Materials Research Express

PAPER

Bismuth/bismuth oxide-incorporated reduced graphene oxide nanocomposite: synthesis, characterisation, and photocatalytic activity

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Keywords: fabrication, bismuth-based nanocomposite, Bi/Bi$_2$O$_3$, rGO, photocatalytic activity

Abstract

This study loaded Bi/Bi$_2$O$_3$ on the surface of reduced graphene oxide (rGO) to perform a two-step facile synthesis of rGO@Bi/Bi$_2$O$_3$ as a bismuth-based nanocomposite. First, Bi/Bi$_2$O$_3$ nanocomposites were synthesised via a solvothermal process using Bi(NO$_3$)$_3$·5H$_2$O as the Bi$^{3+}$ precursor and dimethyl sulfoxide (DMSO) as the solvent. Second, we exfoliated rGO in water to functionalise Bi/Bi$_2$O$_3$ with a few layers of rGO. Obtained nanocomposites were characterised with scanning electron microscopy and X-ray diffraction. We also measured the nanocomposites’ photocatalytic activity using cationic dyes, specifically methylene blue (MB) and rhodamine B (RhB). Additionally, ultraviolet-visible spectroscopy was used to determine the optical properties of rGO@Bi/Bi$_2$O$_3$. Photodegradation was recorded under differing durations of exposure to visible light. Reaction rates were recorded at 14.6 × 10$^{-4}$ min$^{-1}$ and 22.2 × 10$^{-3}$ min$^{-1}$ for MB and RhB, respectively, while photodegradation efficiency was logged at 17% and 81%.

1. Introduction

Water treatment is an increasingly important area of environmental research. In particular, there is considerable interest in applying nanomaterials as a water-treatment method. For example, antifouling nanomembranes based on carbon materials such as reduced graphene oxide (rGO) and cellulose have relevant physical, chemical, and surface properties for water treatment [1–3]. However, antifouling membranes can also comprise inorganic materials in the form of polymers, mixed polymers, metals, and ceramics [4, 5]. Ceramic membranes are typically comprised of aluminum oxide, silicon carbide, and zirconia, all of which have excellent thermal stability, mechanical properties, biological relevance, low production cost, environmental friendliness, and long lifespan [6]. Various fields make use of a nanosheet with improved thermal and mechanical properties, as well as larger surface area; these nanosheets are derived from hybridising PVA nanoparticles (NPs), metal oxide (MO) NPs, polysaccharide products such as chitosan and cellulose derivatives, generating a modified GO surface [7]. Nanoparticles (notably ZnO and CuO NPs) also have important applications in solar-powered devices, specifically in the form of quantum dots due to their small bandgaps [8]. Water desalination treatments often use GO with titanium dioxide, zinc oxide, and magnetite NPs [9–11] that have high water solubility, biological properties, and low cost [12]. In addition, cellulose derivatives such as sodium carboxymethyl cellulose (CMC) have various biological applications [13]. However, CMCs have low solubility and other drawbacks related to unreacted species in the system; to improve solubility, compounds such as glutaraldehyde are typically added, but they are highly toxic [14]. Recent advancements have combined MO nanomaterials and rGO to enhance their suitability for surface functionalization, biomedical implementation, drug systems, and water-soluble applications [15]. Due to their low energy density, these materials can be used as energy storage devices and alternatives to standard batteries [16–18].

Bismuth-based NPs (BiNPs) are potential theranostic agents [19] and have been tested in various clinical procedures, such as diagnostic CT imaging [20] and radiotherapy [21–23]. For the former, BiNPs can improve
device sensitivity and local CT numbers through increasing target absorption and the likelihood of disease detection, while for the latter, the NPs boost radiation effects on target tissue. Recent evidence has suggested that rGO is a radiosensitizing agent [24–27]. Therefore, Bi-based nanomaterials should improve in performance if combined with rGO. This study fabricated an rGO@Bi/Bi$_2$O$_3$ nanocomposite via loading Bi@Bi$_2$O$_3$ onto the surface of rGO. We then measured the nanocomposite’s photocatalytic activity toward dication dyes methylene blue (MB) and rhodamine B (RhB), with the aim of determining its suitability as a radiosensitizer agent.

2. Materials and methods

Potassium permanganate (KMnO$_4$), CMC, ammonium nitrate (NH$_4$NO$_3$), and graphite were provided by Sigma-Aldrich. A Shimadzu UV-2450 spectrophotometer (Shimadzu 6000) and a scanning electron microscope (SEM; JEOL-JSMIT100–30 kV) were used to examine x-ray peaks.

2.1. Fabrication of nanomaterials

2.1.1. Synthesis of Bi/Bi$_2$O$_3$ nanomaterial

To synthesize the Bi/Bi$_2$O$_3$ nanocomposite, 2.0 g Bi(NO$_3$)$_3$, 5H$_2$O (AR grade, Sigma–Aldrich) was dissolved in 30 ml dimethyl sulfoxide (DMSO, Sigma–Aldrich). The mixture was then heated to 190°C, mechanically agitated for 2 h at that temperature [28, 29], and then centrifuged. The resultant precipitate was washed several times with ethanol/acetone (2:1), and then vacuum-dried at 50°C for 12 h, yielding Bi/Bi$_2$O$_3$ as a grey powder.

2.1.2. Synthesis of reduced graphene oxide (rGO) nanostructure

The study generated rGO following methods from Hummers and Offeman [30]. First, 8.0% graphite/H$_2$SO$_4$ was made via combining 8 g ammonium nitrate (NH$_4$NO$_3$) and graphite powder with 98% H$_2$SO$_4$ in an ice bath. Potassium permanganate (KMnO$_4$) was then stirred into the mixture for 2 h at 90°C until completely dissolved, forming a GO precipitate. Subsequently, hydrogen peroxide (48 ml) was added to the solution. The resultant mixture was cleaned with hydrochloric acid (10.0%), and then dried at 45°C for 24 h in double-distilled water (DDW). Graphene oxide (1.0 g) was then sonicated in DDW (100 ml) for 15 min until fully mixed. Ammonium hydroxide (5 ml) and hydrazine hydrate (5 ml) were added to the GO solution, and stirred for 30 min. This mixture was heated to 90°C in a water bath for 45 min with constant stirring. Darkening of the solution indicated that GO reduction was complete. The final rGO sample was collected and used for further analyses [31].

2.1.3. Synthesis of rGO@Bi/Bi$_2$O$_3$

A 50 mg suspension of rGO in DDW was stirred for 3 h before adding 50 mg of Bi/Bi$_2$O$_3$ dropwise, with vigorous agitation. After stirring overnight, the product was washed with water, then ethanol several times, and finally dried at 70°C. Characterisation was performed using SEM, FT-IR, and X-ray diffraction (XRD).

2.2. Photocatalytic activity and electron transfer

Photodegradation of methylene blue (MB) and rhodamine B (RhB) was performed under visible light at differing exposure durations. In a quartz cuvette, 200 μl of stock solution (6.0 mg of rGO@Bi/Bi$_2$O$_3$ in 10 ml DDW) was combined with 100 μl of the appropriate dye (both 1.0 × 10$^{-3}$ M). Double-distilled water was then added until the volume reached 3 ml. The resultant product was exposed to light, and the reaction was followed with UV–vis spectroscopy.

3. Result and discussion

3.1. Characterization of rGO@Bi/Bi$_2$O$_3$ nanocomposite

3.1.1. Microscopic analysis

The surface of rGO appears as a nanosheet (figure 1), with Bi/Bi$_2$O$_3$ comprising mixed nano-spherical and nanorod structures. The rGO@Bi/Bi$_2$O$_3$ nanocomposite was also of mixed composition, with Bi/Bi$_2$O$_3$ decorating the rGO surface. We then used energy dispersive X-ray (EDX) analysis to determine the percentage of each element in the fabricated rGO@Bi/Bi$_2$O$_3$ nanocomposite.

3.1.2. X-ray diffraction (XRD)

Figure 2 shows the characteristic XRD patterns of rGO, Bi/Bi$_2$O$_3$, and rGO@Bi/Bi$_2$O$_3$. The main XRD peak of rGO was 2θ = 25.02 with a layer spacing of 0.34 nm, indicating that GO was successfully reduced to rGO. The rGO nanosheets were generally exfoliated into a monolayer, resulting in a new lattice structure that is indicated by the broad peak [32]. These findings suggest that differences in intercalated oxide functionalities may cause
Figure 1. SEM images of rGO nanosheet (a), SEM and TEM images of Bi/Bi$_2$O$_3$ (b and c), SEM of rGO@Bi/Bi$_2$O$_3$ (d and e), and EDX analysis of rGO@Bi/Bi$_2$O$_3$.

Figure 2. XRD of (a) Bi/Bi$_2$O$_3$, (b) rGO@Bi/Bi$_2$O$_3$, and (c) rGO.
pre-exfoliation of vein graphite directed to different interlayer spacings for GO group content. These findings suggest that differences in intercalated oxide functionalities may cause pre-exfoliation of vein graphite directed to different inter-layer spacing for GO group content. The phase patterns of Bi/Bi₂O₃ were compared to JCPDS 76–1730, which corresponded to the monoclinic phase of Bi and Bi₂O₃ NPs (figure 2(a)). As a result, the creation of a pure phase was established [33].

The nanocomposite rGO@Bi/Bi₂O₃’s XRD patterns corresponded to those of Bi/Bi₂O₃ NPs. This highlighted the presence of Bi/Bi₂O₃ on the rGO surface. The Scherrer formula was used to determine the crystalline size, and the size of Bi/Bi₂O₃ was recorded at 48 nm, which agrees well with the results of TEM investigation.

3.1.3. Zeta potential
We detected suspension stabilities (measured using zeta potential) of rGO and rGO@Bi/Bi₂O₃ in DDW at room temperature, where the stability range was approximately ±30 mV [34]. Nonionic capping reagents and polymers without electrostatic repulsion can be used to determine zeta potential stability. The zeta potentials of rGO and rGO@Bi/Bi₂O₃ were −31 and −40 mV, respectively (figure 3), emphasising the stability of synthesised nanocomposites.

3.1.4. UV–vis spectroscopy
Distinct from GO, the rGO spectrum (figure 4(a)) shows a strong sharp peak at approximately 258 nm, indicating that oxygen functionality has been almost completely removed and a C=C conjugated graphene structure has been established [35]. Electron transfer and bandgap values of the synthesised nanocomposite determined ROS generation via the Tauc equation (equation (1)) [36]:

\[ α \nu = A(\nu - E_g)n \]

where \( α \) = absorption coefficient, \( ν \) = frequency of light, \( h = \text{Planck’s constant} \), \( hν = \text{photon energy} \), \( A = \text{proportionality constant} \), and \( E_g = \text{bandgap} \). Bandgap is calculated as \( n = 1/2 \). To approximate the bandgap using the linear line of the curve, we determined the relationship between \( (αν)^2 \) and \( hν \) (figure 4(b)). Bandgaps for Bi/Bi₂O₃ and rGO@Bi/Bi₂O₃ were 3.0 and 2.6 eV, respectively.

3.2. Photocatalytic activity
We used UV–vis spectroscopy to detect the photocatalytic activity of 6 mg/10 ml rGO/Bi/Bi₂O₃ under various exposure durations to visible light (figure 5). We observed a quenching effect of the nanocomposite under visible light, resulting in characteristic peaks at 664 nm for MB and 560 nm for RhB. The rate constants of the reactions were evaluated using equation (2) [10, 11]:

\[ \ln \left( \frac{C}{C_0} \right) = -k_{obs}t \]

where \( C_0 \) (mg/L) is initial MB or RhB concentration and \( k_{obs} \) photodegradation rate (kobs), proportional to the dye concentration. For MB and RhB dyes, \( k = 14.6 \times 10^{-4} \) and \( 22.2 \times 10^{-5} \text{ min}^{-1} \), respectively (figure 5). Photodegradation efficiency was determined using equation (3) [37]:

![Figure 3. Zeta potential of rGO, and rGO@Bi/Bi₂O₃.](image-url)
where variations in dye absorption peaks were $A_0$ and $A_t$. After 110 min of rGO@Bi/Bi$_2$O$_3$ catalysis, the photodegradation efficiencies for MB and RhB were 17% and 81%, respectively (figure 5). Photodegradation efficiency is determined based on the amount of reactive oxygen species (ROS) such as $^{1}$O$_2$, $^{·}$OH, or O$_2$·$^{-}$ generated. Here, rGO acted as an electron acceptor from the Bi/Bi$_2$O$_3$ conduction band (CB), causing rapid oxidation and formation of superoxide radicals that ultimately converted dyes to CO$_2$ and water [36, 37].

3.3. Photodegradation reaction mechanism of Dyes

Scheme 1 depicts a plausible photocatalysis mechanism for the rGO@Bi/Bi$_2$O$_3$ nanocomposite. Upon Once irradiation with visible light, rGO-Bi/Bi$_2$O$_3$ produces an $e^−$-$h^+$ pair that is stabilised by the electron acceptor rGO [38, 39]. Doping Bi with the Bi$_2$O$_3$ crystal structure decreases the nanocomposite’s bandgap via the Z-scheme mechanism, where the heterojunction between Bi and Bi$_2$O$_3$ increases electron transfer. As OH content increases, the photocatalytic activity of Bi/Bi2O3 also improves [29]. In the presence of the rGO nanosheet, photogenerated electron-hole pairs were efficiently separated, favouring the continuous production of free charge carriers through accepting electrons from Bi/Bi$_2$O$_3$.

Therefore, with charge carriers separated upon the irradiation of rGO@Bi/Bi$_2$O$_3$, electrons in the conduction band (CB) of Bi/Bi$_2$O$_3$ can freely migrate to the rGO surface, where they are captured by adsorbed oxygen (O$_2$) to generate superoxide radicals (O$_2$·$^{−}$). Whereas the holes left in the valence band (VB) of Bi/Bi$_2$O$_3$ then oxidise hydroxide ions (OH$^−$) to generate hydroxyl (OH) radicals. These generates OH and O$_2$·$^{−}$ reactive species radicals degrade MB and RhB into CO$_2$ and H$_2$O [40–42].

4. Conclusion

This study fabricated a bismuth-based nanocomposite (rGO@Bi/Bi$_2$O$_3$) by loading Bi/Bi$_2$O$_3$ on reduced graphene oxide (rGO), then characterized its structure and photocatalytic activity, in comparison with rGO.
We demonstrated that the fabricated nanocomposite can degrade two cationic dyes (methylene blue and rhodamine B) after light exposure. After subjecting the nanocomposite to visible light, we recorded reaction rates of $14.6 \times 10^{-4} \text{ min}^{-1}$ and $22.2 \times 10^{-3} \text{ min}^{-1}$ for MB and RhB, along with photodegradation efficiencies of 17% and 81%. We believe that our study makes a significant contribution because this is the first reported fabrication of combining rGO and Bi/Bi$_2$O$_3$ to generate a nanomaterial with enhanced properties. The characterization we provided here can act as a starting point for further analysis of this nanocomposite, paving the way for multiple potential applications in water treatments and theranostics.
Acknowledgments

The authors would like to thank the Deanship of Scientific Research, Taif University, Taif, Saudi Arabia for supporting this project #1-441-114.

Data availability statement

No new data were created or analysed in this study.

Conflicts of interest

There is no conflict to declare.

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