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Photocatalytic Degradation of Rhodamine B Dye by Bi_2MoO_6 Microspheres under Natural Sunlight Irradation

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ABSTRACT
Removal of dyes from water bodies is a significant concern throughout the world. In this study, Bi_2MoO_6 microspheres were synthesized by a hydrothermal synthetic route at 180°C, and it is effectively characterized by various techniques. The XRD peaks confirmed the orthorhombic planes of Bi_2MoO_6. The microsphere-like morphology was revealed by FESEM and HRTEM. The optical band gap was investigated by UV-vis DRS and showed a reflection edge with corresponding energy at 2.68 eV. The photocatalytic activity of the Bi_2MoO_6 microsphere is tested against the degradation of rhodamine B under natural sunlight irradiation. About 90% degradation of rhodamine B is observed in 90 min with the photocatalytic degradation rate of $0.038min^{-1}$. Results confirmed that the Bi_2MoO_6microspherecould facilitate 90% degradation of RhB dye and followed the first-order kinetic model.

Keywords: Bi_2MoO_6; Solar Photocatalyst; Rhodamine B, Photocatalysis

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INTRODUCTION

Organic dyes in aquatic environments are a significant pollutant due to their extensive usage in textile and other fabric industries (Homem & Santos, 2011; Qin et al., 2021; Rivera-Utrilla et al., 2013). Many water sources are polluted by residual dyes, which enter directly into the aquatic environment through various means like dye industries, textile industries, etc. (Dinh et al., 2017; Michael et al., 2013). Rhodamine B dye is a widely used cationic dye found in its application in coloring fabrics. Rhodamine B is water-soluble, stable in an aquatic environment, non-biodegradable, and cancer-causing in nature, which makes it harmful to humans and living species of aquatic ecosystems.

However, these residual dyes are not quickly metabolized, so they can easily pollute groundwater and surface water, causing harmful diseases in animals and humans. Due to this, several methods have been developed for wastewater remediation. Out of these techniques, semiconductor-based photocatalysts are widely utilized for the photocatalytic

removal of various water pollutants (Akbari et al., 2021; Calvete et al., 2019; Durán-Álvarez et al., 2016). To date, ZnOand TiO_2 nanoparticles are the most commonly used photocatalysts for degrading organic dyes, but they require UV light for photoexcitation as their band gap is large. Recently, bismuth-based photocatalysts have been the most promising and new class of photocatalysts used in wastewater treatment over the last few decades. Their applications cover several areas such as water-splitting, NH_3 production from N_2, reduction of CO_2, and degradation of water pollutants through heterogeneous hotocatalysis. The band structure of these materials provides them with a suitable band gap for visible light-active and a well-distributed valence band in favor of recombination charge, enabling them to act as potential photocatalytic materials for wastewater treatment over metal oxides. Bismuth-based multi-component oxides are usually identified as stoichiometric hybrid oxides of Bi_2O_3 and metal oxides likeTiO_2, V_2O_5, Mo_2O_3, W_2O_3, etc. The Aurivillius layered structure is generally determined by $[Bi_2O_2]^{2+}$ layers combined with metal oxide layers along the c-axis. The Bi_2MoO_6 (n = 1) is the simplest member of the Aurivillius family, which is a promising candidate for the photocatalytic degradation of inorganic and organic pollutants, under solar-light illumination. In this work, we have reported the synthesis of Bi_2MoO_6microsphere as a solar photocatalyst, and its photocatalytic activity was tested on RhB dye degradation under solar light irradiation.

Synthesis of Bi_2MoO_6microsphere

4 mmol bismuth nitrate pentahydrate was mixed in 20 mL of ethylene glycol, and 4 mmol sodium molybdate dihydrate was dissolved in 30 mL of ethyl alcohol. After stirring both the solutions for 30 min separately, the sodium molybdate dihydrate solution was added slowly into the bismuth nitrate pentahydrate solution with continuous magnetic stirring. After 45 min of constant stirring, the mixture was poured into a Teflon-lined stainless-steel autoclave and heated under a controlled temperature of 180°C for 24 h. The finally prepared precipitates were washed with DI water and C_2H_5OH and separated by centrifugation at 10000 RPM for 20 min, and the white product finally obtained was dried in an oven at 50°C.

Methodology for Photocatalytic Experiment

The photocatalytic performance of the Bi_2MoO_6photocatalyst was determined by observing the degradation of RhB dye (10 mg/L) solutions under exposure to natural sunlight radiation. Typically, 100 mL aqueous solution of 10 ppm RhB dye is taken into a 500 mL beaker, followed by the addition of 80 mg of Bi_2MoO_6photocatalysts into it, which was then subjected to continuous stirring for 60 min under the dark condition. After 60 min of dark study, the beaker was kept under sunlight. 2 mL aliquot was taken from the beaker at certain intervals. The change in concentration of the RhB molecule was recorded by UV-vis spectrophotometer (UV-1800, Shimadzu, Japan) at absorbance λ= 553 nm.

RESULTS AND DISCUSSIONS

Characterization of Bi_2MoO_6

XRD analysis

The XRD spectra of pristine $Bi_2MoO_6$was investigated by Bruker AXS advanced diffractometer with a scan range of 1 min^{-1} using graphite monochromatized Cu Kα radiation (1.5418 Å) operated at 40kilovolts. The XRD peaks for Bi_2MoO_6 were detected at 2θ = 11.1°, 28.5°, 32.9°, 36.2°, 47.2°, 55.6°, 58.4°, which are matched to (020), (131), (002), (151), (062), (133), and (262) orthorhombic planes of Bi_2MoO_6 (JCPDS Card No.- 21 1272) (Figure.1). The lattice parameters are calculated to be as *a* = 5.42 Å, *b* = 16.32 Å, and *c* = 5.42 Å, with the average crystallite size of 14.10 nm.

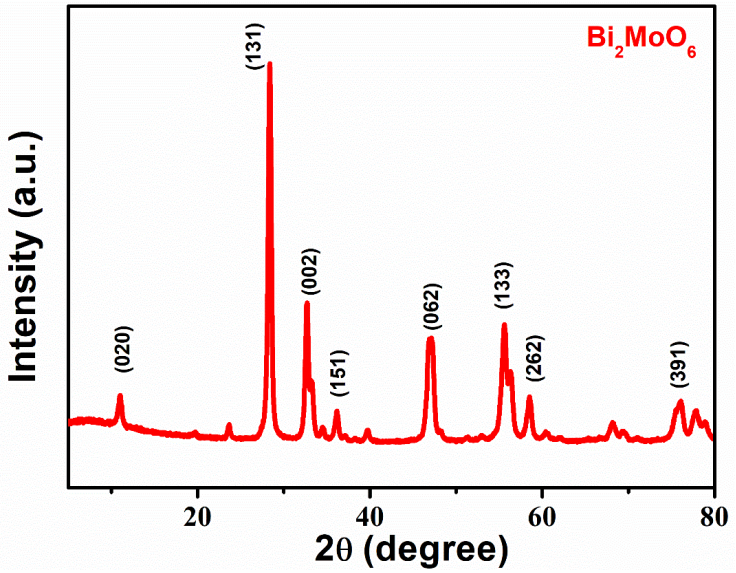

Figure 1: XRD patterns of as-synthesized Bi_2MoO_6 microspheres

Morphology of Bi_2MoO_6

The surface morphology of the Bi_2MoO_6 photocatalyst was investigated by electron microscopy. The FE-SEM image of Bi_2MoO_6 microspheres was recorded by Zeiss FESEM, Ultra-plus 55 shows agglomeration of nanospikes-like structures (Figure. 2a and 2b). Similarly, the morphology of the Bi_2MoO_6microsphere was better displayed from the HRTEM images with their corresponding SAED pattern (Figure. 2c and 2d) are recorded on a JEM-3200FS, JEOL transmission electron microscope.

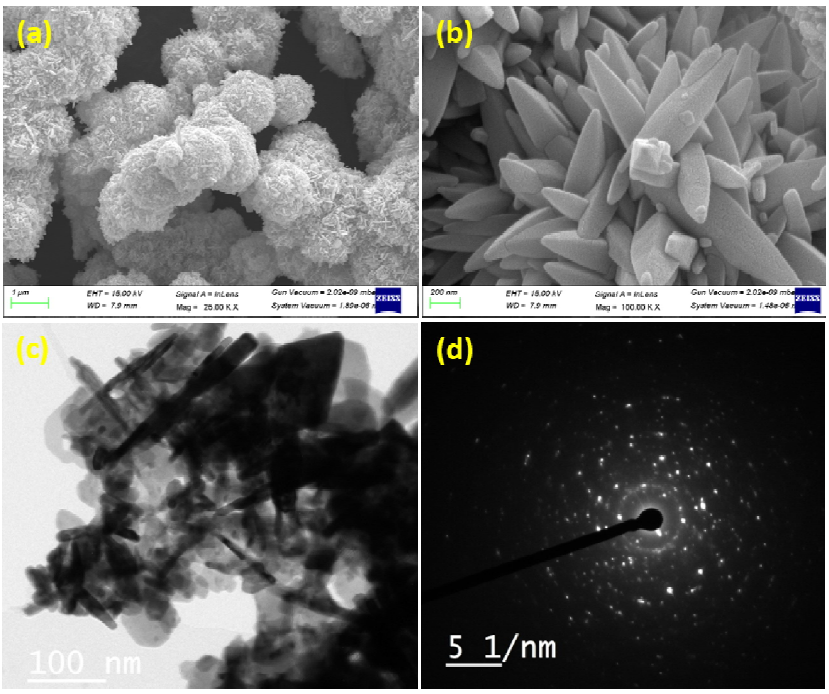

Figure 2: a) FE-SEM image of Bi_2MoO_6microspheres; b)HR-TEM image of Bi_2MoO_6microspheres

UV-vis DRS analysis

The UV-vis DRS studies of the as-prepared Bi_2MoO_6 microspheres were recorded on a Shimadzu UV-2450, Japan spectrophotometer using $BaSO_4$ as reference. The pure Bi_2MoO_6 microspheres absorb in the ultraviolet and visible light region (Figure3). The UV-vis DRS spectra were changed into absorption spectra by using (K-M function) Kubelka-Munk (Kortüm, 1969), and the band gap was calculated from the Taucs plots (Tauc et al., 1966), Figure 3 shows Tauc's plots of Bi_2MoO_6 photocatalyst. The optical band gap of Bi_2MoO_6 was determined to be 2.68 eV.

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (1)$$

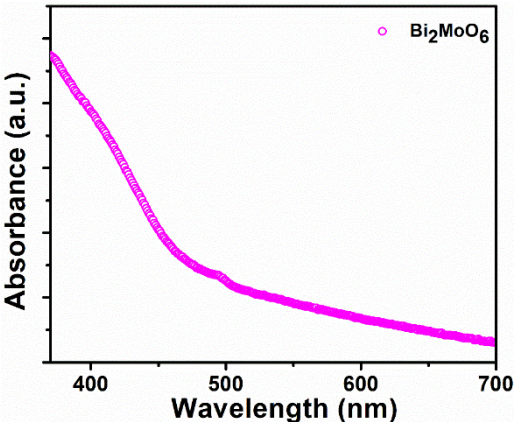

Figure 3: Tauc's plot of pure Bi_2MoO_6

Photocatalytic activity

The impact of photocatalyst dose on the photocatalytic performance was investigated by treating the aqueous solution RhB with different amounts of photocatalyst, i.e., 50–100 mg of photocatalyst per 100mL under the same experimental environment as mentioned above. The degradation rate and removal efficiency were first increased with the increase in the photocatalyst dose from 50 mg (k=0.08 min^{-1}) to 80 mg/100mL (k=0.038 min^{-1}) and then decreased for the dose 100 mg (k=0.011 min^{-1}) (Figure.4a and 4b). The impact of the change in concentration of RhB solution has been investigated by changing the initial concentration of RhB solution from 10 to 30 mg/L. The decrease in the photocatalytic performance was observed with the increase of RhB concentrations (Figures. 4c and 4d). A complete photocatalytic degradation study was performed with a photocatalyst dose of 80 mg per 100 mL aqueous solution of RhB.

The sunlight-mediated photocatalytic degradation of RhB dye (10 mg/L) by the Bi_2MoO_6 microsphere is shown as a curve of C_t/C_0 vs. (t) time (Figure 4). In the dark experiment firstly, the change in concentration of RhB dye was determined by the dark experiment. About 16% of RhB dye was adsorbed on Bi_2MoO_6microspheres (Figure 4a). The self-decomposition investigation of rhodamine B shows negligible results. The Bi_2MoO_6 microspheres show the photocatalytic performance of about 90 % rhodamine B dye degradation after 90 min of sunlight exposure. The degradation kinetics of rhodamine B was modelled by a 1st-order kinetics model. The 1storder kinetics equation is:

$$\ln(C_0/C_t) = kt \quad (2)$$

Where C_0 is the initialdye concentration of dye, and C_t is the dye concentration at any time, whereas k (min^{-1}) (Table 1) is the 1st-order kinetic rate constant for RhB dye photocatalytic degradation. The photocatalytic rate constant of pristine Bi_2MoO_6 (k= 0.038 min^{-1}) (Figure 4b). Figure 4c shows the UV-vis absorption spectra, which shows the change in concentration of

rhodamine B dye during the photocatalytic degradation. The decrease in the intensity of the absorption peak of rhodamine B dye (553 nm) was observed over 90 min period of sunlight irradiation.

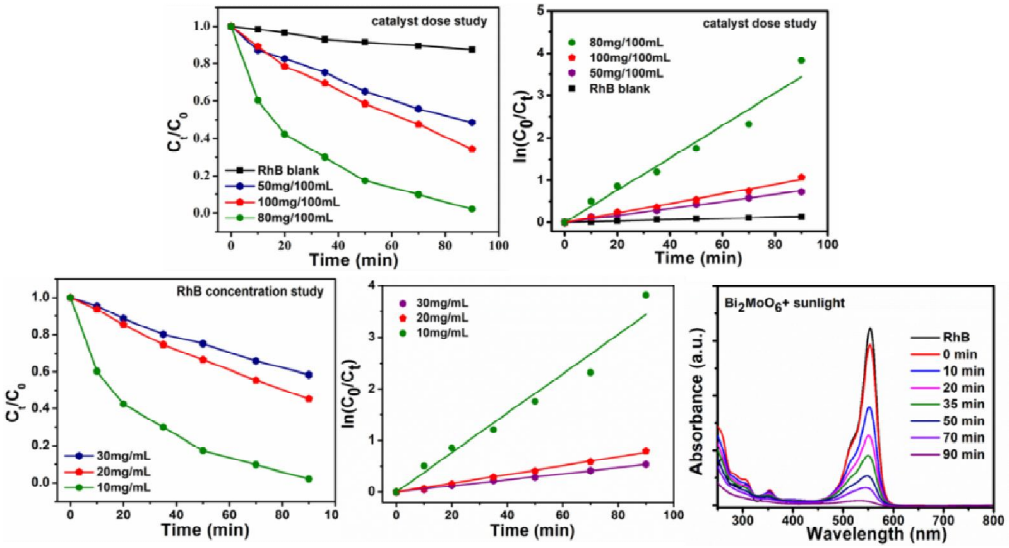

Figure 4: a) Effect of photocatalyst dose on the photocatalytic performance, (b) Corresponding 1st order kinetics curves, (c) Effect of RhB dye concentration on the photocatalytic performance, (d) Corresponding 1st order kinetic curves, e) UV-is absorbance spectra of RhB dye solution.

Table1: Summary of kinetics study of RhB dye photocatalytic degradation

Sample name	Percentage Adsorption	Percentage Degradation	1st-order kinetics (RhB)	
			k (Min^{-1})	R^2
Bi_2MoO_6	16%	90%	0.038	0.994
Blank	NA	10%	0.002	0.983

Reusability of photocatalyst

The reusability of the Bi_2MoO_6 photocatalyst has been tested for three successive cycles for the photocatalytic degradation of RhB dye. A similar type of degradation pattern and degradation rate for all three-cycle obtained (Figure 5a). The chemical stability of Bi_2MoO_6 photocatalyst further confirmed from the XRD pattern and FESEM image of the used photocatalystobtained after the 3rd cycle (Figure 5b and 5c).

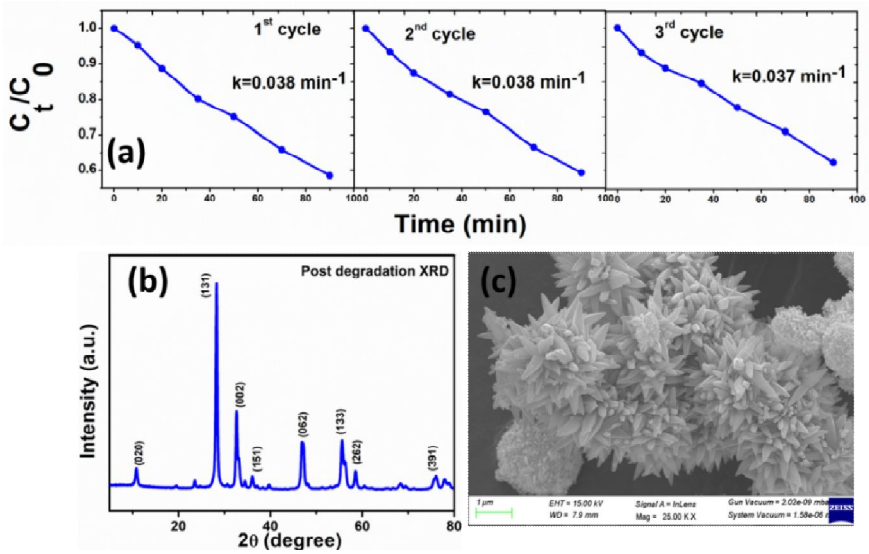

Figure 5: (a) Reusability of the Bi_2MoO_6 up to three cycles; (b) post degradation XRD and (c) SEM image of the re-used photocatalyst.

Reactive oxygen species (ROS) scavenging studies

In order to determine the main active reactive oxygen species responsible for the photocatalytic degradation of RhB, the ROS experiment was performed in the presence of (1mM) ammonium oxalate (h^+), (1mM) chloroform (O_2^-·scavenger) and(1mM) isopropyl alcohol (OH·scavenger) respectively, under the optimized conditions. The radical scavenging experiment confirmed that the O_2^-· radical is mainly responsible for the photocatalytic degradation of RhB (Figure 6).

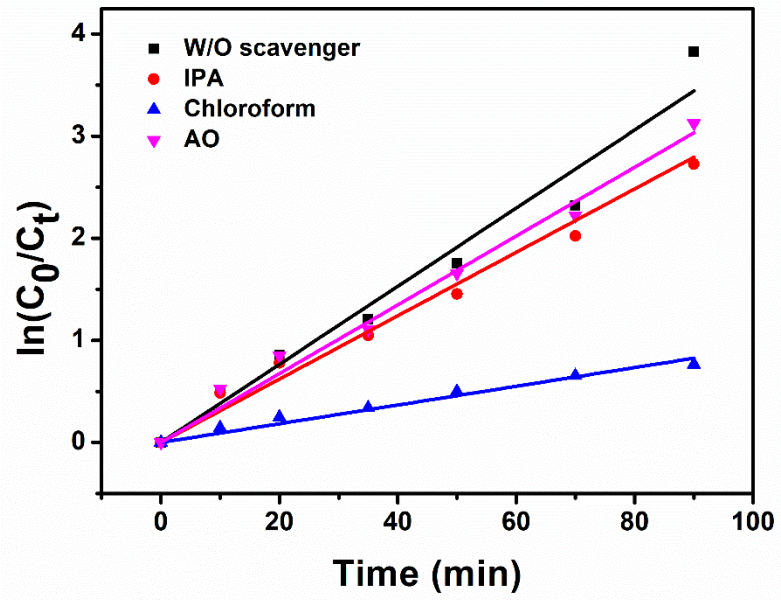

Figure 6: Effect of reactive oxygen species on RhB degradation

Photocatalytic mechanism

The charge transfer in a semiconductor photocatalyst mainly depends on the photocatalysts conduction and valence band positions. The value of the conduction and valence band is calculated by the equation, ECB = χ (AaBb) – 1/2Eg + Eo and EVB = ECB+ Eg where Eg represents the band gap of

Bi_2MoO_6, ECB represents the conduction band potential, EVB represents the potential of the valence band, and Eo value is taken as – 4.50 eV, *i.e.*, the energy of free electrons on the NHE scale. The value χ (AaBb) represents the absolute electronegativity of a semiconductor material of the AaBb type. For Bi_2MoO_6 ,the electronegativity value is calculated to be 5.55 eV. Upon exposure to visible light radiation, the electron excited from the valance band into the conduction band. The conduction and valence bands of Bi_2MoO_6 are calculated as –0.28eV and +2.40eV, respectively. The valance band of $Bi_2MoO_6$was estimated to be +2.38 eV (vs. NHE), which was more negative than the potential of $OH^{\bullet}/H_2O$ (+2.68 eV vs. NHE), which confirm that the photo-generated holes are not capable to oxidize water to yield hydroxyl ($OH^{\bullet}$) radicals in Bi_2MoO_6. The conduction band potential of Bi_2MoO_6 was estimated to be (–0.28 eV vs. NHE),which is more negative than $E(O_2/O_2^{-}\bullet)$ (–0.04 eV vs. NHE)(Li et al., 2018), so it can quickly reduce O_2 to produce superoxide radical $O_2^{-}\bullet$.

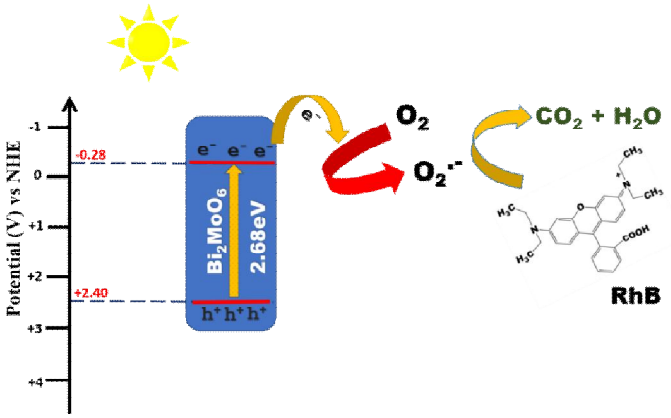

Figure 7: The proposed photocatalytic mechanism over Bi2MoO6 under sunlight irradiation

CONCLUSIONS

A simple hydrothermal synthetic route has synthesized the Bi_2MoO_6 photocatalyst. The Bi_2MoO_6 photocatalyst shows excellent photocatalytic performance towards the degradation of 90 % of rhodamine B (RhB) under sunlight irradiation. The corresponding kinetic rate constant of the Bi_2MoO_6 photocatalyst was 0.038 min^{-1}. Bi_2MoO_6 is an effective visible light photocatalyst option for removing various organic dyes in aqueous media due to its strong photocatalytic activity.

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