting efficiency of the HRG-CdS nanocomposite prepared through a chemical reduction method was ~ 3 times higher than that of pure CdS NPs [191]. Both computational and experimental studies of other sulphides like WS₂, MoS₂, ZnS, SnS₂ have recently shown their effective role in catalyzing the PEC based clean H₂ generation with a relatively good yield [192,193]. The study of the optical properties of WS₂-HRG hybrid has revealed high optical absorption (98 %) and lower band gap (1.75 eV), with good band-edge alignment in PEC experiments [194]. The photocatalyst exhibited good photocurrent density (95 μA/cm² at 1.23 V bias), and 3.3 times higher

performance compared to pristine WS_2 with higher charge transfer ability. HRG-based ZnS heterojunction photo-anode enhanced the PEC performance by improving optical properties and charge separation ability of the composite.

Furthermore, graphene-based ternary nanocomposites have also been prepared and received decent attention [196]. He et al. have prepared HRG-modified WO_3/TiO_2 heterojunction (S-scheme heterojunction) nanocomposite based photocatalyst in a single-step using hydrothermal method [195]. TiO_2 and WO_3 nanoparticles attached closely to HRG in the ternary hybrid forming a stable S-scheme heterojunction (cf. Fig. 14). In this case, HRG not only offered plentiful adsorption and catalytically active sites but also facilitated electron separation and transfer from the conduction band of TiO_2 by creating a Schottky junction between TiO_2 and HRG. Due to this, the ternary $\text{WO}_3/\text{TiO}_2/\text{HRG}$ nanocomposite exhibited a dramatically enhanced H_2 evolution rate of $245.8 \mu\text{mol g}^{-1}\text{h}^{-1}$, which was approximately 3.5-fold higher than that of pure TiO_2 . Bai et al. reported the synthesis of $\text{BiVO}_4/\text{NiO}/\text{HRG}$ photoanode using electrodeposition, solution immersion and spin coating methods [197]. In comparison with BiVO_4 , the photo-current density of the ternary photoanode reached $1.52 \text{ mA}/\text{cm}^2$ at 1.23 V vs RHE, which is 2.41 and 1.39 times higher than that of pure BiVO_4 and binary BiVO_4/NiO photoanode, respectively. Very recently, $\text{VS}_4\text{-MoS}_2\text{-rGO}$

heterostructure was fabricated and explored for the PEC based H_2O splitting. In this ternary composite, MoS_2 was applied to inhibit charge recombination and HRG as a protective layer to improve the stability of the material [198]. The resultant hybrid exhibited 4.5 times higher catalytic activity and stability than bare constituent materials.

In short, it has been established that graphene derivatives including GO, HRG, pristine graphene possesses several extraordinary features such as, high surface area and π conjugated basal plane for high electron mobility and therefore, have been regularly applied as electron sinks for semiconductors based photocatalysts to facilitate exciton separation and later transportation and/or storage of electrons for H_2 for water splitting. Besides, the incorporation of inorganic material on the surface of graphene forms a Schottky barrier, which further enhance the clean H_2 production. So far, extraordinary success has been achieved in designing and creating highly efficient graphene/inorganic nanoparticles-based PEC systems which can effectively split water to generate clean H_2 using sunlight. However, there are still several concerns which need to be addressed to achieve the full potential of these materials for the generating green H_2 fuel. For instance, there is little understanding available on the interfacial contact and bonding between graphene and the semiconductors in the hybrid materials, which still require extensive experimental and theoretical

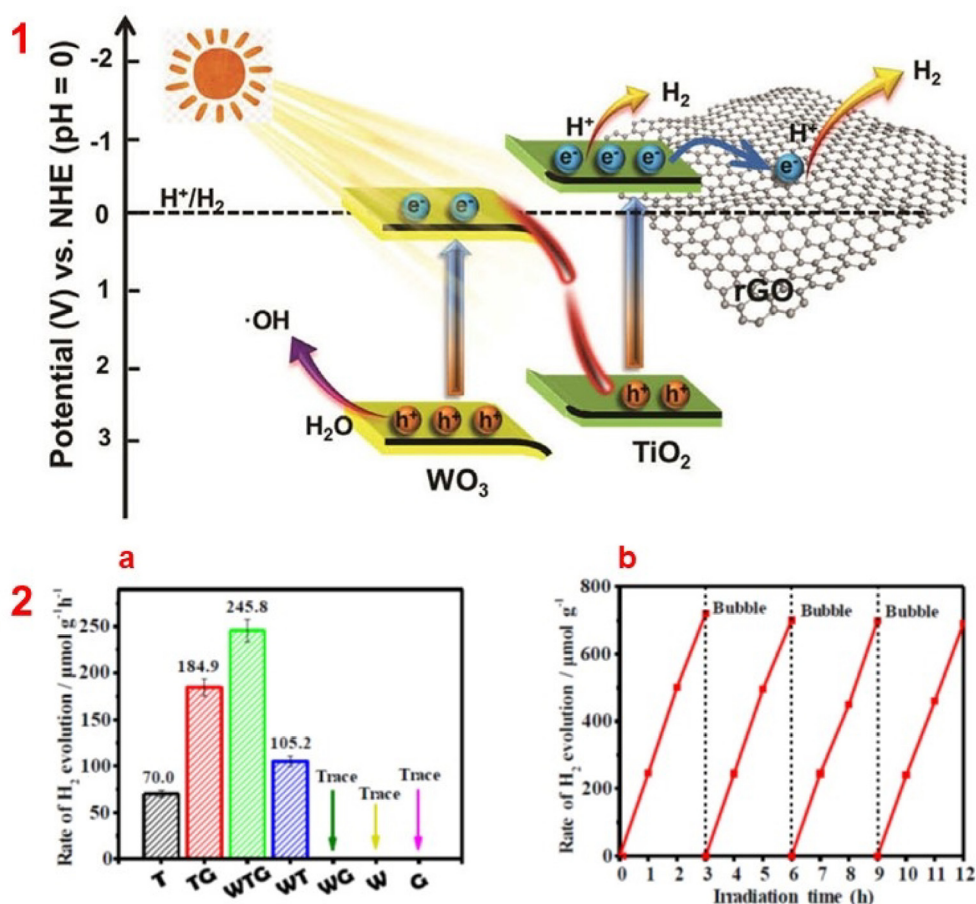


Fig. 14 1) Schematic representation of the S-scheme heterojunction-based charge transfer mechanism in $\text{WO}_3/\text{TiO}_2/\text{HRG}$ hybrid. 2) (a) photocatalytic properties of the bare TiO_2 (T), tungsten oxide (WO_3), HRG (G), $\text{WO}_3\text{-TiO}_2$ (WT), $\text{WO}_3\text{-HRG}$ (WG), $\text{TiO}_2\text{-HRG}$ (TG) and $\text{WO}_3/\text{TiO}_2/\text{HRG}$ (WTG) (b) the stability of the $\text{WO}_3/\text{TiO}_2/\text{rGO}$ composite [195].

knowledge of the electronic structure of the resulting materials. The synthesis of graphene needs to be further enhanced to obtain high-quality graphene with precise size, number of sheets and functionality which can further enhance the charge transport mechanism of the graphene-based photocatalysts. Furthermore, creative designing of the multicomponent graphene-based photocatalysts is required to achieve efficient charge transport in the composite matrix and infuse further charges for the facilitating the reaction at the H₂O-composite interface.

3.2. Photocatalytic degradation of pollutants for environmental remediation

The quality of aquatic environment heavily deteriorates due to the release of sewage water, heavy metal ions, dangerous organic and inorganic pollutants, most of them are non-degradable and highly resistant in nature [199]. Organic pollutants include phenolics, oil bacterial and so on., whereas inorganic contaminants involve metal salts, and heavy metal ions., which remain suspended in water for a very long time either in dissolve or colloidal form [200]. Among these contaminants, industrial effluent based phenolic compounds are the most dangerous materials due to their high toxicity [201]. Conventional water-treatment methods like filtration, sedimentation (physical methods), chlorination, ozonation (chemical methods) are mostly incompetent in removing hazardous pollutants [202]. On the other hand, chemical oxidation processes which are capable of completely mineralizing the contaminants to carbon dioxide, water and inorganic ions. [203]. However, they often require harmful chemicals such as chlorine, hypochlorite, H₂O₂, chloramines, chlorine dioxide, which possibly lead to the formation of several carcinogenic by-products [204]. On the contrary, heterogeneous photocatalysis is a suitable alternative to the conventional treatment processes for the advancement of wastewater treatment technology due to its capability of utilizing sustainable resources like sunlight for water treatment [205]. Photocatalysis require efficient heterogeneous catalysts which are effective in accelerating the rate of reaction by decreasing the activation energy [206]. Ideally, for this purpose, a photocatalyst with high crystallinity, large surface area, low-cost, non-toxic, and should be easy to handle [207] is preferable. In this regard, graphene based photocatalysts have received tremendous recognition in the field of photocatalysis due to high specific surface area, high mechanical strength, good thermal and electrical properties.

These photocatalyst have been extensively used in advance oxidation processes (AOPs), which are highly effective in mineralizing persistent organic contaminants including pesticides, surfactants, phenolic wastes, and hazardous organic dyes [208,209]. These methods are capable of utilizing sunlight for direct disinfection and detoxification of contaminated water. During this process, UV-visible or sunlight generate electron-hole pairs facilitating the formation of reactive oxygen species (ROSS) which are highly reactive and effectively destroy organic and inorganic pollutants. [210]. Particularly, in the heterogeneous AOPs, which are typically performed in aqueous phase, the oxidation of H₂O molecule occurs on the surface of photocatalyst to release OH[•] at the expense of the reduction of O₂ which ultimately generate superoxide radical (O₂^{•-}) [211,212]. A variety of graphene/inorganic

nanoparticles-based nanocomposites have been applied as photocatalysts for the photocatalytic decontamination of wastewater [213]. Since, in most cases, bare nanomaterials-based photocatalyst demonstrate low absorption of light, high-recombination rate, deactivation and agglomeration, which can be effectively prevented by the inclusion of graphene in the nanomaterials-based hybrids [214].

Graphene has been utilized in various capacities to enhance the photocatalytic behavior of active photocatalysts such as, attachment of graphene with the inorganic semiconductors, graphene doping, surface functionalization and fabricating multi-junction nanohybrids. [215,216]. In graphene-based inorganic semiconductors based photocatalysts, the large-surface area of graphene and smaller size of nanoparticles effectively facilitate charge carrier and charge transportation due to the close contact between the components [217]. These constituents also extend the absorption capacity which ultimately enhance the sunlight harvesting. In this type of nanocomposites, size of the nanoparticles, number of graphene layers have significant effect on the resultant photocatalytic properties of materials. This is suggested by the finding of a study by Zhang et al. who have fabricated HRG/ZnO with varied particles size of ZnO using a facile solvothermal method [218]. ZnO with smaller particles size (20–100 nm) exhibited superior photocatalytic properties in the degradation of dyes and reduction of Cr (VI) when compared with the larger size ZnO nanoparticles (50–500 nm) in the hybrid. This was attributed to the small size of nanoparticles which enhanced the interfacial contact between the two precursors. Similarly, shape of nanoparticles in the composites also influence the photo-activity of the catalysts. This is confirmed by Beura et al. when they prepared different morphologies of ZnO nanoparticles in HRG-ZnO nanocomposites [219]. This was achieved by varying the concentration of the precursor in chemical method in which the shape of ZnO was changed from sphere to rod upon increasing ZnO concentration. Spherical shaped ZnO nanoparticles demonstrated high surface area and superior catalytic activity (98.6 %) than the rod-shaped particles (97.1 %) in the degradation of methyl orange. Similarly, ZnO with different shapes and concentration were deposited onto HRG (HRG-ZnO) in a low-temperature chemical etching route to enhance the photocatalytic properties of the resulting hybrids [220]. Several other studies have also pointed towards the importance of the surface exposed facets of the nanoparticles in delivering efficient photocatalytic properties. As an example, in the case of TiO₂, the formation of dominant [221] facets are technologically and scientifically important for photocatalytic applications due to their high surface energy [222]. The tuning of the photocatalytic selectivity of TiO₂ can also be achieve by varying its crystallographic properties such as the percentage of exposed facet [221]. Especially in the presence of graphene, facets controlled TiO₂ based photocatalysts have exhibited enhanced performance or efficient utilization of visible light in photocatalytic applications. For instance, Liu et al. reported considerable enhancement in the photocatalytic degradation of methylene blue (MB) and methyl orange (MO) under both UV and visible light irradiation in the case of chemically bonded HRG-TiO₂ hybrid photocatalysts which consist of exposed {001} facets of TiO₂ nanoparticles over bare P25 [223]. Very recently, the combination of faceted crystal engineering and 3D-printing technology was used for the preparation of the organic-inorganic 3D-

printed visible-light photocatalyst prototypes [224]. For this purpose, two facet crystal nano-architectonics were fabricated by the *in-situ* synthesis of Ag_3PO_4 nanoarchitectures with tuneable-amorphous and faceted-shapes upon 3D-printed graphene/poly(lactic acid) (G/PLA) nanocomposite scaffolds through a green wet-chemistry approach. The as-prepared nanocomposite demonstrated enhanced photocatalytic properties towards the photodegradation of Rhodamine B.

Apart from prominently applied TiO_2 and ZnO , graphene has been combined with various other semiconducting inorganic nanomaterials to obtain efficient binary graphene-based photocatalyst for the degradation of pollutants [226]. These materials include Cu_2O , WO_3 , Mn_2O , Mn_3O_4 , Ag_3PO_4 , ZnFe_2O_4 , ZnWO_4 , $\text{W}_{18}\text{O}_{49}$, SnO_2 , CuFe_2O_4 , BaCrO_4 , SnWO_4 , and many more [227]. In a recent study, Cu_2O nanoparticles were doped with varying contents of graphene (1–4 wt%) using a precipitation method. The characterization of samples revealed the formation of cabbage like morphology of graphene based Cu_2O nanocomposite [225]. In this case, 2 wt% graphene incorporated Cu_2O sample exhibited superior photo-activity towards the degradation of organic pollutants (97.9 % and 96.1 %) for MB and MO after 160 and 220 min, respectively (cf. Fig. 15). In addition, its catalytic performance over visible region (red shift) was also enhanced to an appreciable extent, when compared with that of other samples. The HRG- WO_3 nanocomposites obtained using hydrothermal route demonstrated high photo-catalytic activity towards the degradation of MB which is ~ 6.5 times compared

to pristine WO_3 [228]. The 1D-2D hybrid prepared by loading MnO_2 nanorods over HRG nanosheets (HRG- MnO_2) by hydrothermal process demonstrated enhanced photoactivity towards the removal of coloured dye (neutral red) and a colourless pollutant (ciprofloxacin) from water [229]. The enhanced activity is attributed to the large surface area, close contact of 1D-2D components with abundant reaction sites. Similarly, hausmannite Mn_3O_4 -HRG nanocomposite obtained by solvothermal process showed decent photocatalytic activity in the degradation of MB dye under sunlight [230]. Solvothermal method was also used to prepare a series of octahedral ZnFe_2O_4 /HRG nanocomposites which demonstrated both high adsorption and good visible-light-responsive photocatalyst activities [231]. The hybrid material showed enhanced photocatalytic degradation properties for cationic dyes (MB and RhB) compared to those for the anionic dye (MO). Besides, The hybrid photocatalyst successfully degraded H_2O_2 in the visible-light photocatalytic process to form hydroxyl radicals ($\bullet\text{OH}$), which are mainly responsible for the photodegradation of the organic contaminants. ZnWO_4 nanoparticles were deposited onto the surface of HRG to obtained ZnWO_4 -HRG hybrids which degraded hazardous MB in a neutral medium and showed superior photoactivity than its pristine counterpart [232].

In addition to the aforementioned graphene-based photocatalytic binary nanocomposites, multi-component hybrid materials have also found considerable attention of scientists. The multi-junction nanocomposites offer improved charge car-

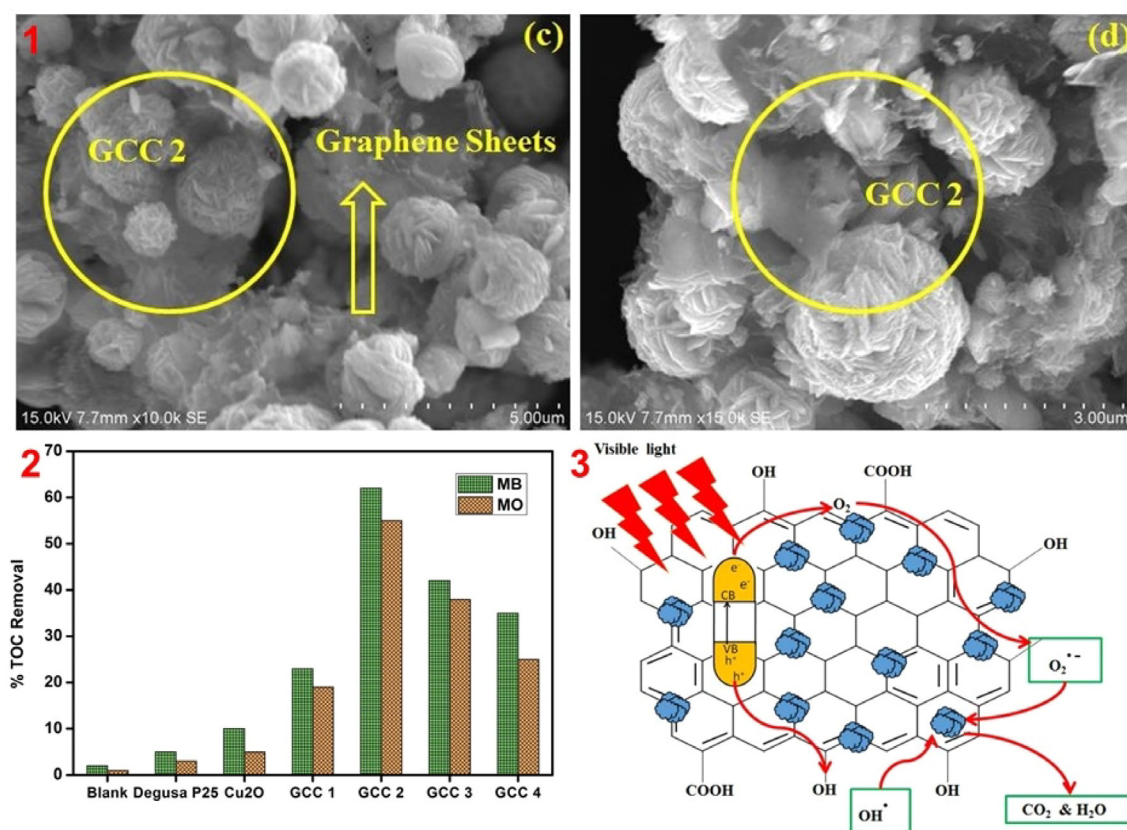


Fig. 15 1c and d, are the SEM images Cu_2O -HRG composites, 2) TOC removal profile for MB and MO dyes, and 3) photocatalytic mechanism of Cu_2O -HRG composites.[225].

rier separation and a fast electron transfer system compared to the pristine semiconductor materials. For instance, a ternary nanocomposites consisting of TiO_2 , silver and graphene has confirmed the benefits of multi-junction nanocomposites [233]. The hybrid was used as photocatalysts for amaranth azo dye degradation, under UV and natural light exposure. The best result for amaranth dye degradation was obtained with the HRG/ TiO_2 -Ag catalyst reached upto 99.9 %. In another study, Dutta et al. have fabricated HRG-based ternary nanocomposites, using glutathione (GSH) as both reducing agent for GO and sulfur donor for CdS synthesis under modified hydrothermal conditions [234]. Among two different colour CdS, the yellow coloured ternary CdS- TiO_2 -HRG has showed maximum efficiency compared to the corresponding red ternary CdS- TiO_2 -HRG or binary photocatalysts for dye degradation under visible light irradiation. The high activity of the composite was attributed to the presence of TiO_2 at the interface of HRG and CdS forming a barrier which prevent the direct contact between HRG and CdS. Due to this, the CdS bandgap is slightly extended (2.15 eV vs 2.04 eV for CdS-HRG), unexpectedly, this has delivered better photocatalytic property simply by diminishing the possibility of the charge-recombination process. Jilani et al. have demonstrated the fabrication of ternary hybrid of Ag nanoparticles with HRG and ZnO nanorods ($\text{Ag-HRG@ZnO}_{\text{NR}}$) using an *in-situ* homogeneous coating of Ag nanoparticles onto pre-fabricated thermally reduced HRG encapsulated ZnO nanorods [235]. The hybrid degraded 2-chlorophenol under sunlight irradiation with high yield. The light harvesting ability of the composite was enhanced due to the customized reduction of bandgap, and the presence of Schottky barrier at the metal-semiconductor interface which possibly promoted charge separation. More recently, ZnSnO_3 /HRG/ MoS_2 hybrid was synthesized and its photocatalytic activity was explored for the mixed dyes degradation under UV-visible light irradiation [236]. The hybrid demonstrated a maximum removal rate of 0.0131 min^{-1} for Rh B degradation, and 0.0153 min^{-1} for MB dye degradation and efficiency was 78 % (Rh B) and 86 % (MB), respectively in 100 min, which is relatively higher than other samples. Apart from ternary, graphene-based quaternary photocatalysts have also demonstrated enhanced photocatalytic activity [237]. Indeed, in some cases, these four-component hybrids have shown better performance than their binary and ternary counterparts. This was confirmed in a study by Divya et al. in which they have prepared TiO_2 / ZnO /HRG/Ag hybrid which showed improved catalytic activity compared to TiO_2 / ZnO /HRG and TiO_2 / ZnO for the degradation of rhodamine B under visible light [238].

The photocatalytic efficiency of a graphene based photocatalysts is mainly dependent on the band structure, which is tailored by various strategies to enhance the stability of the material and to achieve maximum light absorption [239]. One of the strategies for this is the doping of the surface of the graphene with a either a metallic ion or a non-metallic atom such as nitrogen (N), sulfur (S), phosphorous (P). This introduces new bands between the VB and CB and also enhance the surface interactions [240,241]. Chandel et al. reported the preparation of visible-light-driven nitrogen-doped graphene (N-HRG) supported magnetic $\text{ZnO}/\text{ZnFe}_2\text{O}_4$ ($\text{ZnO}/\text{ZF}/\text{N-HRG}$) and $\text{ZnO}/\text{CoFe}_2\text{O}_4$ ($\text{ZnO}/\text{CF}/\text{N-HRG}$) nanocomposites [242]. The doped hybrid material has shown enhanced photocatalytic activity for the degradation of MO

and malachite green (MG) dyes in aqueous solution. The high surface area of the composite enhanced the adsorptive removal of MO and MG dyes. The photodegradation performance of heterojunction photocatalysts was superior to bare photocatalyst after 140 min under visible-light irradiation. In another study, sulfur doped graphene was used to fabricate S-HRG- Ag_3PO_4 composite which showed high photoactivity for a variety of textile dyes and fungicide under solar irradiation [243]. Rawal et al. have used both N and S for co-doping of graphene quantum dots which was further utilized for the formation of heterojunction with TiO_2 [244]. Customized type-II band gap (E_g) alignment was formed with narrowed E_g value that enhanced the photogenerated electron transfer due to π -conjugation. The hybrid showed superior MB degradation up to 99.78 % with 2 to -3 times elevated rate constants as compared to pristine TiO_2 based photocatalyst. Boron (B) was also used for the purpose of preparing doped graphene based photocatalysts, such as the preparation of B-doped HRG (B-HRG) supported by bismuth ferrite (BiFeO_3) hybrid which enhanced the photophysical properties of the resulting materials including the charge carrier separation due to the density state value near to the Fermi energy level in the system [245]. The superior performance of the developed nanocomposite was explored for the degradation tetracycline (TC), and Rhodamine B (RhB) which showed TC (86.7 %) and RhB (99.4 %) degradation efficiency.

All these studies clearly evince towards the enhancement of desirable properties of photocatalytic materials by the inclusion of graphene. The graphene based photocatalysts have demonstrated enhanced absorptivity of pollutants, maximized light harvesting properties, accelerated charge carrier migration, reduced the rate of recombination, and increased photo-efficiency of the resulting materials. As an effective support material graphene inhibited the aggregation of nanomaterials on the surface, thereby enhanced the surface area, inhibited leaching and offered excellent electron scavenging and photosensitizing properties which proved to be crucial for the resulting photocatalysts. Particularly, the combination of graphene with semiconducting metal oxides to obtain multi-components hybrids have demonstrated great success in the enhancement of the photocatalytic properties towards the degradation of pollutants. Therefore, besides other environmental remediation processes, graphene-based nanocomposites have also clearly emerged as promising materials as photocatalysts for water purification. Still, several factors are needed to be addressed to exploit the full potential of the graphene-based materials in photocatalytic applications. Particularly, cost-effectiveness, large-scale preparation of high-quality nanocomposite, complex graphene-based materials with high photostability and efficiency.

3.3. Photocatalytic applications in organic synthesis

The use of visible light to perform organic reactions has progressed vastly for last two decades [246]. This has become possible due to several reasons, including an urge to maximize energy efficiency using visible light of solar spectrum as reagent, technological advancement in the field of light-emitting diodes which are capable of offering high intensity visible light in narrow wavelength, and availability of cost effective light sources for photocatalysis [247]. Moreover, the

development of flow chemistry, and the widescale applications of transparent flow reactors which helped to resolve several challenges in photochemical reactions including large-scale synthesis and reproducibility [248,249]. Conventional photochemical reactions typically apply UV light to directly excite the organic substances and the technique has been in use for more than 100 years [250]. However, this was not popular in the mainstream chemical reactions and always considered as an advance technique which is difficult to perform on regular basis [251]. With the advent of effective photo-redox catalysts, sensitizers, efficient visible light equipments, the photochemical field started to develop rapidly [252,253]. The photochemical reactions are mostly performed in a similar manner in which convention thermal reactions are carried out but with an exception of light source [254].

Due to the lower energy of visible light which is used as a primary source of light, the photochemical reactions demonstrate enhanced selectivity, more predictability and efficient controllability [255,256]. In the presence of light, these reactions typically involve the formation of radicals or highly-reactive radical ion intermediates, which has offered new dimension to the organic synthesis. Hitherto, diverse chemical reactions have been carried out using visible light-based photo-redox catalysis including oxidations, reductions, C–C bond formations, carbon and hetero atom bond formation, and cycloaddition reactions. [257–259]. Usually, a variety of photo-redox catalysts are applied as photochemical reaction including redox-active metal complexes like ruthenium–tris(bipyridine) or iridium–tris(phenylpyridine) salts, organic dyes such as, eosin or rhodamine-6G, (homogeneous catalysts) and different types of semiconducting heterogeneous catalyst like inorganic metal oxides, carbonaceous compounds like graphene and carbon nitride. [260–262].

Among various photo-redox catalysts, graphene/inorganic nanoparticles based nanocomposites have demonstrated great potential in the field of photocatalysis with improved photocatalytic activity [263]. However, a large focus of scientific community was on the graphene-based non-selective photocatalytic reactions such as pollutant degradation, water splitting, and relatively less attention has been given to the selective photocatalytic processes such as organic transformations.[264]. But with the advent of advance organocatalysts and semiconductors based photocatalysts including graphene/inorganic nanoparticles based nanocomposites, selective heterogeneous photocatalysis has progressed rapidly [265]. Particularly, graphene based photocatalyst have been prominently selective photocatalytic reduction of CO₂ and nitroaromatic compounds, oxidation of alcohols, epoxidation of alkenes, hydroxylation of phenol, and selective oxidation of tertiary amines. [83]. The selective reduction of CO₂ will be dealt separately in the following section, however, in the current section recent literature about the selective organic transformations will be highlighted.

The photocatalytic reduction of nitroaromatic compounds produces industrially important amino compounds which are extensively used in the preparation of pharmaceuticals and dyes[266]. Graphene/inorganic nanoparticles based nanocomposites have proven to be effective in the photo-catalytical transformation of these compounds [267]. For example, Liu et al. demonstrated the preparation of HRG–CdS nanocomposites using electrostatic self-assembly method, and subsequent hydrothermal reduction process [268]. In the presence

of ammonium formate as holes scavenger, the nanocomposite showed enhanced photocatalytic activity under visible light irradiation as compared to the pristine CdS. The hybrid system was used as photocatalysts for the selective reduction of a variety of nitroaromatic substances in water. Nickel oxide nanoparticles were deposited onto HRG through simultaneous reduction of GO and nickel precursor to obtain HRG–NiO hybrid [269]. The hybrid showed efficient visible light active photocatalytic activity for the reduction of nitroaromatic derivatives to their corresponding amino compounds. Hydrazine monohydrate provided necessary protons and electrons for the targeted reaction. HRG/copper oxide with variable oxidation number based ternary photocatalyst (HRG/Cu₂O–CuO) was developed for the reduction of nitrobenzene in the presence of hydrazine monohydrate under visible light irradiation [270]. Another multi-component graphene-based hybrid photocatalyst of copper oxide/HRG/titanium dioxide (CuO/HRG/TiO₂) was synthesized and used for the carbon–nitrogen bond formation under visible light irradiation [271]. The efficiency of hybrid photocatalysts was investigated in a pseudo 4-component reaction of salicylaldehyde, malononitrile and secondary amines for the preparation of benzopyranopyrimidines in high yields (75–95 %) under visible light irradiation (60–120 min) in ethanol as the solvent at room temperature.

Selective oxidation of alcohols to carbonyls belongs to an important class of reactions due to the significance of carbonyl compounds like ketones and aldehydes in several industries [272,273]. These types of selective oxidations are conventionally performed under harsh reaction conditions involving strong oxidants, high temperature and pressure [274]. On the other hand, heterogeneous photocatalysts based selective oxidations require mild reaction conditions and benign oxidants like O₂ and H₂O₂ and thus are considered eco-friendly and suitable alternatives to the classical oxidation reactions [275]. For instance, Zhang et al. prepared ternary CdS–HRG–TiO₂ nanocomposites using an *in-situ* strategy on the flatland of GO [276]. In this composite, the presence of TiO₂ helped to maintain the morphology and porosity of the samples, and also facilitated in the tuning of energy band and electron transfer properties, which ultimately prolonged the lifetime of photo-generated charge carriers (cf. Fig. 16a). These nanocomposites were used as photocatalyst for the selective oxidation of alcohols to their corresponding aldehydes. The hybrid nanophotocatalyst demonstrated enhanced photocatalytic activity when compared to its parent binary HRG–CdS composite. The electron transfer in this hybrid occurred through two different routes simultaneously to HRG and TiO₂. This ultimately led to the promotion of interfacial charge transfer and prolonging the lifetime of photo-generated electron hole-pairs (cf. Fig. 16b). In another study, the same group (Zhang and coworkers) have reported the assembly of nanosized ZnS particles onto the 2D platform of GO in two-step wet chemistry process, during which the preparation of HRG and the intimate interfacial contact between ZnS nanoparticles and the HRG sheet were achieved simultaneously [277]. The nanocomposite exhibited visible light photoactivity toward aerobic selective oxidation of alcohols and epoxidation of alkenes under ambient conditions. A novel photoactive porous material of HRG/FeMIL-101 based on FeMIL-101 MOFs was prepared using a hydrothermal method and applied as photocatalyst for the selective oxidation of benzyl alcohol under visible light irradiation [278]. The Fe and MIL-101

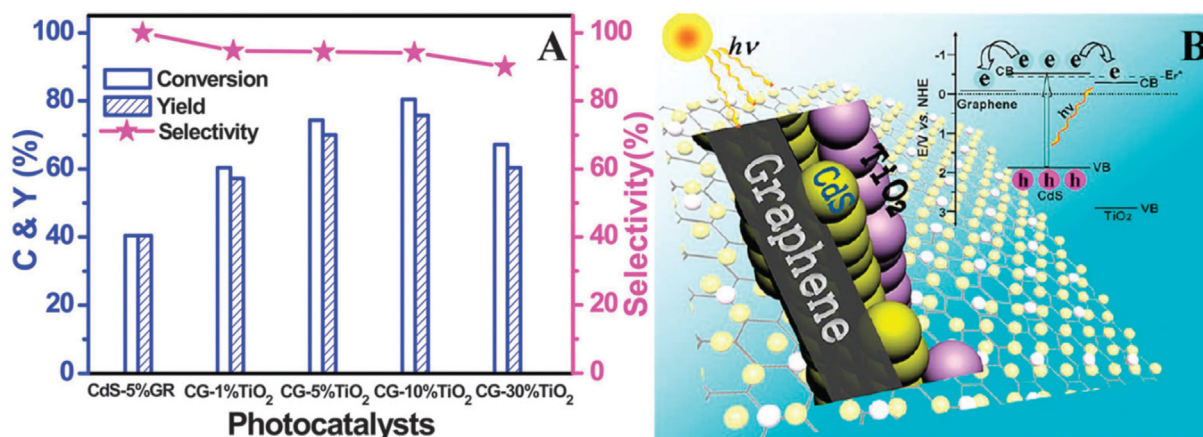


Fig. 16 (A) Photocatalytic selective oxidation of benzyl alcohol to benzaldehyde under the visible-light irradiation over CdS–HRG–TiO₂ and CdS–HRG hybrids. B) illustration of the proposed reaction mechanism for selective oxidation of alcohols over the ternary hybrid; the upper right inset demonstrates the energy band of a ternary hybrid [276].

caused valence fluctuations of $\text{Fe}^{3+}/\text{Fe}^{2+}$ which enhanced the visible-light absorption and maximized the separation efficiency of photogenerated charges.

Apart from the oxidation of alcohols and epoxidation of alkenes, the graphene based photocatalysts were also applied for the selective oxidation of aromatic compounds (photohydroxylation). For instance, the photocatalytic benzene hydroxylation to phenol in the presence of H_2O_2 was performed by applying a variety of graphene- Cu_2O based photocatalysts [279]. The selectivity of phenol was enhanced by tailoring the surface of the Cu_2O nanoparticles on defective graphene using long-chain alkanethiols. In another study, Borah et al. developed VPO@GO hybrid photocatalyst by exploiting the strong interactions between GO and exfoliated $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$. V^{4+} -rich VPO@GO selectively oxidized benzene to phenol at low temperature (60 °C) using H_2O_2 as the oxidant [280]. The reaction afforded 100 % selectivity with a benzene conversion of ~33 % up to 5 catalytic cycles. Cai et al. has carried out selective single-step benzene hydroxylation to obtain phenol in an eco-friendly process. The reaction was performed in water using graphene as catalysts under visible light [281]. The photocatalytic efficiency for benzene hydroxylation was considerably enhanced (greater than 3 times), through engineering the surface wettability of HRG from hydrophilic (with a contact angle of 52°) to hydrophobic (with a contact angle of 127°). Further, HRG– Ag_3VO_4 hybrids were used as photocatalysts for the transformation of phenol to catechol and hydroquinone under visible light irradiation, without using any hydroxylating agents like H_2O_2 [282]. Particularly, the composite photocatalyst demonstrated enhanced selectivity towards catechol under visible light irradiation.

Thus, the combination of graphene with other semiconducting materials have demonstrated enhanced photocatalytic efficiency and selective redox properties due to the extraordinary physicochemical properties of the hybrid materials including, high light absorption capacity, prolonged light absorption range, enhanced charge carrier separation and transport efficiency. Additionally, as a photoelectron reservoir, graphene functioned as an organic dye-like macromolecular photosensitizer. GO can also act as a co-catalyst and a photocatalyst for selective organic transformations. The highlighted

literature clearly demonstrates the availability of wide scope of opportunity in the graphene based selective photocatalytic organic transformations. However, so far, only few semiconducting materials were combined with graphene to obtain photocatalysts for organic transformations, which can be further extended to explore materials to enhance the scope of graphene-based heterogeneous photocatalysts in organic transformations. Moreover, the list of organic reactions being explored using graphene based photocatalysts is not very long, and still there is lot of opportunity to investigate more conventional and complex organic reactions.

3.4. Photocatalytic reduction of CO_2

The environmental remediation process that involves the conversion of CO_2 to solar fuels or useful chemicals is another very important area of research [283]. CO_2 is an abundant greenhouse gas, which accounts for almost three-quarters of global greenhouse gas emissions, thus reduction of CO_2 has great potential in alleviating the issues of global warming and environmental pollution [284]. In this regard, the effective transformation of CO_2 to valuable fuels or chemicals by the efficient utilization of sunlight through photocatalytic process, is one of the attractive approaches which has received tremendous recognition among scientific community [285,286]. Photocatalytic reduction of CO_2 belongs to a process of “artificial photosynthesis”, which employs semiconductors based photocatalysts and reducing agents like H_2O , H_2 and sunlight to convert CO_2 into renewable fuels or chemicals such as CO , CH_4 , CH_3OH , and HCOOH [287]. Photocatalytic CO_2 reduction offers several benefits including renewable energy generation and minimizing the anthropogenic CO_2 level. But the performances of these processes are often affected by low range of light absorption, fast recombination of photogenerated charges, poor selectivity, slow rate of reactions and inefficient reactors [288]. Several approaches have been adopted to overcome these issues such as, the development of highly efficient photocatalyst by tailoring the band gap through morphological controls or doping of non-metals and utilization of co-catalysts [289,290]. Among these strategies, the application of graphene-based materials has received a considerable

recognition in minimizing the inherent flaws of traditional photocatalysts, due to the exceptional photocatalytic properties of graphene including high surface area conductivity and good mechanical strength [291].

At present, the widely accepted mechanism of the photocatalytic reduction of CO₂ is “proton assisted multi-electron reduction process”. In this process, possibly the CO₂ adsorb a single electron and transformed into an unstable anion radical (CO₂⁻), which reacts further with electron (e⁻) and proton (H⁺, released through the oxidation of H₂O) to yield C1 chemical such as CO, CH₃OH etc. [292]. Indeed, the photoreduction of CO₂ is most efficient during multi-electrons transfer reactions in the presence of excess of protons, and efficient adsorption of CO₂ on the surface of the photocatalysts [293]. In addition, well-aligned band gap edges, controlled surface morphology and conductivity of the photocatalysts also play vital role in accelerating the photocatalytic reduction of CO₂ [294]. Notably, when graphene is combined with semiconductor materials the work function/Fermi level of resulting hybrids usually remained below the edge of the conduction band (CB) of the involved semiconductor. Due to this, when the light is irradiated, the photogenerated electrons can efficiently flow to the graphene-based hybrids and reacts with CO₂ at the active sites of the photocatalysts to generate possible products. Whereas, the leftover holes in the VB of the semiconducting material facilitate the oxidation of water [295].

Typically, the photocatalytic properties of semiconducting materials such as metal oxides are enhanced by combining them with noble metals like Ag, Au, Pt., which are considered as efficient electron sink and possess strong extracting properties of photogenerated electrons. However, the large-scale applications of noble-metals as co-catalysts are often hindered due to their high-cost. After the advancement of the low-cost, high-quality synthesis of graphene, the graphene derivatives and their composite materials have successfully replaced the noble metals in many cases. Particularly, the combination of graphene and widely used metal oxides semiconductors have gained immense attention. Shehzad et al. have developed a simple two-steps method to prepare HRG-TiO₂ involving partial reduction of GO and subsequent vacuum thermal treatment to reduce it to HRG [296]. The hybrid photocatalyst was tested for the reduction of CO₂ with H₂O, which has yielded high amounts (4 times) of CH₄ (12.75 μmol g⁻¹ h⁻¹) and CO (11.93 μmol g⁻¹ h⁻¹). In this case the photocatalyst has shown high adsorption of CO₂ which is possibly due to the hydrophilic nature of HRG by virtue of the presence of oxygenated groups on the surface [297]. Several studies have suggested that excess of graphene in composites negatively influence the photocatalytic properties of the resulting hybrid photocatalysts, due to the possible hinderance in the absorption of light [298]. While the less amount of graphene is not capable of separating the excited charges, therefore, optimization of graphene content is necessary for efficient photocatalytic properties [299]. In this regards, HRG-TiO₂ based ternary composite was developed by the incorporation of WSe₂ to obtain HRG-TiO₂-WSe₂ hybrid by an ultrasonic method [300]. The hybrid demonstrated a suitable band-gap of 1.62 eV for the photodegradation under ultraviolet UV/Visible light irradiation. In this case, the loading of graphene is optimized and 8 % of graphene content in the hybrid has shown high photocatalytic activity towards the CO₂ reduction to CH₃OH and yielded a total CH₃OH of 6.3262 μmol g⁻¹ h⁻¹ -

after 48 h. Very recently, new-modelled ternary nanocomposites AgFeNi₂S₄-HRG-TiO₂ were prepared using a Pechini method [301]. The photocatalytic properties of the hybrids were directly evaluated by the output of CH₄ production. The highest methanol yields were found after 48 h of irradiation under the UV light, and the yields were 8.679 %, 6.349 %, while the CH₄ yield was reduced when visible light was used as irradiation source.

Apart from TiO₂, graphene based ZnO nanocomposites have also been prepared. The preparation of few-layer graphene was *in-situ* deposited on the surface of ZnO, which was used as photocatalysts for CO₂ reduction. The hybrid demonstrated the enhanced performance than the pristine ZnO. This was due to the intimate interfacial contact and Schottky junction between ZnO and graphene. In another study, a ternary nanocomposite (Bi₂O₃-HRG-ZnO) was prepared using ultrasonic techniques. This was evaluated for the photocatalytic reduction of CO₂ in a reactor, for the production of CH₃OH [302]. 8 % loading of graphene demonstrated the highest photoactivity, achieving a total CH₃OH yield of 7.250 μmol g⁻¹ h⁻¹ after 48 h. Moreover, cuprous oxide (Cu₂O) and cupric oxide (CuO) which are p-type semiconductors with narrow band gaps (ca. 2.2 and 1.2 eV, respectively) were also extensively investigated for visible-light-active photocatalysis for the reduction of CO₂ [303]. Various studies have suggested that the exposed facets of active sites have outstanding influence on the photocatalytic performance of the semiconducting materials. Cu₂O nanoparticles with varied morphologies (different facets) and oxidation states were deposited onto HRG to obtained a series of Cu₂O-HRG nanocomposites which were evaluated for the photocatalytic reduction of CO₂ [304]. Among them, the rhombic dodecahedra Cu₂O-HRG demonstrated the maximum CH₄ yield (355.3 μmol g⁻¹cat) which is ca. 4.1–80.8 times superior to cubic, octahedral hybrids after 20 h under visible light irradiation. Similarly, in another study, octahedron Cu₂O nanocrystals-based ternary photocatalyst (HRG-Ag-Cu₂O) (Ag/Cu₂O@rGO) was successfully prepared by the combination of water bathing with gas-bubbling-assisted membrane reduction process [305]. In this case, Ag nanoparticles which consists of low fermi energy enriched the photogenerated electrons Cu₂O octahedral nanocrystals. While the conjugation of HRG nanosheets with Ag-Cu₂O nanoparticles, further enhanced the capturing of photoelectrons and also improved the adsorption-activation capacities for reactants. The hybrid exhibited enhanced performance during the selective photocatalytic reduction of CO₂ with H₂O into CH₄, and yielded highest amount of CH₄ (82.6 μmol g⁻¹ h⁻¹) with a high selectivity of the desired product (95.4 %).

Occasionally, other semiconducting oxides have also been used, such as, BiVO₄ quantum dots (QDs) supported onto the HRG to form BiVO₄ QDs-HRG hybrid nanocomposites employing hydrothermal process by Chen and his group [307]. The hybrid was used as a photocatalyst for the reduction of CO₂ to CO or CH₄. It was found that upon inclusion of 0.2 % HRG (0.2 is the mass ratio of HRG to BiVO₄ QD), the photocatalytic activity was improved up to 3.5 times when compared with bare BiVO₄ QDs. The improved activity is ascribed to the effective photoelectron transfer and transport in the HRG. Mateo and co-workers [308] utilized NiO/Ni nanoparticles (NPs) deposited on graphene (NiO/Ni-HRG) nanocomposites for the reduction CO₂ to CH₄. The

graphene-based nanocomposite i.e. NiO/Ni-HRG exhibited superior CH_4 production rates, compared to the Ni or NiO NPs supported on various other supports such as silica-alumina. Additionally, perovskite quantum dots combined with GO i.e. $\text{CH}_3\text{NH}_3\text{PbBr}_3/\text{GO}$ nanocomposite was used for the photo-electrochemical conversion of CO_2 into solar fuels. The conversion was attempted in non-aqueous media and it was found that the presence of GO in this nanocomposite i.e. $\text{GO}/\text{CH}_3\text{NH}_3\text{PbBr}_3$, enhanced the conversion and the photo-electrochemical reduction of CO_2 much better than bare MAPbBr_3 and the CO formed was $1.05 \mu\text{molcm}^{-2}\text{h}^{-1}$ and $0.268 \mu\text{molcm}^{-2}\text{h}^{-1}$, respectively.

The application of doped graphene, which is obtained using a variety of non-metals such as nitrogen, boron and phosphorus for the preparation of nanocomposites have also received decent recognition for the photocatalytic reduction of CO_2 [309]. This is further confirmed by incorporating TiO_2 nanoparticles onto boron doped graphene (B-HRG) to obtain B-HRG- TiO_2 hybrid photocatalyst [306]. In this case, doped HRG enhanced the electron locality with efficient directional transfer of electrons under light irradiation. The photocatalyst (B-HRG- TiO_2) have shown high photocatalytic activity towards the reduction of CO_2 to CH_4 when compared with the parent composites (TiO_2 -GO, TiO_2 -HRG) due to the electron transfer efficiency, suitable band gap alignment and enhanced reaction sites on surface (Fig. 17). In another study, nitrogen doped graphene (N-HRG) was used to prepared a hybrid photocatalyst (N-HRG- TiO_2) which was applied for the photocatalytic reduction of CO_2 which exclusively yielded CO [310]. Compared to bare TiO_2 and pristine N-HRG, the N-

doped hybrid photocatalyst has demonstrated high conversion and selectivity to solely produce CO, whereas, the former compounds have yielded a mixture of CH_4 and CO. The highest production rate of CO ($8 \mu\text{mol/gTiO}_2/\text{h}$) was achieved when the doped-photocatalyst was used.

Thus, the coupling of graphene with other semiconducting materials have garnered extensive recognition in the field of photocatalysis for the reduction of CO_2 for environmental remediation which is clearly represented by the publication of large number of studies in recent years. The inclusion of graphene in the semiconducting composites effectively reduced the hole recombination, facilitated CO_2 adsorption due to the π - π conjugation between graphene and CO_2 , facilitated the activation of CO_2 molecule, enhanced surface area and light absorption. In addition, graphene has also helped to enhance the selectivity towards production of solar fuels like methane and ethane, which are highly demanded energy sources. Despite of this, the rates of production of the photocatalytic reduction of CO_2 on graphene-based hybrid semiconductors still remain very low ($\mu\text{mol/g h}^{-1}$), due to some fundamental and essential problems which required specific attention of scientific community [311]. The efforts are required to fabricate multi-component graphene-based hybrids in which each of the component should be separately optimized to enhance the photocatalytic properties. So far, only few studies have been published on the theoretical calculations of charge carrier dynamics within the photoactive ingredients and at their interfaces with graphene, which require special attention. Furthermore, the photostability of the graphene-based composites are needed to be enhanced. This can be achieved by the inclusion

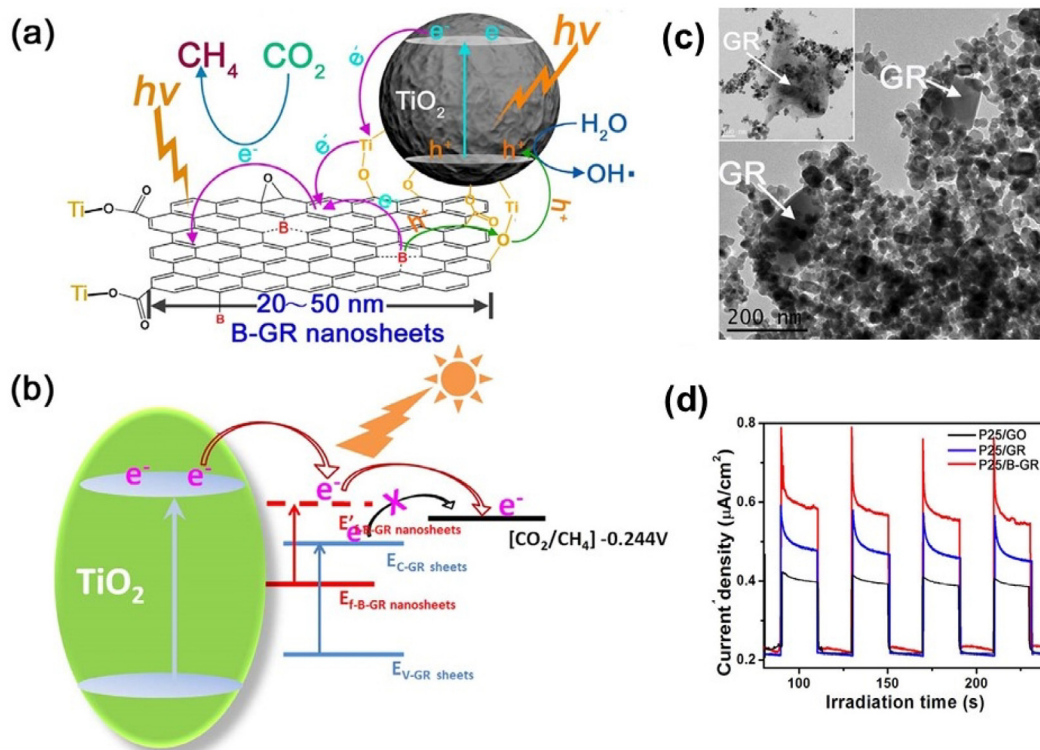


Fig. 17 (a) Schematic illustration of photo-excited electrons and holes transfer among TiO_2 and B-HRG, (b) electrons transfer between TiO_2 and HRG, (c) TEM images for TiO_2 -HRG, (d) transient photocurrent responses of TiO_2 -GO, TiO_2 -HRG and TiO_2 -B-HRG in $0.5 \text{ M Na}_2\text{SO}_4$ aqueous solution under solar irradiation [306].

of water oxidation co-catalyst into the hybrids, which will accelerate the consumption of photogenerated holes leading to the enhancement in photoactivity and stability of the graphene-based hybrid photocatalysts. Apart from these, the underlying photocatalytic mechanism for the reduction of CO₂ over graphene-based photocatalysts is still less understood. There is still less control on the tuning of product selectivity in the conversion of CO₂ due to the lack of proper understanding.

4. Summary and perspectives

Graphene/inorganic nanoparticles based semiconductor photocatalysts have been extensively investigated over the last decade. The number of studies exploring the potential of these materials for various photocatalytic environmental remediation processes have been increasing steadily. In addition to the discussion of selected studies in the text, some other examples of the application of graphene-based nanocomposites in H₂ production, pollutants degradation, organic transformation and CO₂ reduction are provided in the Table-1. Till date, several crucial factors related to the enhancement of the photocatalytic properties of these materials have been explored, which has further offered an array of opportunities for designing next-generation, advanced graphene-based photo-catalysts towards the enhancement of the performance of artificial photosynthetic processes. The tailoring of the band-gap of graphene would provide tremendous scope in photocatalysis, to some extent, success has been achieved in this regard by adopting few effective strategies including the application of doped-graphene, graphene-nanoribbons and graphene-nanomeses in the preparation of photocatalytic composites. Particularly, the doping of graphene with non-metals, such as nitrogen has delivered great success in preparing highly active engineered graphene-based photocatalysts. Moreover, graphene offers improved and extended absorption range of solar light, however, the synergistic effect between graphene and the semiconducting components involved in the hybrids is still poorly understood, which may offer valuable information and may further enhance the application of graphene for photocatalytic applications.

Additionally, there is still lack of control over the morphology of graphene-based nanoarchitectures, which may further enhance the photocatalytic role of graphene-based hybrids. Nanostructures should be engineered to improve the light absorption, mass transportation and for increasing the active sites. For instance, the creation of hollow structured, high surface area materials, such as, the utilization of graphene aerogels, preparation of graphene wrapped materials may offer additional sites for photon entrapment which will further enhance the light absorption capacity of the resulting hybrid. In this regard, the combination of graphene derivative such as 3D graphene with semiconducting materials has significantly improved the specific surface area, optical properties, stability, active sites, and charge transportation ability of hybrids which increased the photocatalytic activity of the graphene-based composites for environmental remediation processes. However, the mechanisms on how to increase the charge separation rate among these materials and suppressing of charge recombination have not been clearly understood yet.

Particularly, the advancement in the designing of robust graphene-based materials has surely offered great progress on the graphene-semiconductor composite photocatalysts for solar energy utilization for environmental remediation. However, the ability to accurately optimize the structural and electronic properties of each component is still at the level of infancy. This type of control over the structural properties of composites will further enhance the interfacial electron transfer at the nano-level, which is very crucial for over all photocatalytic properties of the graphene-based hybrid photocatalysts. In this regard, so far, the most commonly applied method in the literature for the preparation of graphene-based composites is based on the random dispersion of solid semiconducting materials on the surface of graphene, which is often referred as “hard” integration. However, using this approach the graphene is just randomly introduced in the hybrid, and thus unable to display its full potential due to aggregation and wrapping of sheets. This leads to poor interfacial contact between the components, which seriously hampers the effective transfer of photogenerated electrons, leading to the diminished photocatalytic properties of the resulting materials. Therefore, the advancement in the preparation approaches is highly desirable to exploit the full potential of the structural and electronic properties of graphene in the composites for superior photocatalytic performance.

The researchers are mainly focused on binary or ternary systems for the preparation of graphene-based hybrids. However, the combination of graphene with multi-component materials is most promising which will offer great opportunity to generate advanced 3D nanoarchitectures with diverse photocatalytic properties. Nevertheless, graphene-based hybrid photocatalysts have so far demonstrated great talent as robust materials for addressing a variety of environmental and energy-related problems. But, still its comprehensive ability is yet to be exploited, and the research in this field requires great enthusiasm of researchers from both academia and industry to overcome the challenges for the development of multifunctional graphene-based photocatalysts for the effective transformation of solar energy to chemical energy. We hope that we were able to shed some light on this vast topic, but a large area of this research still remains in the dark.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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