

Synthesis and Photocatalytic Activity of GO/Bi₂FeMoO₆ Composite under Visible Light Irradiation

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Abstract: Graphene Oxide (GO) with Bi₂FeMoO₆ composite has been successfully synthesized to GO by modified Hummer's method and GO/Bi₂FeMoO₆ composite by Co-precipitation method and followed by calcination using stoichiometry ratio of bismuth nitrate [Bi(NO₃)₃.5H₂O], nitric acid (HNO₃), ammonium molybdate [(NH₄)₆Mo₇O₂₄.4H₂O], ferric chloride hexahydrate [FeCl₃.6H₂O], ferrous sulphate hepta hydrate [FeSO₄.7H₂O] and graphite flake as a precursor materials. The synthesized GO/Bi₂FeMoO₆ composite were characterized with X-ray diffraction (XRD), UV-DRS, FE-SEM and EDX. The photocatalytic activity of GO/Bi₂FeMoO₆ composite was evaluated using the photocatalytic degradation of Methylene blue under Visible light irradiation at room temperature.

Keywords: Graphite flake, Methylene blue, Visible light, Calcination, Co-precipitation

1. Introduction

Nowadays, with the development of modern industries the environmental problem serious and have attracted more and more attention. Water pollution is one of the serious issues among all of them which need to be highly noticed, because the clean water is a necessary for us. Lot of water source polluted with industry effluent. The textile, lather, paper, food, pharmaceutical and cosmetic industries produced over 70,000 tones of commercial dyes annually [1-3]. Among many solutions for water purification, semiconductor based photocatalysis technique is an efficient and low cost strategy for the treatment of water pollutants. Photocatalysis of semiconductors under sun light energy has attracted worldwide researchers because they can apply it for the splitting of water and degradation of organic pollutants [4-5]. Visible light driven photocatalyst has accounted for approximately 43% of solar energy, while that of UV radiation has taken up only 5% [4,6].

Recently, Fe₃O₄ nanoparticles have emerged as a new type of catalyst, which show higher catalytic activity than conventional heterogeneous catalysts due to their chemical stability. These materials have been widely used as mild and efficient catalysts for many organic transformations including Suzuki reaction [7], Friedel-Crafts acylation [8], Sonogashira-Hagihara reaction [9], Paal-Knorr reaction [10], thiolysis of epoxides [11], dehydrogenation of ethylbenzene [12], N-Boc protection of amines [13], and syntheses of heterocycles [14] a-aminonitriles [15] sulphonamides [16] and quinoxalines [17]. Although a number of nanostructured magnetite (Fe₃O₄) has been reported for decorating Bi₂WO₆ [18], TiO₂ [19], CdS [20], and ZnO [21]. The heterojunction composite exhibit excellent properties in photocatalysis.

The enhanced photocatalytic properties are attributed to the transfer of photoexcited electrons from the TiO₂ conduction

band to graphene, increasing the efficiency of electron-hole separation. TiO₂/GO was explored as the photocatalyst for photodegradation of MB dye under either UV or visible light irradiation. The graphene component in TiO₂/GO not only promoted charge separation and increased the adsorption of dye molecules, but also extended the light adsorption to visible light [22]. However, TiO₂ as the photocatalyst is a high band gap (~ 3.2 eV) semiconductor and responds only to the ultraviolet light ($\lambda < 400$ nm), which limits the efficient utilization of solar energy for TiO₂ photocatalysis [23]. However, thus it is very urgent to develop new photocatalytic materials responding in the visible light with large surface area. There are a number of researchers studying photocatalytic activities of Bi₂MoO₆ under visible light irradiation [4-7] due to Bi₂MoO₆ with 2.9 eV narrow energy gap is typical Aurivillius-phase perovskite with its structure containing perovskite layers ($Am^{-1}BmO_3m^{+1}$) between Bi₂O₂ layers of bismuth oxide family with corner-shared octahedral structure [1, 2, 4]. It was found that Bi₂MoO₆ is very interesting due to its unique physical properties for using as dielectric material, gas sensors, ionic conductors, luminescent material, and photocatalyst for water splitting under visible-light irradiation [4-6]. This work synthesized the GO/Bi₂FeMoO₆ composite via Co-Precipitation method and evaluated the photocatalytic activity under visible light irradiation and reported first time in this paper.

2. Experimental

2.1 Materials

Graphite Flakes (Sigma Aldrich), Sodium nitrate [NaNO₂], Potassium permanganate [KNO₃], Hydrogen peroxide 30% [H₂O₂], Sulphuric acid 98% [H₂SO₄], Hydrochloric acid 35% [HCl], Ortho phosphoric acid [H₃PO₄], Bismuth Nitrate [Bi(NO₃)₃.5H₂O], Nitric acid [HNO₃ 78%], Ammonium molybdate [(NH₄)₆Mo₇O₂₄.4H₂O] and Ammonium

hydroxide [NH₄OH], Ferric chloride [FeCl₃.6H₂O], Ferrous sulphate [FeSO₄.7H₂O]. All chemicals received from Merck India except Graphite flake received from Sigma Aldrich USA and used without further purifier

2.2 Synthesis of Graphene Oxide by modified Hummer's method

Graphite flakes (2 g) and NaNO₃ (2 g) were mixed in 80 mL of H₂SO₄ (98%) and 10 ml of H₃PO₄ in a 1000 ml round bottom flask kept under at ice bath (0-5°C) with continuous stirring. The mixture was stirred for 4 hrs at this temperature and potassium permanganate (12 g) was added to the suspension very slowly. The rate of addition was carefully controlled to keep the reaction temperature lower than 15°C. The mixture is diluted with very slow addition of 200 ml distilled water, The ice bath was then removed and kept under stirring for 2 hrs at room temperature. The above mixture is kept in a reflux system at 90°C for 1h. After 1h, change the temperature to 30°C which gives brown colored solution. Again after 10 min, change it to 25°C, and maintain the temperature for 2 hrs. The solution is finally treated with 40 ml H₂O₂ by which color changes to bright yellow, 200 ml of water is taken in two separate beakers and equal amount of solution prepared is added and stirred for 1 hr. It is then kept without stirring for 3-4 hrs, where the particles settles at the bottom and remaining water is poured to filter. The resulting mixture is washed repeatedly by centrifugation with 5% HCl and then with distilled water several times until it forms gel like substance (pH- neutral). After centrifugation the gel like substance is vacuum dried

2.3 Synthesis of GO/ Bi₂FeMoO₆ composite

Step1. Weighed the 1.5g of Graphene oxide prepared from modified hummers method and dispersed into 200 ml of distilled water and then sonicated 1 hours for uniformly dispersed

Step2. Synthesis of Fe₃O₄ -Bismuth molybdate-Graphene composite to 4.75 g of bismuth nitrate (0.49M Bi(NO₃)₃.5H₂O) was dissolved in 20 ml of diluted nitric acid (1.5M HNO₃). The solution was then added drop wise into the aqueous solution containing 0.035M of ammonium molybdate (0.86 g/20 ml (NH₄)₆Mo₇O₂₄.4H₂O) under vigorous stirring and the solution of sonicated Graphene Oxide(step1) is added to the reaction mixture and then added the aqueous solution of aqueous solution of FeCl₃.6H₂O (4.32 g/50ml) and FeSO₄(2.22g/50ml) and During the co-precipitation step, pH of the mixed solution was precisely controlled by adjusting the amount of ammonia solution added. The pH values were kept at 3.0 in the preparation of GO/Bi₂FeMoO₆ composite. The reaction of the solution continuously constant stirred vigorously at room temperature for 12h. And again the reaction mixture reflex with constant stirring at 98°C for 4 h, the precipitate was filtered to obtain a solid product. The solid product was dried and then it was calcined at 475°C for 5h to yield the GO/Bi₂FeMoO₆ composite.

3. Characterization

The crystalline structure of the GO/Bi₂FeMoO₆ composite was investigated by powder X-ray diffraction (XRD, PanAlytical, X-Pert pro, Netherland) with Cu Kα (λ-1.54218 Å) radiation. The size and morphology of the product were obtained with a scanning electron microscope (FESEM-CARL Zeiss Germany, Model Ultra 55 FESEM, Gemini column, 1nm Resolution, detector is INLENSE), EDX (Oxford company, model 20 nm X Ma) UV-Vis diffuse reflectance spectra of the sample were obtained in the range 300 – 800 nm using a UV-vis spectrophotometer (UV2550, Shimadzu, Japan) barium sulphate (BaSO₄) was used as a reflectance standard.

4. Photo Catalytic Test

Organic pollutant such as Methylene blue were chosen for photocatalytically evaluate the photocatalytic activities of the as synthesized catalyst. A 400 W HgX lamp was used as the light source to provide the simulated solar light. The experiments performed at an ambient temperature. The photocatalysts (0.05 g) were added into 50 mL of organic pollutant (5 ppm) solution, and suspension was magnetically stirred for 30 min in the dark to reach an adsorption-desorption equilibrium with the photocatalysts. At a given time intervals, a 3 mL solution collected and then analyzed on UV-Vis spectrophotometer during the photo degradation process. The concentration of Methylene blue were determined by monitoring the variations in the main absorption centered at 664nm.

5. Results and Discussion

Fig.1. represents the powder XRD pattern of GO/Bi₂FeMoO₆ composite shows the characteristic XRD peaks centered at 2θ = 10⁰, 26.10⁰, 28.86⁰, 32.14⁰, 33.18⁰, 35.4⁰, 41.12⁰, 48.64⁰, 53.37⁰, 58.82⁰, 60.85⁰, 68.20⁰ which can be indexed as (020), (260), (131), (133), (002), (042), (311), (202), (151), (191), (262), (400) respectively. The peaks can be indexed to (020), (131), (200), (002), (151), (042), (202), (260), (133), and (262) planes sequentially of orthorhombic Bi₂MoO₆ (PDF#21-0102). For the GO/Bi₂FeMoO₆ composites, the peaks at 35.4⁰, 41.12⁰, and 68.20⁰ correspond to the (311), (400), and (440) planes of cubic Fe₃O₄ (PDF#26-1136), respectively.

The very high peak suggests that the material is highly crystalline. XRD peaks revealed that the crystalline phase was nanosized. The average crystallite size was calculated from the XRD line boarding using Debye Scherrer relationship given in the Eq.(1)

$$L = 0.9\lambda / (\beta \cos\theta) \quad (1)$$

where L is the crystallite size, β is the full width at half maximum line width (FWHM) and λ was the wavelength of X-rays. The average crystalline size of the GO/Bi₂FeMoO₆ calculated from diffraction peaks found to be 43- 46 nm.

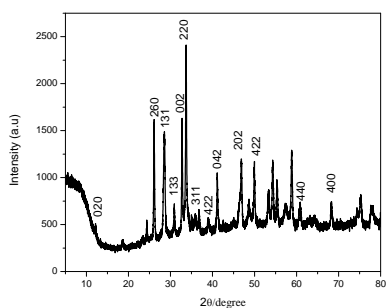


Figure 1: XRD pattern of GO/Bi₂FeMoO₆

Fig.2. shows Diffuse-reflectance spectroscopy (DRS) is an important method for charactering the electronic state, optical state and calculates the band gap of semiconductor materials. The DRS spectra of as synthesized of GO/Bi₂FeMoO₆ composite and the band gap of synthesized catalyst calculated, The adsorption edges of Bi₂MoO₆, Magnetite graphene Oxide(MGO), GO/Bi₂FeMoO₆ composite are located around 490nm, 540nm and 580nm respectively. Their band gaps are estimated to be 2.39eV, ~1.87eV, ~1.58eV respectively, which suggests enhancement the photocatalytic activity of GO/Bi₂FeMoO₆ compared to pure Bi₂MoO₆ and MGO due to the reason of small band gap samples photocatalytic capability enhanced, and all synthesized samples exhibited an intense absorption in the visible light range, which suggests the property of being photoactive under visible –light irradiation. The bang gap was mainly influenced by the coordination of oxygen ions to a molybdenum ion. The synthesis materials Bi₂MoO₆, Magnetite graphene Oxide(MGO), GO/Bi₂FeMoO₆ composite in this study exhibited a narrower band gap compared with that reported by Kudo and co-workers. Generally narrow band gap materials suggests to the good semiconductors were preferred for efficient charge separation, the photocurrent generated to the sample measured which correlates with photocatalytic activity.

$$\text{Band gap energy } (E_g) = h \cdot c / \lambda \quad (2)$$

Where E_g , h , c , λ are band gap energy, plank constant, speed of light, cut of wavelength respectively.

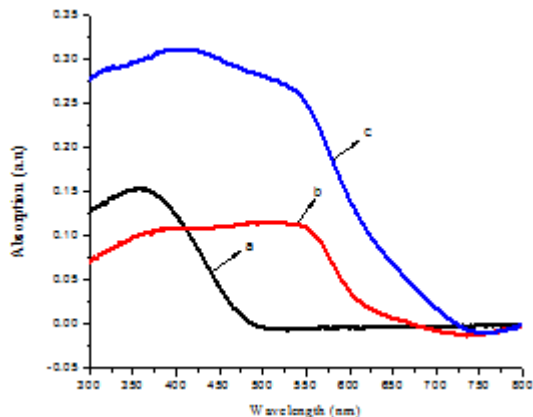


Figure 2: UV-DRS spectra for (a) Bi₂MoO₆ (b) Magnetite Graphene Oxide (c) GO/Bi₂FeMoO₆ composite

The surface morphology of γ -Bi₂MoO₆ NP's was investigated by field emission scanning electron microscopy (FESEM). The FESEM images of Bi₂MoO₆, Magnetite graphene Oxide(MGO), GO/Bi₂FeMoO₆ is depicted in Fig.3. The Fig.3(a) shows the FESEM images of Bi₂MoO₆ NP's clearly observed to the octahedral shapes and with particle size of 47 nm. The Elemental composition and purity of compound confirmed by energy dispersive X-ray (EDX) analysis, the EDX spectrum of Bi₂MoO₆ sample shows the presence of Bi, Mo and O only due to no other elements present which contain perfect sample synthesized without any other impurities. The Fig 3(b) shows the MGO images with EDX analysis and Fig 3(c) shows GO/Bi₂FeMoO₆ NP's clearly observed the Bi₂FeMoO₆ composite on GO surface with flower like morphology and EDX analysis which contain perfect sample without any other impurities.

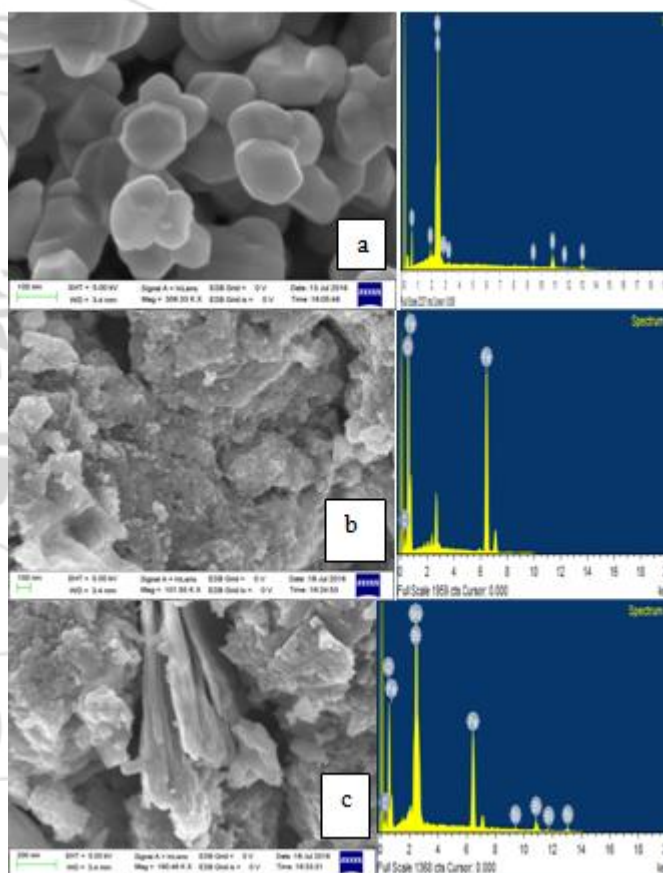


Figure 3: FE-SEM images with EDX spectra of (a) Bi₂MoO₆ (b) Magnetite Graphene Oxide (c) GO/Bi₂FeMoO₆ composite

6. Photocatalytic Effect

General photocatalytic degradation of dyes by a photocatalyst is critically depends on particle size, crystallinity, morphology, band gap energy, charge recombination, efficient charge separation and the value of photocurrent indirectly reflects the semiconductor's ability to generate and transfer a photogenerated charge carrier under irradiation, which correlates with the photocatalytic activity, this properties

characterized with relevant instruments. The GO/Bi₂FeMoO₆ had good photocatalytic property because XRD revealed to nanosized and good crystallinity, FE-SEM revealed to flower like shape, UV-DRS revealed to narrow band gap and good efficiency for charge separation. Fig.4. shows the photocatalytic activity of as prepared GO/Bi₂FeMoO₆ was evaluated under visible light irradiation over degradation of Methylene blue were chosen as representative model pollutant. The establishment of adsorption – desorption equilibrium was obtained under continuous stirring 30 min before the degradation reaction was carried out, evaluated degradation under visible light irradiation measured to UV-Visible spectrometer to the cut off filter 664nm. Fig .4(c) shown that the GO/Bi₂FeMoO₆ composite spectra are more efficient in photocurrent generation compared to pure Bi₂MoO₆ catalyst. Therefore, the GO/Bi₂FeMoO₆ composite enhanced the charge carrier transfer and reduced the electron hole recombination with large surface area of GO. It is assumed the interaction between Bi₂FeMoO₆ and GO are more favorable for enhancing the photocatalytic activity of GO/Bi₂FeMoO₆ composite.

$$\% \text{ of degradation} = (A_0 - A_t) / A_0 * 100 \quad \text{Eq (4)}$$

Where A₀ and A_t are respectively initial absorbance and absorbance at time 't'

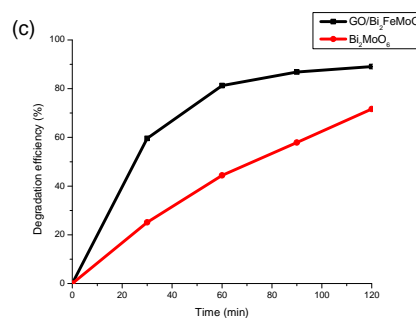
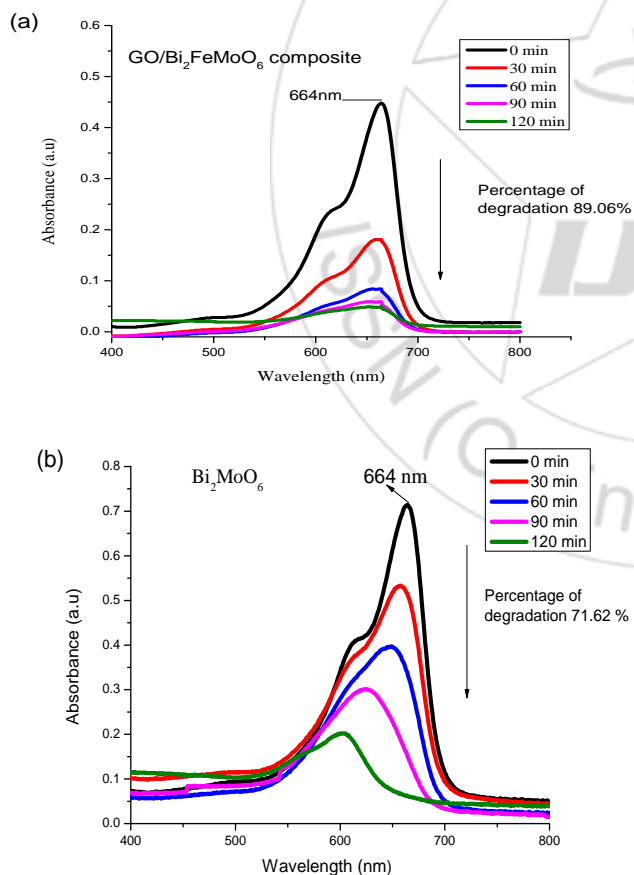


Figure 4: Degradation of methylene blue dye under Visible light irradiation (a) GO/Bi₂FeMoO₆ composite (b) Bi₂MoO₆ (c) Photocatalytic comparison between Bi₂MoO₆ and GO/Bi₂FeMoO₆ composite under visible light irradiation as a function of the % of degradation verses time

7. Conclusion

The synthesis of GO/Bi₂FeMoO₆ was successfully synthesized by the Co-precipitation method by controlled specific pH condition and followed by calcination treatment. Formation of GO/Bi₂FeMoO₆ composite catalysts was well confirmed by XRD and EDS analysis, the photocatalytic activity of GO/Bi₂FeMoO₆ composite spectra are more efficient in photocurrent generation compared to pure Bi₂MoO₆ phase. Therefore, the GO/Bi₂FeMoO₆ composite enhanced the charge carrier transfer and reduced the electron hole recombination. It is assumed the interaction between Bi₂FeMoO₆ and GO are more favorable for enhancing the photocatalytic activity of Bi₂FeMoO₆ composite.

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