Chapter 6 Graphene-Based Photocatalysts for the Elimination of Pollutants in Water



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Abstract Water is an essential part of living things as the life cycle, and water cycle are inextricably linked. The development of industrialization caused the water to become hazardous by emitting dyes, pollutants, organic wastes and other harmful chemicals into the water bodies. It's a big challenge to treat wastewater for human health and to preserve the ecosystem. In recent years, graphene-based photocatalytic materials have gained much attention to eliminate liquid pollutants. This is due to the tremendous optical, electrical and physicochemical properties of this unique twodimensional material. On integration with other semiconducting, metallic or polymeric materials, graphene remarkably boosts the photocatalytic activity of materials toward contaminants destruction. The high charge carrier mobility, high surface area and excellent mechanical strength of graphene-based nanocomposites make them suitable for photocatalytic applications. This book chapter will focus on the recent significant advances in developing graphene-based photocatalytic materials. The principle of photocatalysis, the basic properties of graphene and the mechanism of how the photocatalytic efficiency against the removal of the liquid pollutant can be enhanced when coupled with graphene has been discussed in this book chapter. Furthermore, current challenges and future recommendations for developing graphene-based photocatalysts are also discussed.

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6.1 Introduction

The demand for fresh water has increased manyfold in the last decade due to increased world's population. According to the report published by United Nations in 2018 on World Water Development, there will be a one-third increase in the demand for drinkable water by 2050 [1]. As clean water is primarily required for various industries and pharmaceutical companies, and households. After use, the release of the water into the environment without treatment adversely affects aquatic as well as human life. Thus, it is highly desirable to treat wastewater using a suitable technique so that it can be reused which can also solve the problem of water scarcity.

To remove the impurities and harmful water pollutants from the waste water, various techniques have been developed with the technological advancements [2]. The waste water can be treated in three effective ways as follows.

- (i) Biological treatment,
- (ii) Physical treatment, and
- (iii) chemical treatment.

Biological treatment of water involves the use of various microbes to degrade the biodegradable water pollutants through biological process. This type of treatment degrade the water pollutant and produce the water, CO_2 and other chemicals. The challenge in this type of water treatment lies in requirement of large area, slow treatment process and bring water to its natural appearance of clean water. Furthermore, physical treatment of water involves physically filter the water using filtration method, sedimentation etc. which again put forward the challenge of slow treating process. It is appreciable in the physical treatment method that no chemicals are used while treating the waste water with physical methods. An another way is chemical method which involves treatment of water through chemical reaction. Oxidation, precipitation, and adsorption are examples of chemical wastewater treatment.

The photocatalytic treatment of wastewater using nanomaterials has gained a lot of attention due to its potential to solve environmental issues, the biggest challenge of the twenty-first century [3, 4]. Many nanomaterials show inherent confinement quantum effects, high surface-to-volume ratio, and large surface area which are favourable to increase the photocatalytic reaction.

Various fundamental issues related to photocatalysts that still need to be resolved before implementing them for large-scale industrial applications. For example, high cost, low efficiency, mismatch of the band gap, recombination of charge carriers and low absorption of solar energy [5]. On absorption of light photons having energy greater than the band gap of the material, the electrons and holes get separated and reside in the conduction band (CB) and valence band (VB), respectively (Fig. 6.1). These separated charge carriers (electrons and holes) migrate towards the surfaceactive sites wherein they combine with the adsorbed water molecules or moisture to generate highly reactive species such as OH', O_2^{--} , OOH', etc. Further, these highly reactive species react with the pollutant species to mineralize them into CO₂ and water. One could improve the photocatalytic performance of the nanomaterials by addressing the following three key points [6, 7];



Fig. 6.1 Photoexcitation of the semiconducting materials and subsequent oxidation and reduction reactions for generation of radical species

- (1) Absorption of the broad solar spectrum,
- (2) Effective separation of the charge carriers, and
- (3) Facilitated movement of the separated charge carriers towards the surface-active sites.

Various attempts have been made to improve the efficiency of the photocatalysts such as doping with cationic or anionic species [8], coupling with the metal nanoparticles (NPs) [9] or other semiconductor photocatalysts [10], exfoliation [11] and surface modifications to improve the porosity, surface area, and active facets of the photocatalysts [12, 13]. Despite such modifications at the lab scale, the commercialization of such photocatalytic subsystems for wastewater treatment needs to achieve a certain criterion in terms of cost, efficiency and environmental impact is yet to be realized [14]. Among various two-dimensional support materials, graphene-based materials are the most reliable due to their low cost, high stability and excellent efficiency.

6.2 Basic Properties of Graphene-Based Materials

The carbonaceous materials exhibit unique structural, electrical, and redox properties and tend to add an attractive feature to photocatalysis. The carbonaceous and graphene-based photocatalytic materials have attracted immense attention due to the unique flexible sp² hybridized carbon network [15, 16]. Graphene-based materials show promising applications in various fields, such as energy storage [17], biosensors [18], photocatalysis [19], antibacterial and antimicrobial activity [20] etc. The graphene-based nanomaterials showed excellent electron mobility and electrical conductivity, high optical transparency, and good chemical and thermal stability. Due to the promising electronic and optical properties of graphene-based nanocomposites they are highly demanding in the field of photocatalysis.

Graphene is a two-dimensional layered honeycomb-like structural material formed by sp² hybridized carbon atoms. Graphene is a fascinating material with a large surface area, good electrical conductivity, high intrinsic electron mobility and optical transmittance [21, 22]. The two most widely studied derivates of graphene are graphene oxide (GO) and reduced graphene oxide (RGO) [23]. Furthermore, the modified graphene derivatives (graphene, GO and RGO) with other materials such as metals or non-metals or semiconductors, metal–organic frameworks (MOF's) aerogels, etc., offer an outstanding platform for photocatalytic applications. It was found that the modified graphene-based derivative exhibits better photocatalytic and adsorption properties as compared to the pristine graphene [24].

6.3 Synthesis and Properties of Graphene-Based Composites

There are several chemical and physical methods for designing and developing graphene-based composites. Although the chemical vapour deposition and physical exfoliation methods can produce high-quality graphene materials, they show poor dispersion and contact angle due to insufficient functional groups making them less suited for photocatalytic applications [25, 26]. The chemical oxidation of graphene modifies its surface with many oxygen functionalities (hydroxyl, epoxides, carboxyl groups) responsible for increased interlayer distance, thereby allowing better solubility and adsorption of the organic pollutants [26]. In GO, the hydroxyls and epoxides groups are extensively occupied on the basal planes, while the aldehyde, ketone and carboxylic groups are mainly located on the edge of GO [27]. The oxygenated functional groups of GO affect its mechanical, electronic, and electrochemical properties and improve its dispersion in solvents. However, the high dispersion of GO in both aqueous and non-aqueous solvents is challenging during its recovery after the treatment process. Also, the presence of a large number of oxygen functionalities in the GO dimmish its electrical conductivity, which is inappropriate for photocatalytic activity.

To overcome this drawback of GO, further reduction of the oxygen functionalities was made by various techniques. The RGO exhibits similar properties as pristine graphene with restored hexagonal honeycomb-like structure and electrical conductivity due to abundant conjugated π -bonds that were not there in GO [28]. However, with the reduction of oxygen functionalities in RGO, there will be a reduction in the repulsive forces between the sheets, causing lower interlayer distance [29]. The aggregations or restacking due to strong π - π interactions could reduce some potential active sites of RGO nanosheets. However, to prevent the aggregation of RGO nanosheets various strategies have been used such as surface modification, composite formation, in-situ reduction etc.

Muiva and coworkers prepared multilayered graphene/zinc oxide (MLG/ZnO) nanocomposite using ex-situ casting of ZnO and MLG nanopowders [30]. The MLG wasobtained via a green route from cellulose extracted from corn husk. The extracted cellulose was pyrolyzed at 800 °C for 2 h under a nitrogen atmosphere (Fig. 6.2). The carbonized corn husk (CH-C) was mixed homogeneously with KOH and pyrolyzed again in a nitrogen atmosphere to activate the carbon material (CH-CA). Finally, the activated material was treated with H_2SO_4 to etch out intercalated K⁺ ions resulting in highly porous and activated MLG nanosheets. Furthermore, the prepared nanocomposite was used for the photocatalytic degradation of congo red (CR) and rhodamine B (RhB) under natural sunlight irradiations.

Recently, our group has synthesized a ternary nanocomposite of 2D-2D GCN/RGO heterojunction decorated with Au nanostars (NST) using a hydrothermal synthesis route (Fig. 6.3) [31]. A chemical reduction method was used for the synthesis of the Au NST. The mixture of the Au NST, protonated GCN and GO with negative surface charge was treated hydrothermally to synthesize the composite with strong electrostatic interactions. Further, a series of nanocomposites were synthesized by varying the weight ratio as 1, 2, 3, and 5 wt%. It was found that the



Fig. 6.2 Schematic presentation for the synthesis of multilayered graphene/ZnO nanocomposite and its photocatalytic activity for the degradation of organic pollutants. Reproduced with permission from Ref. [30] Copyright 2022, Elsevier Science Ltd.

optimized catalyst ACG2 showed the highest efficiency for the degradation of the methylene blue (MB) and tetracycline (TC) dyes. Similarly, other ternary nanocomposites synthesized using the hydrothermal synthesis route have been reported in the literature for the degradation of organic pollutants such as RGO/ZnO/MoS₂ and CNT/Zno/MoS₂ [32], Ag₃VO₄/Cu-MOF/RGO [33], AgFeO₂-graphene/Cu₂(BTC)₃ MOF [34], CdS/RGO/BiOI [35], and GCN/graphene/TiO₂ [36].

Furthermore, another synthesis strategy (chemical reflux method) was adopted for the fabrication of RGO nanocomposite with Fe₃O₄@polypyrrole [37]. The free radical polymerization of the pyrrole monomer using ammonium persulfate as an initiator in an acidic solution of GO, resulted in the formation of polypyrrole/RGO (PPy/RGO) nanohybrid. Further, the chemical reflux method was used for the coating of Fe₃O₄ nanorods onto the PPy/RGO nanohybrid as shown in Fig. 6.4a. The XRD patterns show the presence of the characteristic peaks of GO and further the appearance of a broad peak at 24.5° in the PPy/RGO hybrid indicated the successful reduction of GO into RGO (Fig. 6.4b). Similarly, the change in the intensity ratio of D-band due to the defect-filled nature of graphitic carbon at 1347 cm⁻¹ and G-band due to



Fig. 6.3 Schematic representation for the synthesis of Au NST/GCN/RGO nanocomposites. Reproduced with permission from Ref. [31]. Copyright 2021, Royal Society of Chemistry

stretching vibration modes in graphitic carbon sheet at 1582 cm^{-1} in Raman spectra indicate a reduction of GO into RGO as shown in Fig. 6.4c. The downward shift of the D and G bands in the representative nanocomposite, Fe₃O₄@PPy/RGO signifies the strong interactions between Fe₃O₄ and PPy/RGO hybrids.

In another report, a quaternary nanocomposite consisting of NaYF₄:Yb/Er@CdS core—shell nanostructures decorated with Au NPs supported on RGO nanosheets has been synthesized using the multistep hydrothermal method for the removal of the pharmaceutical pollutant, ciprofloxacin (CIP) [9]. The rational design and development of the catalyst showed the efficient absorption of the broadband solar spectrum (visible and NIR regions). The carbonaceous 2D material, RGO, not only acts as the support for the NPs but plays multiple roles, such as electron acceptor and transporter. In addition, the RGO nanosheet adsorbs the pollutant molecules onto the



Fig. 6.4 a Schematic presentation of the synthesis of Fe₃O₄@PPy/RGO nanocomposite, b XRD patterns and c Raman spectra of GO, PPy/RGO and Fe₃O₄@PPy/RGO nanocomposite. Reproduced with permission from Ref. [37]. Copyright 2021, Elsevier Science Ltd.

surface, thereby facilitating their photocatalytic degradation. Other quaternary photocatalytic materials are also reported in the literature for the removal of the organic and inorganic contaminants from the wastewater, for example, $Ag_2CrO_4/TiO_2/Au/RGO$ hybrid biofilm [38], Carbon QDs/RGO-S@GCN/B@GCN [39], etc.

6.4 Photocatalytic Degradation of Organic Pollutants

Various intermediates and radical species are generated after photoexciting the graphene-based photocatalysts. These species are responsible for destroying both organic and inorganic components of pollutants in wastewater. Table 6.1 summarizes the recent reports on the photocatalytic degradation of organic pollutants using graphene-based nanocomposites. Peng et al., have synthesized 2D-2D GCN/GO nanocomposite using a hydrothermal synthesis route through π - π stacking interactions [40]. Further, the Ag NPs were uniformly deposited onto GCN/GO nanocomposite through the *in-situ* reduction method. As-synthesized nanocomposite was used for surface-enhanced Raman scattering (SERS) detection of biomolecules (adenine) and adsorption and photocatalytic degradation of organic pollutants (methylene blue).

A TiO₂/GO nanocomposite synthesized using the hydrothermal method was used to treat mineral processing wastewater photocatalytically [41]. The UV–Vis diffuse reflectance spectroscopy (DRS) analysis showed an extraordinary improvement in the absorption of the TiO₂ in the visible region after loading 18% of GO (Fig. 6.5a). Furthermore, the photocurrent measurements showed the higher photocurrent density of the 18% TiO₂/G nanocomposite as compared to the bare graphene nanosheets indicating the efficient separation of the charge carriers for better photocatalytic performance (Fig. 6.5b). The representative nanocomposite showed a degradation efficiency of 97.03% in 190 min under visible light irradiations (Fig. 6.5c). The improved photocatalytic performance of the catalyst was attributed to the huge specific surface area, low electron-hole suppression rate and extended absorption in the visible range. The bare GO shows a high rate of removal of the dye for an initial 30 min that could possibly be due to the adsorption process. However, the removal rate decreases significantly with further increases in time. Figure 6.5d depicts the EPR spectra suggesting that the higher intensity in 18% TiO₂/G nanocomposite under visible light irradiations is due to high oxygen vacancies in the samples. The EPR analysis showed that the 18% TiO₂/G photocatalytic material can be easily excited under visible light to generate electrons responsible for its high photocatalytic performance.

In another report, Graphene-based ZnCr layered double hydroxide (LDH) nanocomposites were utilized for the sonophotocatalytic performances for the degradation of rifampicin dye [42]. For this purpose, the ZnCr LDH and its nanocomposite with RGO were synthesized using a facile co-precipitation method., The maximum degradation efficiency of 87.3%, was achieved for rifampicin dye within 60 min of visible light irradiation. The high photocatalytic performance of the ZnCr

Photocatalysts	Light source	Pollutants concentration	Reaction time	Year (Ref.)
Ag NPs/GCN/GO nanocomposite	Visible light (405 nm)	RhB (1 × 10 ⁻⁶ M)	60 min	(2022) [40]
Corn husk multi-layered graphene/ZnO nanocomposite	Natural sunlight	RhB, CR and DOX (1.25 × 10^{-5} mol L ⁻¹)	RhB (86%), CR (100%) and DOX (90%) in 180 min	(2022) [30]
Indium hydroxide/Nitrogen-doped graphene aerogels	High-pressure mercury lamp (400 W)	<i>p</i> -NP (20 mg L ⁻¹)	98% in 180 min	(2022) [44]
B doped RGO supported bismuth ferrite	300 W Xenon lamp	TC and RhB $(10 \text{ mg } \text{L}^{-1})$	TC (86.7%) and RhB (99.4%) in 90 min	(2022) [45]
RGO-TiO ₂ (photocatalysis linked with Fenton process)	shortwave light (UV254), black light (UV365), UV LED torch (UV395), visible light (400–700 nm) and sunlight	PA (200 mg L ⁻¹)	100% in 24 min (UV254), 22 min (UV365), 19 min (UV395), 18 min (VIS), 15 min (sunlight)	(2022) [46]
3D graphene/Cd _{0.5} Zn _{0.5} S hybrids	300 W Xenon lamp ($\lambda >$ 420 nm)	CIP (5 mg L ⁻¹)	95% removal in 15 min	(2022) [47]
ZnCr LDH/RGO nanocomposite	LED lamp (visible light)	RIF (15 mg L ⁻¹)	87.3% removal in 60 min	(2022) [42]
TiO ₂ /graphene nanocomposite	300 W Xenon lamp	$\begin{array}{c} \text{PBX} \ (20 \ \text{mg} \\ L^{-1}) \end{array}$	97.03% in 130 min	(2022) [41]
Graphene- AgNPs@GCN	Visible light	$\begin{array}{c} \text{MB} \ (5 \ \text{mg} \\ L^{-1}) \end{array}$	88.5% in 140 min	(2022) [48]
FeTiO ₃ /GO nanocomposite	150 W Xenon lamp	Phenol $(50 \text{ mg } \text{L}^{-1})$	100% in 150 min	(2021) [49]
ZnSnO ₃ /graphene aerogel	Simulated sunlight	$CIP (100 mg L^{-1})$	100% in 120 min	(2021) [43]
Fe ₃ O ₄ NRs-polypyrrole/RGO	Two 250 W tungsten-halogen lamps	$\begin{array}{c} \text{ACP} (1 \text{ mg} \\ \text{L}^{-1}) \end{array}$	84% in 120 min	(2021) [37]

 Table 6.1
 Summary of graphene-based photocatalysts for degradation of pollutants in wastewater

(continued)

Photocatalysts	Light source	Pollutants concentration	Reaction time	Year (Ref.)
RGO/Zno/MoS ₂ ternary nanocomposite	Visible light (100 W)	Aniline (80 mg L ⁻¹)	100% in 120 min	(2020) [32]
RGO-Bi ₂ WO ₆	85 W CFL bulbs (450–650 nm)	LVX (80 mg L^{-1})	74.3% in 120 min	(2020) [50]
Ag ₃ VO ₄ /Cu-MOF/RGO	Visible light	AB92 (10 mg L^{-1})	80% in 120 min	(2020) [33]
AgFeO ₂ -graphene/Cu ₂ (BTC) ₃ MOF	Natural sunlight	AMC and DCF (5 mg L^{-1})	AMC (92.9%) and DCF (91.4%) in 150 min	(2020) [34]
Carbon QDs/RGO-S@GCN/B@GCN	300 W Xe lamp (450 mW cm ⁻² , 380-780 nm) and direct sunlight	CMP (10 mg L ⁻¹)	Visible light 90% in 120 min) and sunlight (99.2% in 90 min)	(2020) [39]
Ag ₂ CrO ₄ /TiO ₂ /Au/RGO biofilm	125 W Hg lamp	$\begin{array}{c} \text{MB} \ (10 \ \text{mg} \\ \text{L}^{-1}) \end{array}$	97% in 52 min	(2020) [38]
RGO-N-ZnO	500 W tungsten halogen lamp	$\frac{\text{MB (10 mg}}{\text{L}^{-1}})$	98.5% in 120 min	(2020) [51]
GO/TiO ₂	500 W Xenon lamp	$\begin{array}{c} MB \ (5 \ mg \\ L^{-1}) \end{array}$	92% in 60 min	(2020) [52]
N doped graphene/TiO ₂	300 W mercury lamp	BPA (20 mg L^{-1})	100% in 60 min	(2020) [53]
GO-derived C-doped SrTiO ₃	500 W Xenon lamp	$\begin{array}{c} \text{MB (8 mg} \\ \text{L}^{-1}), \text{MO} \\ (3.3 \text{ mg } \text{L}^{-1}), \\ \text{RhB (4.8 mg} \\ \text{L}^{-1}), \text{phenol} \\ (9.4 \text{ mg } \text{L}^{-1}) \end{array}$	Over 95% of MO, MB, and RhB, and 70% of phenol and BPA in 3 h	(2020) [54]
Lanthanum-substituted Zn spinel ferrite @RGO	UV lamp (0.6 mW cm^{-2})	$ \begin{array}{c} \text{RhB} (30 \text{ mg} \\ \text{L}^{-1}) \end{array} $	100% in 60 min	(2020) [55]
GCN/graphene/TiO ₂	300 W Xenon lamp (300 mW cm ⁻²)	TC (15 mg L^{-1}), CIP (3 mg L^{-1}), BPA (5 mg L^{-1}) and RhB (20 mg L^{-1})	TC (83.5%) in 80 min, CIP (61.7%) in 60 min, BPA (79.5%) in 70 min and RhB (98.0%) in 50 min	(2020) [36]

Table 6.1 (continued)

(continued)

Photocatalysts	Light source	Pollutants	Reaction	Year
1 hotocatalysts		concentration	time	(Ref.)
Bi ₂ S ₃ -BiVO ₄ graphene aerogel	$300 \text{ W Xe lamp} \\ (\lambda > 420 \text{ nm})$	$\begin{array}{c} {\rm Cr}~({\rm VI})\\ (50~{\rm mg}~{\rm L}^{-1})\\ {\rm and}~{\rm BPA}\\ (10~{\rm mg}~{\rm L}^{-1}) \end{array}$	99% removal of Cr (VI) and BPA in 120 min	(2020) [56]
GO/ZnO-Ag nanocomposite	Natural sunlight	$\frac{\text{MB} (3.13 \times 10^{-5} \text{ M})}{10^{-5} \text{ M}}$	100% in 40 min using GO/ZnO-Ag	(2020) [57]
CuO-TiO ₂ /RGO	UV light (312 nm)	$\begin{array}{c} \text{MO} \ (10 \ \text{mg} \\ L^{-1}) \end{array}$	99% in 90 min	(2019) [58]
SnO ₂ aerogel/rGO nanocomposite	40 W UV lamp (370 nm)	MO (1 × 10 ⁻⁵ M)	84% in 60 min	(2019) [59]
GO/TiO ₂	Hg lamp	RhB (10 mg L^{-1}) and AG25 (40 mg L^{-1})	100% in 120 min (RhB) and 97% in 180 min (AG25)	(2019) [60]
Graphene based NiAlFe LDH	500 W Xe lamp	$\begin{array}{c} \text{CIP} (10 \text{ mg} \\ \text{L}^{-1}) \end{array}$	93% in 120 min	(2019) [<mark>61</mark>]
SnS ₂ /RGO	65 W CFL lamp ($\lambda > 400 \text{ nm}$)	RBB and RBR (10 ppm)	99.7% (RBB) and 97% (RBR) in 150 min	(2019) [62]
Porous graphene/ZnO	Natural sunlight	$\begin{array}{c} \text{MO} (13 \text{ mg} \\ \text{L}^{-1}) \end{array}$	100% in 150 min	(2019) [63]
CdS/RGO/BiOI	500 W Xe lamp ($\lambda > 420$ nm)	$\begin{array}{c} \text{MDHB} \\ (20 \text{ mg } \text{L}^{-1}) \end{array}$	~80% in 240 min	(2019) [35]
Ordered Porous TiO ₂ -Pt/RGO	$300 \text{ W Xe lamp} \\ (\lambda > 420 \text{ nm})$	$\frac{\text{MO}(20 \text{ mg}}{\text{L}^{-1}})$	82% in 120 min	(2019) [<mark>64</mark>]
RGO-ZnTe	Solar simulator	$TC (10 mg L^{-1})$	~70% in 45 min	(2019) [65]

AB92 = acid blue 92; ACP = acetaminophen; AG25 = acid green 25; AMC = amoxicillin; BPA = bisphenol A; CMP = Chloramphenicol; CIP = ciprofloxacin; CR = congored; DCF = diclofenac; DOX = doxycycline; GCN = graphitic carbon nitride; GO = graphene oxide; LDH = layered double hydroxide; LVX = levofloxacin; MB = methylene blue; MDBH = methyl 3,5-dichloro-4-hydroxybenzoate; MO = methyl orange; NPs = nanoparticles; *p*-NP = p-nitrophenol; PA = picric acid; PBX = potassium butyl xanthate; RBB = remazol brilliant blue; RBR = remazol brilliant red; RGO = reduced graphene oxide; RhB = rhodamine B; RIF = rifampicin; TC = tetracycline



Fig. 6.5 a UV–VIS-DRS spectra, b photocurrent-time (I-t) plot, c photocatalytic activity under visible light and d EPR spectra of GO and 18% TiO₂/G nanocomposite. Reproduced with permission from Ref. [41] Copyright 2022, Elsevier Science Ltd.

LDH/RGO nanocomposite was attributed to the enhancement in the production of active hydroxyl (OH) radical species under visible light irradiations. The radical scavenger studies confirm that the OH radical plays the most significant role in degrading the dye molecule. Furthermore, the ultrasonication process benefits the process by preventing the agglomeration of the catalyst in solution, improving mass transport and increasing the availability of the active sites by continuously cleaning of the catalyst surface.

A macroscopic ZnSnO₃/graphene aerogel structure has been synthesized that showed excellent adsorption and degradation of the CIP from wastewater under visible light irradiations [43]. The catalyst synthesized with an optimized mass ratio (1:2) of the ZnSn(OH)₆ to GO, denoted as ZGA-4, exhibits the 100% removal efficiency of the pollutant. The improved photocatalytic performance of the catalyst was ascribed to the optimized interfacial and electronic band structures responsible for the separated photogenerated charge carriers and immensely produced active species such as OH⁻ and O₂⁻⁻⁻ radicals, as shown in Fig. 6.6.

The graphene-based materials play a major role in enhancing the photocatalytic activity of the semiconducting materials for the degradation of organic pollutants. Various intermediates and radical species are generated after photoexciting the graphene-based photocatalysts. These species are responsible for destroying both



Fig. 6.6 a UV–VIS diffuse reflectance spectra; b Tauc's plots; c Mott-Schottky diagram and d band gaps of the ZGA nanocomposites. Reproduced with permission from Ref. [43] Copyright 2021, Elsevier Science Ltd.

organic and inorganic components of pollutants in wastewater. Table 6.1 summarizes the recent reports on the photocatalytic degradation of organic pollutants using graphene-based nanocomposites.

6.5 Summary and Future Perspective

In summary, graphene-based materials open new opportunities in the advanced photocatalysis process. The outstanding physical and chemical properties of graphene-based photocatalysts such as large surface area, high electron conductivity, abundant surface-active sites, high mechanical strength and good adsorption and reusability properties make it the most reliable candidate in the field of photocatalysis. This chapter discusses various strategies, such as surface modification, doping, and multijunction formation, to improve the photocatalytic performance of graphene-based materials. Coupling the two-dimensional carbonaceous materials (graphene, GO and RGO) with other nanomaterials like metal oxides and metal nanoparticles exhibit synergistic improvement in the photocatalytic efficiency and stability of the catalyst. Also, the optimized amount of graphene-based materials in

the catalyst tunes the bandgap to enhance the light absorption of the catalyst. From the above discussion of the literature on binary, ternary, and quaternary composites of graphene-based materials, it can be concluded that the appropriate modification could result from highly efficient materials for adsorption and photocatalytic treatment of wastewater. The production of cost-effective, photostable and efficient graphenebased materials at a large scale is most desirable and challenging as well. Thus, more work needs to be done by researchers to ensure the commercialization of such materials for large-scale photocatalytic applications. There are extensive opportunities in the research area to extend the perspective of graphene-based materials for wastewater treatment.

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