The Efficacy of Graphene oxide and Reduced Graphene oxide with Metal oxides for photodegradation of dyes

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Abstract

As a successful technology for the treatment of waste water, the employment of photocatalyst for the destruction of synthetic and organic contaminants, such as dyes and chemicals, has evolved. In this research, we have primarily concentrated on photocatalytic materials based on two-dimensional carbon nanostructures, such as graphene oxide (GO) or reduced graphene oxide (rGO), which have high oxygen functionality, significant surface areas, and efficient adsorption sites. By altering the level of valence band and conduction band, the composites of GO/rGO outperform electron-hole pairs recombination rate and minimise energy gaps, improving the photodegradation performance of metal oxides composites.

Introduction

Colored organic compounds are frequently discarded in wastewater at the end of the production process in a number of industrial operations, including textile, food, tannery, paper, printing, and cosmetic. These dyes affect the aquatic ecosystem by colouring the water and blocking light from penetrating, which reduces photosynthesis and lowers the amount of dissolved oxygen in the water. Additionally, this kind of pollutant may have genotoxic impacts on fauna, flora, and human health in addition to having carcinogenic, hypersensitive, and other negative effects [1-5]. Dyes are synthetic organic molecules, including azo, sulphur, nitro, triphenylmethane, acidic, and basic ones. The industries of leather, textiles, and biology all benefit from the usage of brilliant green (BG), a dye based on triphenylmethane. However, drinking water tainted with BG can harm people and result in hypertension, heart, lung, and kidney problems, as well as cancer that can be passed on to future generations [6-12]. Methylene blue (MB) can induce eye burns in both people and animals, which is one of its many major negative effects. When consumed, MB stimulates the digestive system and causes nausea, vomiting, and diarrhoea. In addition, it can cause convulsions, cyanosis, methemoglobinemia, dyspepsia, and tachycardia. To maintain ecological balance, it is crucial

to remove methylene blue and other colours from contaminated water due to the negative effects that MB has on people, animals, and aquatic life [13-15]. Therefore, it is very important to get rid of this contaminant from water. Adsorption, ion change, membrane separation, chemical precipitation, photocatalytic method, and other techniques have all been developed in the field of wastewater treatment to treat various types of wastewater [16].

In this regard, the environmentally friendly and cost-effective way of removing the dye from water bodies is photodegradation of the dye under the stimulation of light [17]. The design and prospective uses of nanostructured semiconductor materials for energy, the environment, and water sanitization have recently been examined. However, before the photocatalysts are commercially feasible for extensive industrial applications, a number of basic difficulties need to be resolved. Due to their ability to break down organic dyes when exposed to light, these semi-conductor photocatalysts are among the most promising photocatalysts and offer an affordable and simple method for water filtration. On the photocatalyst surface, electron-hole pairs are produced as a result of light absorption during the photocatalytic reaction. Charge carriers produced by photosynthesis migrate toward the catalyst surface and produce reactive oxygen species [18-21]. Finally, the dye molecule is broken down by these reactive oxygen species. For instance, the application of TiO_2, which is regarded as one of the greatest photocatalysts, is constrained by the rapid recombination of electron-hole pairs and the mismatch between the band gap energy and solar radiation spectrum. The photocatalyst must be activated by UV light due to the wide band gap of TiO_2 (3.2eV), which severely restricts the technology's ability to be used in real-world situations [22-24]. At the moment, there is a lot of focus on creating composite systems and heterostructures based on semi-conductors for visible light driven photocatalysis. The practical limitations on their photocatalytic capabilities, however, include low visible light absorption, a wide band gap energy, and rapid electron-hole pair recombination. As a result, the design and development of semiconductor nanocomposite (NC) materials has recently become a very promising field of study.

Designing graphene oxide (GO) semiconductor composites has received particular attention in an effort to boost the photocatalytic performance of the photocatalyst, notably for water remediation. Graphite oxide sheet, often known as GO, is the end result of the chemical exfoliation of graphite. It is a 2D material made up of an atom-thick sp^2 carbon network. With its exceptional mechanical properties, huge theoretical surface area ($2630 m^2/g$), high transparency, and distinctive two-dimensional long-range conjugation structure, graphene makes an excellent platform for the grafting of various semiconductor materials. It also makes

it possible for the transport of photogenerated charge carriers, which is made possible by its excellent electrical (104 $Ohm^{-1}cm^{-1}$) and thermal (3000 W/Mk) conductivity, as well as its diverse derivatives with fascinating surface properties [25-30]. Semiconductor materials may be adhered to the surface of graphene oxide, where photogenerated electrons are then transferred. enhancing the efficiency of the photocatalytic process. Because of its distinctive characteristics, such as ease of synthesis, vast surface area, layered structure, and excellent thermal and chemical durability, graphene oxide (GO) is a significant member of the carbon family [31-35]. Due to its exceptional qualities, GO is widely employed in a variety of applications, including bio-applications, sensors, photovoltaics, energy and electronic devices, catalysis, and more. Because of its hydrophilic characteristics and the abundant oxygen groups on its basal and edge surfaces, graphene oxide has the advantage of being able to interact with and absorb organic compounds and dyes in water treatment applications. In addition to interacting with water and other polar solvents, functional groups like epoxy, hydroxyl, and carboxyl groups also exhibit π-π stacking interactions [36-43]. In addition, it is simple to reduce these functional groups to generate reduced graphene oxide (rGO). Additionally, access to functionalized graphene-based heterostructure NCs is greatly facilitated by these oxygen-containing functional groups [44-48]. This new material finds significant application in heterogeneous catalysis and support due to its tuneable band gaps and effective intercalation of different compounds. By combining with semiconductor photocatalysts, GO and rGO can be used to create certain hetero structure composites with adjustable size and pore architectures, size distributions, and morphologies.

In this chapter, we discuss the recent development of research on the use of semiconductor NCs materials utilising GO and rGO in the photocatalytic degradation of synthetic organic dye. In chronological sequence, the production method, characterisation, and photocatalytic activity of some representative samples as well as the mechanism of photocatalysis of those materials with regard to some Organic dye degradation are described. Additionally, we have attempted to identify the main obstacles and potential areas for further improving the photocatalytic activity for industrial applications of the graphene oxide based photocatalysts.

Synthesis of GO and rGO

Jianguo Song et al [49] synthesized GO through the Hummer's method. In further specifics, 108 mL of H_2SO_4 and 12 mL of H_3PO_4 were combined with 5 g of graphite and 2.5 g of NaNO3

and swirled in an ice bath for 10 min. 15 g of $KMnO_4$ were then gradually added so that the mixture's temperature stayed below 5°C. The suspension was then agitated for 60 minutes and reacted for 2 hours in an ice bath before being stirred once more for 60 minutes in a 40°C water bath. The mixture was heated to a steady 98°C for 60 minutes while water was continuously added. Additional deionized water was added until the suspension had 400 mL in it. After 5 minutes, 15 mL of H_2O_2 was added. The reaction product was centrifuged and repeatedly rinsed with deionized water and 5% HCl solution. The product was then dried at 60°C. Anastasiia Kobyliukh et al [50] synthesized GO through modified Hummer' method.

Ning Cao et al [45] synthesized GO and rGO through Hummer's method. In 400 mL of water, 400 mg of GO was dissolved using ultrasonication for 30 minutes. A uniform brown GO aqueous solution was produced as a result. By removing NH_3H_2O, the pH of the suspension was brought down to 10. The weight ratio of hydrazine hydrate and GO was maintained at 10: 7 after amounts of the compounds were added to suspension and heated at 80°C for 24 hours. Gradually, a kind of dark flocculent substance precipitated from the solution. Using high-quality filter paper, the product was obtained. The finished black product was then dried for 24 hours at 80°C after being cleaned with methanol and water. By heating GO in a vacuum chamber in an inert atmosphere, such as nitrogen, it is possible to reduce GO by thermal treatment while mostly preserving the hexagonal lattice structure of the carbon atoms. Combination or hybrid methods combine chemical and thermal reduction to achieve a greater degree of reduction, which leads to the transition into graphene to obtain a higher ratio of carbon to oxygen. Fig. 1 shows the schematic route of the production line for GO and rGO.

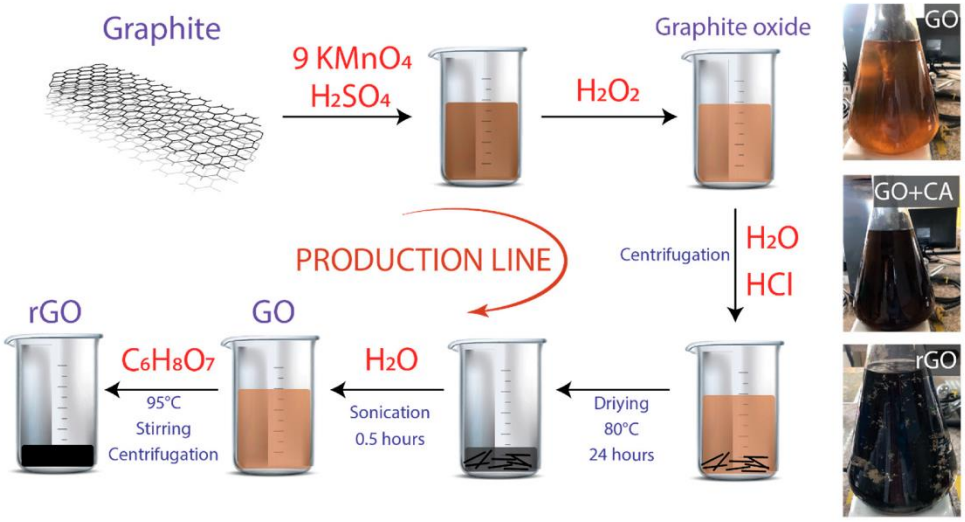

Fig. 1. Schematic representation of the procedure. The starting material is graphite powder. Inset:optical images of graphene oxide (GO), GO plus citric acid (CA), and reduced graphene oxide (rGO). (re-printed from Ref.45)

Properties of GO and rGO

Hydroxyl, carbonyl, epoxy and carboxyl functional groups are among the several oxygen functionalities found in GO [51,52]. By changing the oxygen functionality, it is possible to change the band gap of GO. Partially oxidised GO can serve as a semiconductor, but fully oxidised GO can work as an electrical insulator. The UV-vis absorption spectra were used to calculate the band gap energy of GO, which was found to be 3.26 eV. The hybrid structure's outstanding absorptivity and spatial charge separation are facilitated by the good mechanical strength, distinctive electrical properties, high catalytic activity, low density, wide surface area, and efficient electron-transporting capabilities of GO [53,54]. In order to improve photocatalytic activity, GO also functions as an excellent electron acceptor to increase photo-induced electron transfer [55].

rGO is superior than GO in terms of its strong features and potential applications, including better optical performance, increased electron mobility, higher conductivity, chemical stability, better adhesiveness, a larger surface area, superior thermal conductivity, and improved flexibility [56]. rGO can work well with metal oxides as a co-catalyst to improve photocatalytic redox capabilities under visible and UV light sources. It can also efficiently separate photo-generated electrons to surpass the rate of electron-hole recombination because of its greater electrical mobility. However, GO or rGO accelerates the photocatalytic degradation process due to their -interaction with organic dyes and the formation of hydrogen bonds amongst organic contaminants. Preventing electron-hole recombination can increase the photodegradation efficiency of photocatalysts based on GO/rGO [57]. This can be done by doping with metal oxide nanoparticles (NPs), which can change the band gap of the materials. For instance, it has been discovered that the integration of rGO on metal oxide NPs improves photodegradation activity due to improved charge separation and enhanced active or reactive sites, which in turn slows down the pace at which electrons and holes recombination [58-61].

Metal oxides - GO NCs as photocatalyst

When semiconducting metal oxide photocatalysts like ZnO, TiO_2, V_2O_5, and many more absorb light, photocatalysis occurs. When electrons move from the lower energy valence band to the higher energy conduction band, electron-hole pairs are produced. Through migration, the

newly formed electron-hole pairs start redox reactions with oxygen and water that break down the organic pollutants adsorbed on the surface of the photocatalyst. In order to increase the photodegradation efficiency GO was loaded on the metal oxide NPs. This might be explained by the fact that metal oxide-GO NCs have higher surface area that is active than GO alone. Additionally, GO sheets are capable of holding excited electrons from the metal oxide's conduction band to valence band with ease. As a result, the metal oxide-GO NC has a greater energy gap between the conduction band and valence band, which inhibits electron-hole pair recombination [62,63].

Beaula Ruby Kamalam et al [63] synthesized V_2O_5 nanorods (NRs) and V2O5-GO NCs by sonochemical process. GO was prepared by Hummer's method. To investigate the photodegradation of Victoria blue (VB) dye using the as-synthesized NRs and NCs under UV, visible and direct sun light. A standard stock solution was prepared with a dye concentration of 10 mg in 1L (10 ppm). About 10 mg of GO- V_2O_5 NCs was dispersed in 100 mL of VB dye solution. The bandgap for GO, V_2O_5 NRs, and GO- V_2O_5 NCs was estimated from the UV-Vis spectrum and is 2.2 eV, 2.22 eV, and 2.15 eV, respectively. GO- V_2O_5 NCs are a viable option for visible-light driven photocatalyst due to their low bandgap energy. The photocatalytic degradation efficiency was maximum in V_2O_5-GO NCs under direct sunlight. The electrons in V_2O_5 nanorods' valence band are stimulated to the conduction band and finally reached the go state during exposure to direct sun light. The effective transport of electrons from the conduction band of V_2O_5 to GO was demonstrated by the observed PL quenching for the GO-V_2O_5 nanocomposite. Since GO's relative energy level location is where the conduction band of V_2O_5 is located, GO functions as an electron quencher and slows down the pace at which charge carriers are recombined by V_2O_5 nanorods. In this way, GO advances the separation of charge carriers in V_2O_5 and serves as a sink for photogenerated electrons. During the photodegradation process, these electron-hole pairs generate hydroxyl radicals ($OH^{\bullet}$), superoxide radicals (O_2^-), and numerous other oxygenated reactive species. The degradation efficiency and the detailed photocatalytic mechanism is represented in Fig. 2.

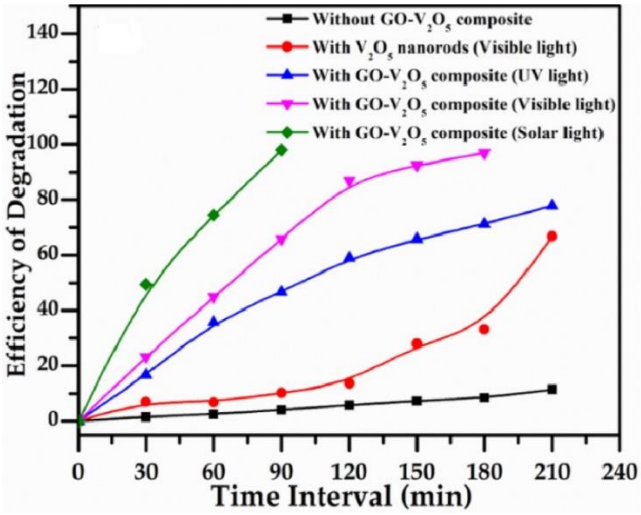

Fig. 2(a). Degradation efficiency of V_2O_5 NRs and V_2O_5-GO NCs under UV light and solar light (re-printed from Ref.64)

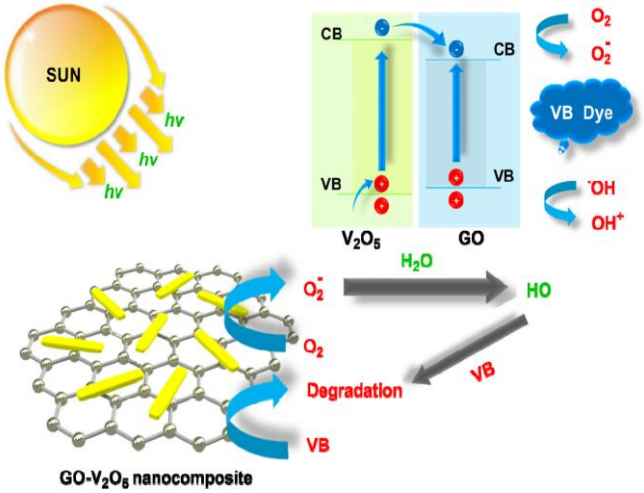

Fig. 2(b) Photocatalytic mechanism of V_2O_5-GO NCs (re-printed from Ref.64)

Ahmar Umar et al [36] synthesized GO through Hummer's method and Fe_3O_4-GO through chemical precipitation method. Fig 3 (a-f) represents the morphological structure of the as-prepared Fe_3O_4 NPs, GO, and Fe_3O_4-GO NCs. The nanoparticles are round and tightly packed due to high-density growth. Figure 3(c) depicts a typical TEM picture of Fe_3O_4 nanoparticles, which verifies the spherical shape morphologies. The typical FESEM and TEM pictures of the generated Fe_3O_4-GO nanocomposite are shown in Figures 3(e) and (f), respectively. These images proved that the GO sheets are adorned with nanoparticles. The TEM image shown in Figure 3(f) shows that the Fe_3O_4 nanoparticles are evenly distributed across the surface of the GO nanosheets. The TEM image revealed that the size of the nanoparticles are in the range of 11 ± 2 nm.

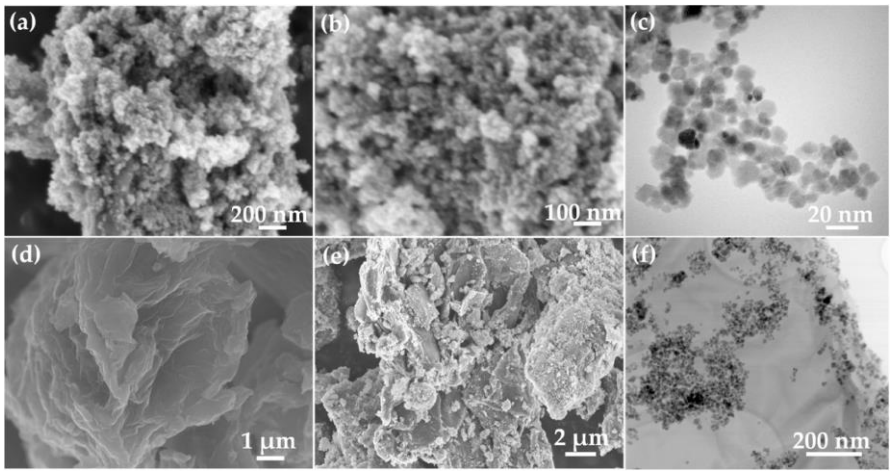

Fig. 3. Typical (a, b) FESEM images and (c) TEM image of Fe3O4 nanoparticles, (d) FESEM image of GO and (e) FESEM and (f) TEM images of Fe3O4-GO nanocomposite. (re-printed from Ref.36)

The energy band gap of GO was calculated using Tauc's plot and it was found to be 2.1 eV. After the addition of Fe_3O_4 NPs on GO the bandgap was reduced to 1.59 eV. The photocatalytic efficiencies of GO and Fe_3O_4 - GO nanocomposites towards Methylene blue (MB) under sunlight irradiation as shown in Fig. 4.

Photoirradiation excites the valence band electrons of the Fe_3O_4 to the conduction band to reduce the molecular O_2 to superoxide ions. In the valence band, holes are created as a result of this, and when H_2O is involved, the radicals OH are created. When the dye sample was continuously irradiated for 210 min, the degradation efficiency of GO towards MB dye was determined to be 75%. The greatest degrading efficiency of 91% for Fe_3O_4-GO, however, was seen after 30 minutes. This might be explained by Fe_3O_4-GO NCs having larger surface area that is active than GO. Additionally, electron-hole pair recombination is prevented in Fe_3O_4-GO NCs by the GO sheets, which also improve the energy difference between the conduction band and valence band in these materials. As a result, Fe_3O_4-GO NCs outperformed GO in terms of photocatalytic activity.

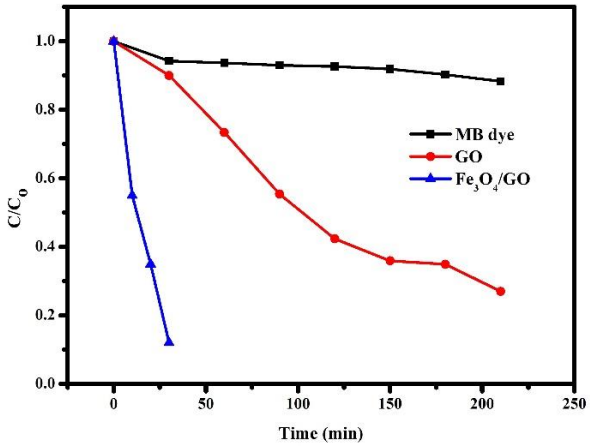

Fig. 4. Degradation efficiency of GO and Fe3O4-GO nanocomposites under sunlight (re-printed from Ref.36)

Beaula Ruby Kamalam et al [64] synthesized nanocomposites were synthesized using sonication assisted simple solution mixing method by loading of α-MoO_3 on GO sheets. GO was prepared through Hummer's method. TEM images revealed that the α-MoO_3 NRs decorated on the GO sheets (Fig. 5 a-d). The band gap values of the graphene oxide, α-MoO_3 and GO-MoO_3 were 2.4 eV, 3.0 eV and 2.96 eV respectively suggesting that the NCs are sensitive to visible region of wavelength.

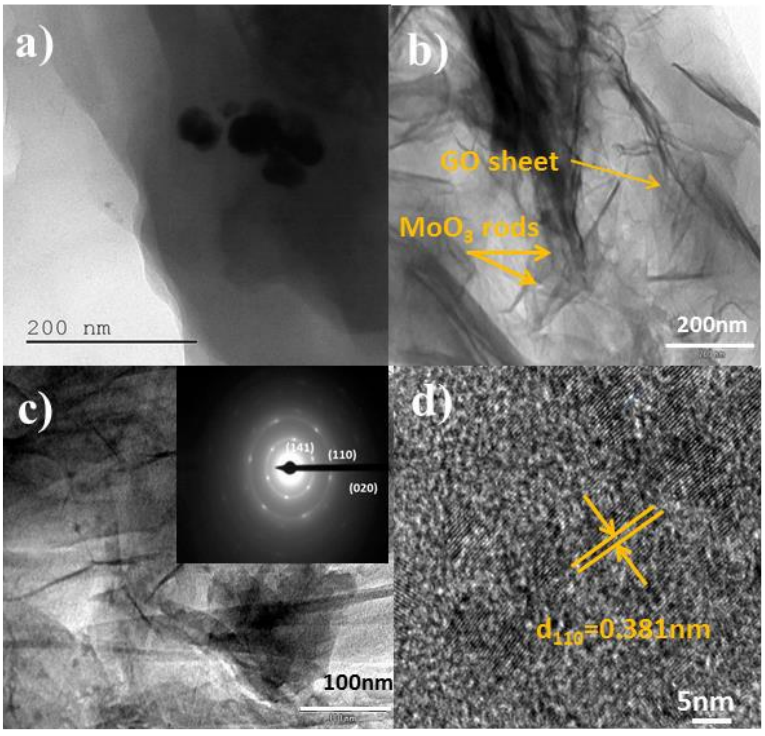

Fig.4 TEM images of (a) GO sheet (b) GO-MoO_3 (5 wt%) (c) GO-MoO_3 (10 wt %) (d) HRTEM images of GO-MoO_3 (5 wt%). Inset in c) SAED pattern of GO-MoO_3 (10 wt %). (re-printed from Ref.65)

Photocatalytic degradation efficiency of VB dye in the presence of as-synthesized NCs under visible light irradiation. The degradation efficiency of MoO_3 NRs was found to be 27% in 150 mins and GO-MoO_3 NCs was found to be 89% in 90 mins respectively (Fig. 5 a & b). The remarkable performance and enhanced absorptivity of the GO-MoO_3 nanocomposites are clearly responsible for the adsorption of dye molecules on the catalytic surface. The presence of graphene oxide may be the cause of the improvement in the speed of charge transportation and the separation of the charge carriers. As a result, the electrons produced by - MoO_3 are transported from graphene oxide's conduction band to molybdenum trioxide. Therefore, it is claimed that graphene oxide functions as an excellent electron acceptor in order to lower the recombination rate.

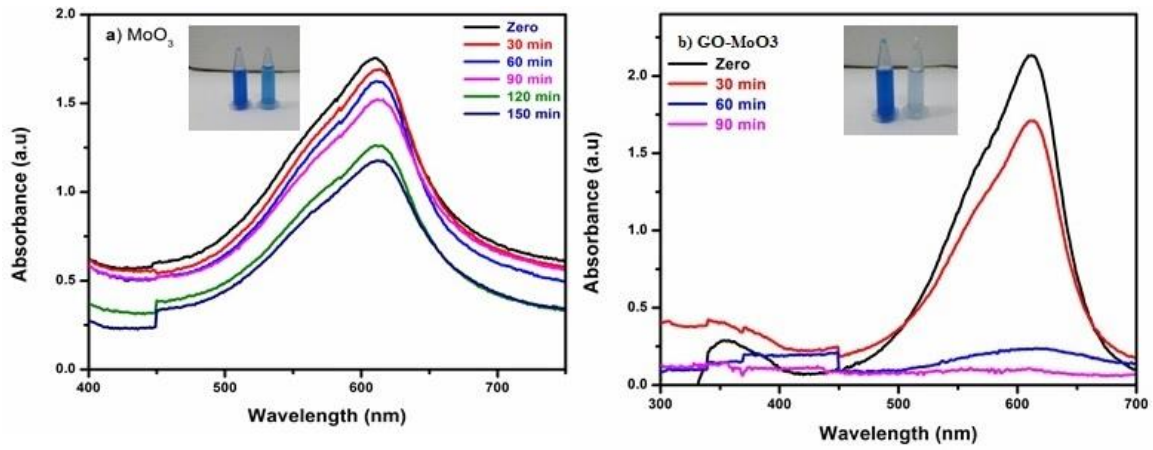

Fig. 5. Photocatalytic degradation VB dye under sunlight in the prensence of (a)MoO_3 & (b) GO-MoO_3 (re-printed from Ref.65)

Nathir. A. F., et al [27] synthesized GO-ZnO NCs embedded Ag and Cu NPs was synthesized through simple one pot method. SEM images represents the massive volume of ZnO nanoparticles is positioned over and between GO sheets (Fig. 6a) without any agglomeration. Fig. 6(b) and 6(c) shows the presence of Ag and Cu NPs on GO-ZnO NCs.

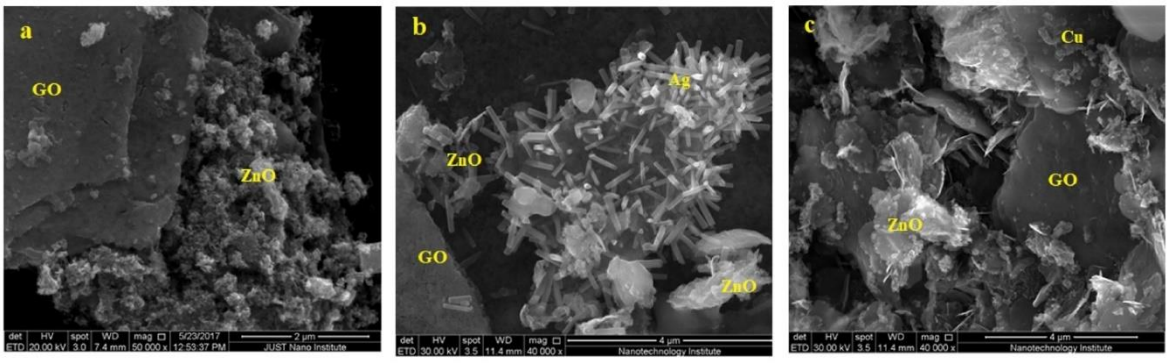

Fig. 6. SEM images of (a) GO−ZnO, (b) GO−ZnO−Ag, and (c) GO−ZnO−Cu (re-printed from Ref.27)

The photodegradation efficiency of MB dye was examined in the presence of as-synthesized GO−ZnO, GO−ZnO−Ag, and GO−ZnO−Cu NCs under sunlight irradiation is represented in Fig. 7 (a-c). The degradation efficiency of GO-ZnO was found to be 84% in 90 mins. After the addition of Ag NPs, it was found to be 100% in 40 mins and Cu NPs it resulted to be 50% in 90mins. The inclusion of silver nanoparticles, which reduced the recombination of electron-hole pairs, and the influence of one-dimensional ZnO nanorods, which increased light-harvesting capacity and significantly increased the photoactivity of the catalyst, are credited with this unusual discovery. Ag nanoparticles' synergistic effect on the activity of ZnO through electron and hole trapping had an impact on the increase in hydroxyl radical generation. The decrease in the degradation efficiency may be attributed to the electrical conductivity is higher in Ag than Cu NPs.

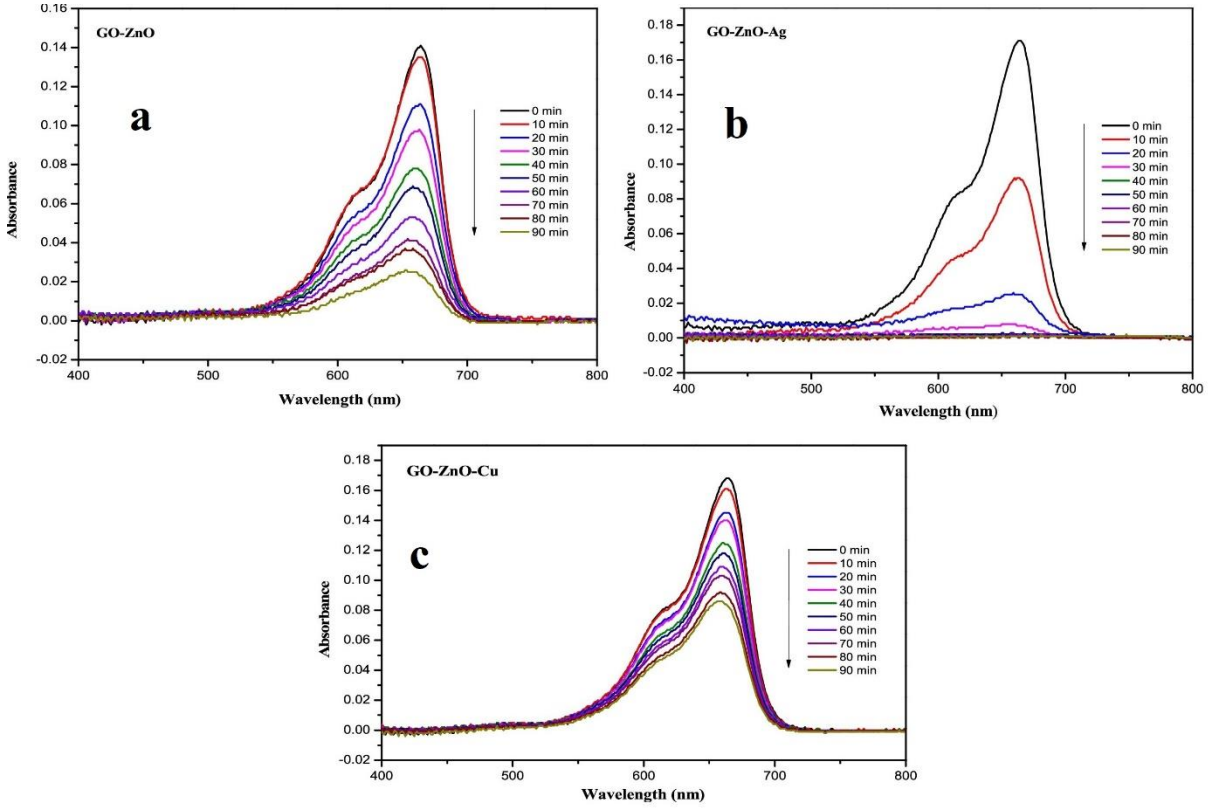

Fig. 7. Photocatalytic activity of (a)GO−ZnO, (b)GO−ZnO−Ag, and (c)GO−ZnO−Cu nanocomposites in degrading the MB dye (re-printed from Ref.27)

Metal oxides - rGO NCs as photocatalyst

In order to remove both organic and inorganic pollutants, carbon-based materials have typically been used in adsorption processes. Activated carbon is one of the most widely used adsorbents. The utilisation of rGO for dye adsorption has recently increased. Due to various faults in the graphitic domains and the persistence of surficial oxygen functions, rGO is considered effective

for the adsorptive removal of dyes. rGO often engages in interactions, electrostatic interactions, hydrophobic association, and structural conjugation with dyes. Numerous dyes can bind to rGO thanks to these interactions. rGO with a wide surface area and high porosity are preferred in order to increase the adsorption capacity; this is possible by carefully monitoring the quality of the GO precursor and the reduction technique [65,66].

Siong et al [67] synthesized rGO at different reduction temperatures via an environmentally friendly solvothermal approach. By removing functionalities that are oxygenated from the surface, the rGO produced at 160^{o}C clearly demonstrated the partial restoration of the sp2 hybridization. Evaluations were made of the impacts of the initial dye concentration, catalyst loading, light intensity, and solution pH. When 60 mg of catalyst, 50 ppm of dye at pH 11, and 60 W/m^2 of UV light source were utilised, it was shown that rGO-160 could produce a greater adsorptive removal (87.39%) and photocatalytic degradation (98.57%) of MB dye. After five consecutive cycles, there was no discernible decline in the MB photodegradation activity of rGO-160 (Fig. 8).

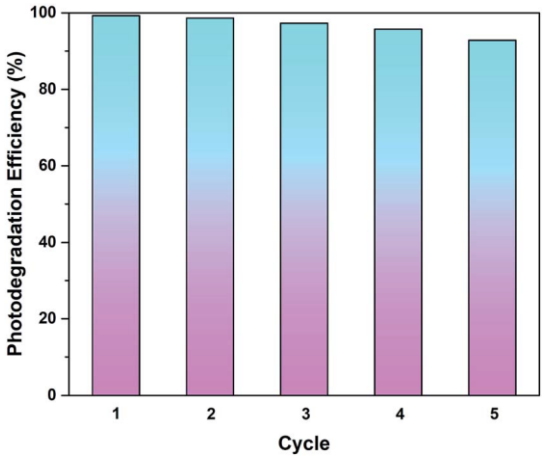

Fig. 8. Recycling tests of rGO-160 for the photocatalytic degradation of MB dye (re-printed from Ref.68)

M. Jarvin et al [15] successfully synthesized Mn_3O_4-rGO NCs through simple solvothermal method as shown in Fig. 9. The as-prepared NCs was used as a photocatalyst to degrade MB dye under sunlight. The pristine Mn3O4shows the efficiency of 34 % and the Mn_3O_4-rGO NC show the efficiency of 60% at 120 mins. The band-band transition that caused the strong emission to be seen at 424 nm can be seen in the PL spectra of Mn_3O_4 and Mn_3O_4-rGO NC. When compared to bare Mn_3O_4, the Mn_3O_4- rGO exhibits a peak intensity that is somewhat lower but still high. Due to edge defects in rGO, which cause a drop in peak intensity, excited

electrons are trapped into the surface via typical flaws. This will reduce the recombination of electrons and holes, enhancing the photocatalytic activity of Mn_3O_4-rGO NC.

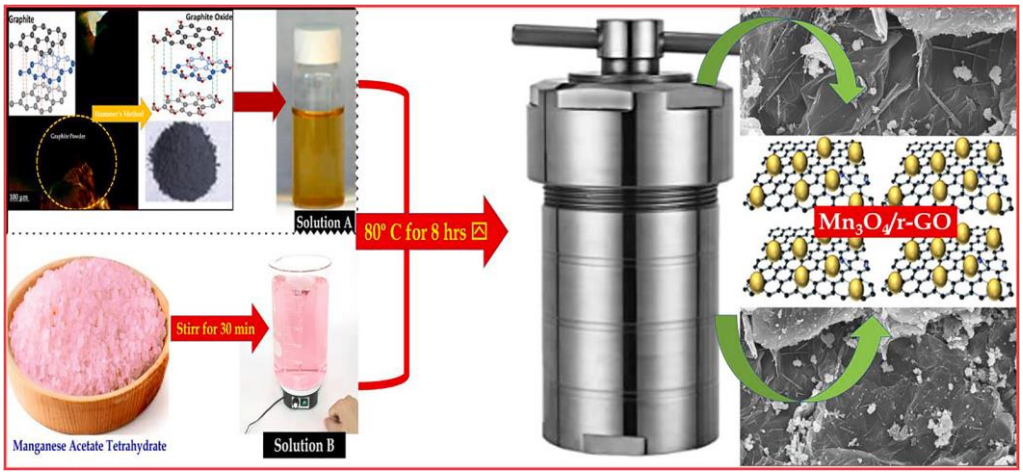

Fig. 9. Schematic representation of the synthesis of Mn3O4–rGO NC (re-printed from Ref.15)

R. Fatima et al [47] synthesized transition metal oxides (TMO's) and their composite with rGO through facile co-precipitation method (Fig. 10). GO was prepared via Hummer's method.

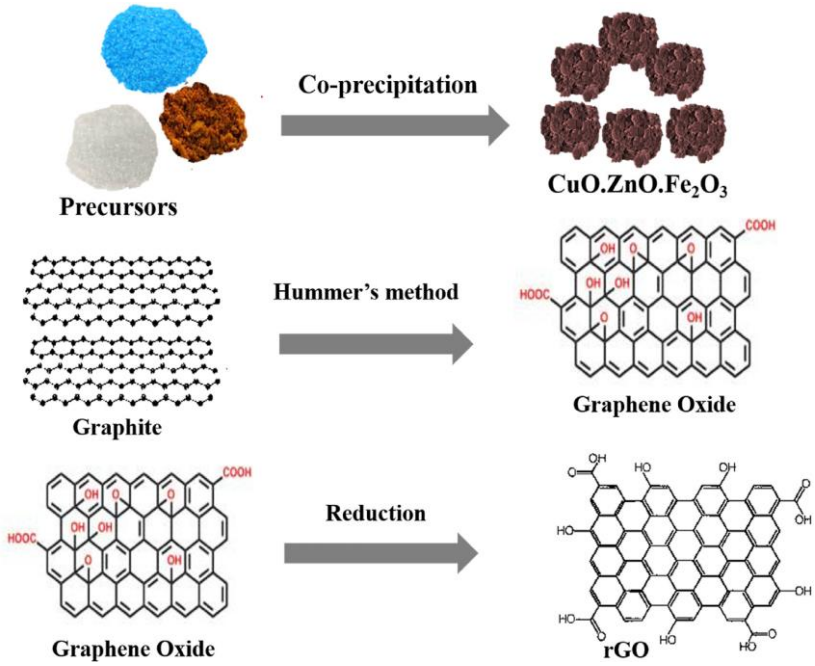

Fig. 10. Schematic illustration of mixed metal oxides CuO.ZnO.Fe_2O_3, GO and rGO (re-printed from Ref.47)

The photogenerated electron is excited toward the photocatalyst's conduction band. By directing electrons toward the high energy level, the hybrid of different metal oxides and

carbonaceous nanomaterials like GO, rGO, and CNTs can lessen the recombination of photogenerated electrons and holes. The oxygen molecules that were adsorbed on the photocatalyst's surface were converted into superoxide radicals (O_2^-) and hydroxyl ions were transformed into OH oxidant radicals. The stacking properties of the carbonaceous materials rGO and CNTs make them an effective instrument for snatching electrons from the conduction band of mixed metal oxides and advancing redox reactions. In order to lessen photocorrosion, rGO provides an active site that postpones the recombination of photogenerated electrons and holes. Under UV irradiation, the CuO.ZnO.Fe_2O_3/rGO NCs exhibit the highest rate of MB dye degradation, 87%, in 90 minutes.

Conclusion

From the above mentioned research reports it can be seen that photocatalytic degradation of organic pollutants, such as dyes and compounds that are toxic to humans and aquatic and terrestrial organisms as well as carcinogenic to humans, is crucial from both a human and environmental standpoint. Degradation by photocatalysis is an effective technique for getting rid of these harmful substances found in waste water. pH value, catalyst dosage and temperature play a significant role in photocatalysis. Additionally, rGO has a superior conductivity behaviour, which narrows the band gap to provide an intermediary energy level that encourages the PC to display its activity in the visible area and improves separation and reusability. It has also been discovered that external magnets may successfully separate nanocomposites having magnetic characteristics, such as rGO doped with iron nanoparticles or iron oxide. It may be possible for the current water treatment facilities and other water purification systems to use photo catalysis technology. When combined with other cutting-edge water treatment techniques like membrane technology, adsorption, etc., photo catalysis may provide synergistic benefits.

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