Visible light driven photocatalytic nanocomposite for the degradation of Rhodamine B in water

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Abstract. Parallel to the fast growing of population around the world, there has been a rapid increase in the amount of toxic organic waste that end up in water bodies, which is a threat to human health and to the environment. Because of this, there is need for the development of materials that are able to degrade them while using the sunlight. In this work, a Bi₂O₃/rGO/MoO₃ composite was successfully synthesized by a solvothermal method under ambient pressure and low temperature. SEM, STEM and XRD techniques were used to characterize the morphological and crystallographic properties of the composite. It was demonstrated that the amount of GO in the synthesis of the composite has a great effect in the photocatalytic activity and it was found that the best ratio between Bi₂O₃ and GO was 300:1. The synthesized composite photocatalyst with ratio of 300:1 presented and enhanced photocatalytic activity for Rhodamine B as it was able to degrade around 70 % after 240 min under visible light irradiation, compared to pristine Bi₂O₃ that was able to degrade around 55 %. Results from this study illustrate the fabrication of a new ternary composite, which shows promising results for its application in the degradation of organic pollutants in water.

1. Introduction
Parallel to the fast growing of population around the world, there has been a rapid development of industry bringing with it an increased amount of industrial and household wastewater containing toxic organics that are persistent even after purification treatments, resulting in an increased harm to the health of human beings and animals [1], [2]. As a consequence, the interest in photocatalytic materials has been growing in the last decade due to its great application in environmental pollution degradation using solar energy [3]. However, most of the semiconductor oxide photocatalysts generally have a wide band gap and consequently they are active only under the illumination of ultraviolet (UV) light (which is about 5% of the solar light [4]) restricting its industrial application. The most common example is TiO₂, which has an excellent chemical stability, is non-toxic and has an excellent photocatalytic activity; however, pure TiO₂ only absorbs UV light and has a fast recombination process of photogenerated electron-hole pairs limiting its practical application [5]. Therefore, the development of visible light driven photocatalysts has been a topic of increasing interest among researchers. Recently, bismuth based photocatalysts, such as Bi₂O₃, Bi₂S₃ and BiOX (X= Cl, Br, I), have attracted interest because they present narrow band gaps and good photocatalytic activities under visible light [6]. Specifically, Bi₂O₃ is an important material because it presents interesting electrical and optical properties, which makes it a promising material in the field of photocatalysis as it presents a band gap between 2.6 and 2.9 eV [7], [8]. In the same context, MoO₃ is a material that present a band gap of 2.9 eV and it also present good chemical stability, is nontoxic and
it presents an excellent capacity to adsorb dyes which is a desirable property for photocatalytic purposes, however, it present the drawback of fast recombination time of electron-hole pair compromising its applicability in photocatalytic purposes [9], [10]. One way to overcome such drawback is its coupling with other semiconductors that have a similar band structure in order to construct heterojunction or Z-scheme systems [11]-[13] and one material that has proven to be an efficient component for the enhancement of the efficiency of photocatalysts is graphene, as it present unique optical an electrical properties [14].

Herein, in this work we present the development of a visible light driven Bi\textsubscript{2}O\textsubscript{3}/rGO/MoO\textsubscript{3} (BiMoGO) photocatalytic nanocomposite for the degradation of Rhodamine B (RhB) in aqueous solution. Particularly, we study the influence of the Bi\textsubscript{2}O\textsubscript{3} and rGO ratio in the photocatalytic performance of the samples. The photocatalytic activity of the composites was evaluated for their ability to degrade RhB under visible and UV light irradiation. In addition, the samples were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM).

2. Experimental

2.1. Reagents

Bismuth (III) nitrate pentahydrate (99.99 %), sodium citrate tribasic dihydrate (99 %), ammonium hydroxide (28-30 %), thiourea (99 %), rhodamine B (RhB) and sodium molybdate dihydrate (99 %) were purchased from Sigma-Aldrich. N,N-Dimethylacetamide (DMAc) was purchased from Merck. All reagents were of analytical grade and were used without further purification and all solutions were prepared using deionized water (18.2 M\textsubscript{Ω}·cm).

2.2. Synthesis of bismuth (III) oxide (\textit{Bi}_{2}\textit{O}_{3})

Firstly, 1.323 g of sodium citrate were dissolved in 150 mL of deionized water, then 1.455 g of bismuth (III) nitrate pentahydrate were added into the solution and was put into a ultrasonic bath for 10 min. Then the solution was stirred for 2 h and then the pH was adjusted to 9 with ammonium hydroxide and was left under constant stirring for another 2 h. Finally, the solution was transferred into a Teflon-lined autoclave and was put in an oven at 180 ºC for 24 h. Afterward, the solution was filtered and wash with water and anhydrous ethanol several times and the precipitate was dried in a vacuum desiccator overnight. Once the powder was dry, it was heated with a temperature ramp of 5º C/min until 360º C, once the temperature was reached it was maintained there for 3 h, then it was left to cool down naturally.

2.3. Synthesis of graphene oxide (GO)

Graphene oxide was synthesized through a modified Hummer method. Briefly, 2 g of graphite were added to a mixture of sulfuric acid/nitric acid (3:1 v:v) and was put in an ultrasonic bath for 1.5 h. Then potassium permanganate was added to the solution and the temperature was raised to 40º C and was left under magnetic stirring for 2.5 h. Afterwards, a certain amount of deionized water was added and the temperature was raised to 90º C and left under magnetic stirring for 24 h. Finally, more water was added and then a certain amount of hydrogen peroxide was added into the mixture until the color of the solution turned from dark brown to light brown. Then the solution was washed with deionized water until a neutral pH was obtained. Once the solution was neutral, the sample was freeze dried.

2.4. Synthesis of Bi\textsubscript{2}O\textsubscript{3}/rGO/MoO\textsubscript{3} (BiMoGO) composite

Different amounts of GO were dissolved in 30 mL of deionized water in order to achieve different ratios of Bi\textsubscript{2}O\textsubscript{3}/GO (100:1, 200:1, 300:1 and 400:1), the amount of Bi\textsubscript{2}O\textsubscript{3} used was 300 mg. Once the GO was completely dissolved, the solution was mixed with 30 mL of DMAc and put into a 3-necked flask and was stirred until a homogeneous solution was obtained. In a separate beaker, 15 mg of sodium molybdic dihydrate and 4.8 mg of thiourea were dissolved in 5 mL of deionized water, after a homogeneous solution was obtained it was added drop wise into the GO/DMAc solution and kept under constant stirring for 10 min. Then Bi\textsubscript{2}O\textsubscript{3} was added into the solution and was stirred for 5 min and it was put into a ultrasonic bath for 5 min. Next, the 3-necked flask was put into an oil bath preheated at 150º C and was put into reflux for 10 h. Finally the solution was left to cool down naturally, filtered and washed with deionized water and ethanol several times and the precipitate was
left to dry in a vacuum desiccator at room temperature. The obtained composites were labeled 100:1, 200:1, 300:1 and 400:1 depending on the ratio between Bi₂O₃:GO used.

2.5. Characterization of Bi₂O₃ and BiMoGO
The morphology of the as obtained particles was studied using a Nova NanoSEM 200 (FEI Company, USA) Scanning Electron Microscope with an acceleration voltage of 15 kV. X-ray diffraction pattern recorded from 20° to 80° were obtained by an Empyrean (PANalytical, USA) X-ray diffractometer using CuKα radiation (λ = 1.5406 Å).

2.6. Photocatalytic activity test
The photocatalytic activities of Bi₂O₃ and BiMoGO composites were evaluated by degradation of Rhodamine B (RhB) under visible (λ from 390-600 nm) and UV (λ from 300-380 nm) light irradiation. The photocatalytic system for catalytic reactions includes a 300 W Xe light source (MAX-303, Asahi Spectra) with an illumination area of 16x16 mm, the nominal power of the lamp used was of 100%. In a typical photocatalytic experiment, 40 mg of the powder photocatalyst were dispersed in 80 mL of a solution of RhB of 10 ppm and put into an ultrasonic bath for 2 min. Before being irradiated, the suspensions were magnetically stirred in the dark for 30 min to complete the adsorption-desorption equilibrium between the photocatalyst and the dye. Then the solution was exposed to visible or UV light irradiation under magnetic stirring. For the degradation analysis, 0.5 mL of the suspension was taken from the reaction at given time intervals during the process, the solution was centrifuged at 13,500 rpm for 5 min, then the UV-vis spectra of the centrifuged solution was recorded using a spectrophotometer. All photodegradation experiments were carried out at 25°C.

3. Results and discussion

3.1. Bi₂O₃ and BiMoGO characterization
Figure 1 shows the representative SEM and STEM images of the as obtained Bi₂O₃ and BiMoGO (300:1) composite. From Figure 1a it can be seen that the Bi₂O₃ particles have a spherical form of diameter around 2 µm that is composed of annealed worm-like nanorods with diameter of 100±15 nm. This is an interesting feature as it leaves gaps between adjacent nanorods increasing the surface area. Fig. 1b and 1c show structure of BiMoGO. Here, it is shown how the rGO sheets cover the Bi₂O₃ particles creating the composite. This is more evident in Fig. 1c where it can be seen how the rGO sheets appear to be translucent and in the center there are darker areas corresponding to the Bi₂O₃ particles, confirming that the composite is being formed.

Figure 1. Representative SEM images of a) Bi₂O₃ and b) BiMoGO (300:1) and representative STEM image of c) BiMoGO (300:1).

Figure 2 shows the XRD patterns of a) Bi₂O₃ and b) BiMoGO (300:1). From Fig. 2a, it can be seen that Bi₂O₃ material shows well-defined peaks and high crystallinity. Pattern matching was performed using the PDF card 01-071-0465 for Bi₂O₃ with spatial group P21/c (14), the obtained cell parameters are a = 5.8496 Å, b = 8.1648 Å, c = 7.5101 Å, α = γ = 90° and β = 112.977° corresponding to a monoclinic crystal structure. The pattern from Fig. 2b can be indexed to spatial group P21/c (14) corresponding to monoclinic Bi₂O₃ and spatial group C2/c (PDF card 01-084-1466) with cell parameters a ≈ 29.1940 Å, b ≈ 8.0830 Å, c ≈ 16.8160 Å, α = γ = 90° and β ≈ 95.472° corresponding to monoclinic Mo₉O₂₆ which is a MoO₃ phase with oxygen vacancies. The observed, the calculated and the difference profiles of the
XRD data have been obtained by Rietveld analysis. Lattice parameters, unit cell volume, crystallite size and the goodness of fitting parameter ($\chi^2$) are listed in table I. The fit between observed and calculated profiles has been found to be relatively good which confirms the structural stability. Presence of Bi$_2$O$_3$ and MoO$_3$ phases was confirmed to be present in the composite material, in which the MoO$_3$ phase has oxygen vacancies present.

Table I. XRD data obtained by Rietveld analysis for pure Bi$_2$O$_3$ and composite BiMoGO (300:1). Lattice parameters, unit cell volume of P21/c and C2/c phases, crystallite size and the goodness of fitting parameter ($\chi^2$).

| Material       | Spatial group | a (Å)  | b (Å)  | c (Å)  | V (Å$^3$) | $\alpha$ (º) | $\beta$ (º) | $\gamma$ (º) | $\chi^2$ |
|----------------|---------------|--------|--------|--------|-----------|--------------|-------------|--------------|---------|
| Pure Bi$_2$O$_3$ | P21/c         | 5.84   | 8.16   | 7.51   | 330.57    | 90.00        | 112.97     | 90.00        | 8.40    |
| BiMoGO (300:1)  | P21/c         | 5.83   | 8.15   | 7.44   | 326.89    | 90.00        | 112.97     | 90.00        | 1.46    |
|                | C2/c          | 29.19  | 8.08   | 16.81  | 3915.69   | 90.00        | 95.47      | 90.00        | 1.46    |

3.2. Bi$_2$O$_3$ and BiMoGO characterization

The photocatalytic activities of Bi$_2$O$_3$ and BiMoGo with different Bi$_2$O$_3$:GO ratios were evaluated by the degradation of RhB in water under visible light irradiation. The changes in RhB concentration were monitored by the maximal absorption in UV-vis spectra at 553 nm, as shown in Figure 3a, where the variation of the RhB concentration (C/CO) is plotted against time. Here one can see that the variation in the Bi$_2$O$_3$:GO ratios of the composites have a great effect in their photocatalytic activity, with the ratio 300:1 being the one with the best performance and degrades around 70% of the total concentration after being irradiated for 260 min with visible light and the material with the lowest degradation percent is pristine Bi$_2$O$_3$.

The evaluation of the photocatalytic activity under UV light irradiation was also performed, as shown in Figure 3b. Here it can be seen that, as in the case of degradation under visible light, the photocatalytic activity of the composites with different Bi$_2$O$_3$:GO ratios varies, having the best activity with the composites with 300:1 and 400:1 ratio with a complete degradation of RhB after 120 min irradiation.
It is known that the catalytic process is closely related to the adsorption and desorption of dye molecules on the surface of catalyst; thus, it is desirable to have a higher surface area of photocatalyst in order to create more available surface sites exposed to the solution enhancing the transportation of the reactant molecules to move into and off the active sites increasing its photocatalytic activity. We achieved this by modifying the surface of Bi$_2$O$_3$ particles with rGO sheets. As can be seen in Fig. 3, in all cases the concentration of RhB decreased considerably (20 - 30 %) after 30 min of stirring in the dark, with BiMoGO (300:1) being the one with the highest adsorption and with the best photocatalytic activity. Moreover, the heterojunctions between rGO and MoO$_3$ promotes the migration of the photogenerated electrons into the Bi$_2$O$_3$ matrix causing a delay in the electron-hole recombination time, which is reflected as an enhancement of the photocatalytic activity, as the results from Fig. 3b suggest. Another interesting feature of the BiMoGO composite is the presence of oxygen vacancies in MoO$_3$ nanoparticles. It is known that when metal oxides, such as MoO$_3$, ZnO, TiO$_2$, WO$_3$, etc., present oxygen vacancies, their photocatalytic activity is enhanced and their visible light absorption is favored [15-18]. Because of this, we attribute the enhanced photocatalytic activity of BiMoGO (300:1) when irradiated with visible light.

4. Conclusion
A visible light driven Bi$_2$O$_3$/rGO/MoO$_3$ (BiMoGO) photocatalytic composite was successfully synthesized using solvothermal method under ambient pressure and low temperature. The prepared BiMoGO composite material exhibit enhanced degradation ability of RhB solution (70 %) than the pristine Bi$_2$O$_3$ (55 %) material after 260 min under visible light irradiation. The increased photocatalytic activity is owed to the percolation of photogenerated electrons through the rGO network, which causes a delay in the recombination time between electron-hole pairs, and to the enhanced ability of MoO$_3$ nanoparticles to absorb visible light irradiation cause by the surface oxygen vacancies. This confirms the potential application of BiMoGO composite for the degradation of pollutant organic molecules present in water under visible light irradiation.

5. References
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