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Full Length Article

Bismuth oxyiodide incorporated reduced graphene oxide nanocomposite material as an efficient photocatalyst for visible light assisted degradation of organic pollutants

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ABSTRACT

Herein, Bismuth oxyiodide (BiOI) – reduced graphene oxide (rGO) photocatalysts were prepared *via* simple hydrothermal method. The BiOI-rGO photocatalyst exhibited high crystallinity with tetragonal phase of BiOI. In addition, the electronic interaction between rGO sheet and BiOI reduced the band-gap value from 1.86 eV of bare BiOI to 1.51 eV of BiOI-rGO (6 wt%) photocatalyst. More interestingly, the rGO showed a strong influence on tailoring the morphology of BiOI to different nanostructures with different rGO loading (wt%), which further reflected differences in the photocatalytic activity. A significant quenching in the photoluminescence intensity of rGO supported BiOI photocatalyst confirmed the effective suppression of electron-hole pair recombination. The optimized rGO (4 wt%) loaded BiOI photocatalyst significantly improved the photocatalytic activity (~85%) towards the degradation of methyl orange (MO) dye compared to that of pristine BiOI (~29%). Thus, around three folds enhancement in the photocatalytic activity of BiOI–rGO (4 wt%) catalyst was mainly attributed to ultrafast separation of electron–hole pairs and rapid transportation of carriers by rGO support. The superior photocatalytic activity demonstrated by this newly synthesized BiOI-rGO photocatalyst makes it's a potential candidate for environmental remediation process.

1. Introduction

Semiconductor photocatalysts have gained much attention in the field of solar energy conversion process, such as photocatalytic splitting of water to produce H_2, solar cells and photocatalytic degradation of harmful organic pollutants, etc., [1–4]. The conventional TiO_2 is the most extensively investigated semiconductor photocatalyst for the decomposition of organic pollutants [5–10]. However, because of its large band-gap energy (3.2 eV), it can respond only in the UV region of the solar spectrum, which further confines the photocatalytic application in visible region [11]. In order to utilize the abundant visible light in the solar spectrum, it is of crucial importance to develop the photocatalyst that can work under visible light illumination with high efficiency. Thus, the degradation of organic pollutants under visible light illumination is considered to be a promising approach. Recently, several visible light photocatalysts, such as CdS, AgI, Bi_2O_3, g-C_3N_4, Cu_2O, $BiVO_4$ and Ag_2CO_3 have been used for photocatalytic degradation of organic pollutants [12–16].

Recent years, Bismuth oxy halides BiOX (X = Br, Cl, and I) are considered to be as potential visible light photocatalysts due to their excellent electrical and optical properties. [17–20]. Among them, BiOI is a promising photocatalyst due to is low bandgap energy (1.8 eV) compared to that of BiOBr and BiOCl [21]. However, rapid electron-hole pair recombination greatly affects the photocatalytic activity of BiOI towards photocatalytic applications [22]. In order to maximize the photocatalytic efficiency of BiOI, several efforts have been put forward, such as doping of metal with BiOI and addition of co-catalysts to form nanocomposites, etc., [23,24]. For example, BiOI-TiO_2 nanocomposites were synthesized using electrochemical deposition and demonstrated as a visible light photocatalysts for photoelectrochemical water splitting [24]. Sun et al. has developed a BiOI/BiOCl heterojunction photocatalyst with enhanced photocatalytic activity under visible light illumination [25]. A novel Bi_2S_3/BiOI nanocomposite produced via simple facial approach exhibited an excellent photocatalytic activity for methyl orange dye degradation [26]. Very recently, *p-n* junction heterostructured BiOI/$La_2Ti_2O_7$ photocatalyst was designed with high photocatalytic activity [27].

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In order to further enhance the photocatalytic activity of BiOI photocatalyst, graphene has been utilized as a potential two dimensional solid support for efficient separation and transportation of charge carriers. Graphene, a single layer of graphite has attracted major attention in various fields due to its excellent physicochemical properties, such as high surface area, better electrical conductivity and high carrier mobility etc. [13,28,29]. Dai et al. has synthesized ternary C_3N_4/BiOI/graphene-oxide nanocomposite for photocatalytic degradation of methylene blue dye [30]. Graphene oxide (GO) was used as an electron transporting layer to transfer the photoexcited electrons from C_3N_4 to BiOI and thereby, suppress the electron-hole pair recombination. Quantum sized BiOI nanoparticles were decorated on reduced graphene oxide sheets and employed as an efficient visible light photocatalyst for methyl orange dye degradation [31]. Likewise, three dimensionally constructed BiOI-GO composite was designed using self-assembly approach and the resultant visible light active 3D BiOI-GO composite showed improved photocatalytic phenol degradation than BiOI and P-25 [32]. Very recently, reduced graphene oxide supported BiOI-AgI photocatalysts were synthesized by simple precipitation method for the efficient degradation of rhodamine B dye under solar light irradiation [33]. In addition, visible light responsive $Bi_7O_9I_3$/reduced graphene oxide composites were developed and exhibited an enhanced photocatalytic activity [34].

In the present work, different wt% of reduced graphene oxide (rGO) loaded BiOI photocatalysts were synthesized using simple hydrothermal technique. The photocatalytic performance of prepared BiOI-rGO photocatalyst was evaluated for the photocatalytic degradation of methyl orange (MO) dye under visible light illumination. Most importantly, introducing different wt% of rGO as a solid support for the BiOI photocatalyst might plays a significant and crucial role in tailoring the morphological nanostructure and the band-gap of BiOI, which further reflected on the photocatalytic activity towards the photodegradation of MO.

2. Experimental details

2.1. Materials

Graphite flakes [particle size + 100 mesh (≥75% min)] was purchased from Sigma-Aldrich. $Bi(NO_3)_3{\cdot}5H_2O$ and KI were obtained from SRL Chemicals, India. All other reagents and solvents were of analytical reagent grade and used without any further purification.

2.2. Synthesis of graphene oxide (GO)

GO was synthesized from graphite flakes using well known modified Hummer's method [35]. In a typical procedure, 2 g of graphite flakes and 1 g of $NaNO_3$ were added into 46 mL of conc. H_2SO_4 and stirred for 30 min. To this, 6 g of $KMnO_4$ was added slowly under ice cold condition to prevent the temperature not exceeding more than 20 °C. Then this suspension was stirred at room temperature for 30 min. Further, 92 mL of DI water was slowly added into the reaction mixture and heated up to 98 °C for 30 min. To remove the excess $KMnO_4$, appropriate amount of 3% H_2O_2 was slowly dropped into the mixture until no bubbles were observed. The mixture was centrifuged and washed with Milli-Q water several times until pH reached up to neutral. Finally, the collected products were freeze dried.

2.3. Synthesis of BiOI and BiOI-rGO photocatalysts

The BiOI-rGO photocatalyst was synthesized using simple hydrothermal method. 1 mmol of $Bi(NO_3)_3{\cdot}5H_2O$ was dissolved in 17 mL of ethanol and slowly dropped into 17 mL of DI water containing 1 mmol KI under constant stirring. To this mixture, a required amount of GO was added and stirred for 30 min. Then this suspension was transferred into the 50 mL Teflon-lined autoclave, heated at 150 °C for 8 h and cooled to room temperature. Finally, orange colour precipitates were collected, washed with DI water and ethanol several times and dried at 60 °C. Different weights of rGO (2, 4 and 6 wt%) was loaded with BiOI by hydrothermal method. For comparison, a bare BiOI photocatalyst was also synthesized according to the previous report [36].

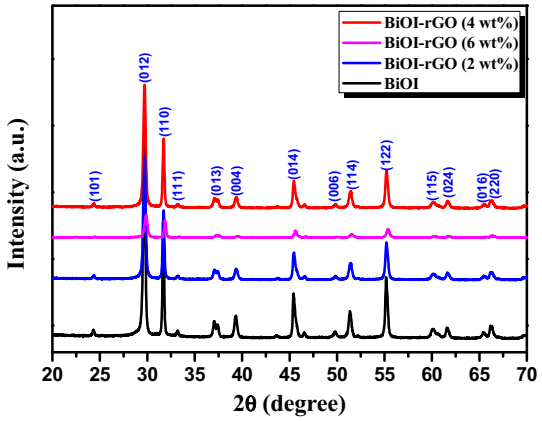

Fig. 1. XRD patterns of BiOI, BiOI-rGO (2 wt%), BiOI-rGO (4 wt%) and BiOI-rGO (6 wt%) photocatalysts.

2.4. Characterization studies

X-ray diffraction (XRD) studies were carried out by (PANaltical X'pert powder diffractometer) using Cu Kα radiation. The morphological studies were obtained through Field Emission-Scanning Electron Microscopy (FEI Quanta FEG 200 HR-SEM). The optical absorption spectra of photocatalyst recorded in diffuse reflectance mode was occurred from Analytikjena specord 210 plus, integrating sphere accessories. Photoluminescence spectra were taken using Horiba Fluorolog@3 spectrophotometer. Fourier Transform Infrared (FT-IR) spectra for the photocatalysts were monitored using Agilent, Cary 660, USA.

2.5. Photocatalytic experiments

The photocatalytic activity for the photocatalysts were evaluated for the degradation of aqueous methyl orange (MO) dye solution under visible light illumination. A 250 W Xenon lamp (Oriel instrument) was used as a light source (λ > 400 nm). 80 mg of photocatalyst in 80 mL of MO (10 mg/L) was suspended in 100 mL glass beaker. Before light illumination, MO dye with catalyst was stirred under dark condition to attain adsorption–desorption equilibrium. At a given time interval, supernatant was collected, centrifuged and transferred to 3.5 mL of quartz cuvette for measuring the UV–vis absorbance value. The MO photodegradation was monitored through UV–visible spectrophotometer (Specord-210 plus, Analytikjena, Germany). The rate of mineralization was analyzed using Total Organic Carbon (TOC) analyzer (Shimadzu, TOC-L, Japan).

3. Results and discussion

3.1. XRD patterns

The XRD patterns of the prepared BiOI and BiOI-rGO photocatalysts are depicted in Fig. 1. Both BiOI and BiOI-rGO exhibit the high intense diffraction peaks at 2θ = 24.4°, 29.7°, 31.7°, 33.2°, 37.0°, 39.4°, 45.4°, 49.8°, 51.5°, 55.2°, 60.1°, 61.7°, 65.5° and 66.3°

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