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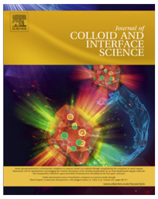

Regular Article

Bismuth oxyfluoride/bismuth oxyiodide nanocomposites enhance visible-light-driven photocatalytic activity

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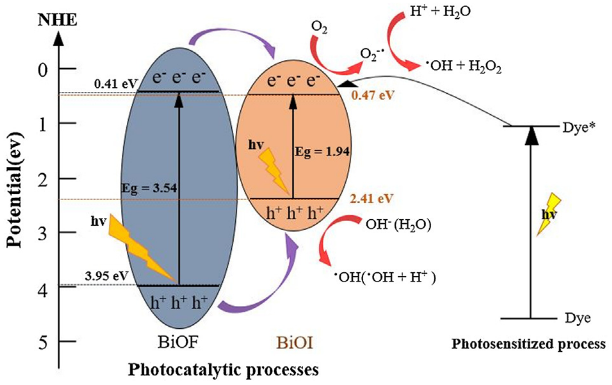
GRAPHICAL ABSTRACT

Schematic of the band-gap structures of BiOF/BiOI and the possible charge separation processes.



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ABSTRACT

This is the first paper to report a series of bismuth oxyfluoride/bismuth oxyiodide (BiO_pF_q/BiO_xI_y) nanocomposites with different F/I molar ratios, pH values, and reaction temperatures that were synthesized through a template-free and controlled hydrothermal method. These nanocomposites were characterized through scanning electron microscope energy dispersive microscopy (SEM-EDS), transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier-transform infrared (FT-IR), X-ray photoelectron spectroscopy (XPS), Brunauer–Emmett–Teller (BET), and diffuse reflectance spectroscopy (DRS). Under visible-light irradiation, the BiO_pF_q/BiO_xI_y composites exhibited excellent photocatalytic activities in the degradation of crystal violet (CV) and 2-hydroxybenzoic acid (HBA). The order of rate constants was BiOF/BiOI > BiOI $\gg$ BiOF. The photocatalytic activity of BiOF/BiOI composites reached a maximum rate constant of 0.2305 h^{-1}, 1.2 times higher than that of BiOI and 100 times higher than that of BiOF. Thus, the derived BiOF/BiOI is crucial for photocatalytic activity enhancement. After the removal of CV in the third cycle, no apparent deficits in photocatalytic activity were observed, and the observed deficit was 8.2% during the fifth run. Overall, the catalytic activity and stability observed for the proposed composites were determined to be adequate under visible-light irradiation. For various scavengers, the noted quenching effects demonstrated that reactive $O_2^{\bullet -}$ has a notable role in the degradation of the applied CV.

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1. Introduction

Scholars have devoted considerable attention to semiconductor photocatalysis energized by visible light, because this is an effective approach to overcome problems linked to environmental pollution and energy production. A photocatalyst that is effective, low-cost, and environmentally friendly is paramount for practical photocatalysis applications [1]. Relevant research has focused primarily on the elimination of toxic constituents from wastewater. Scholars have used various systems to photodegrade crystal violet (CV) dyes and thus to produce active species such as BiO_xCl_y/BiO_mI_n [2], BiOBr/BiOI [3], $BaTiO_3$ [4], BiOI [5], Bi_2WO_6 [6], $PbBiO_2Br/BiOBr$ [7], BiOI/GO [8], $Bi_2SiO_5/g\text{-}C_3N_4$ [9], and $SrFeO_{3-x}/g\text{-}C_3N_4$ [10]. The incorporation of heterostructures can effectively improve a photocatalyst's photocatalytic activity in a facile manner; this strategy may enable tuning photocatalyst electronic properties to particular desired levels and efficient photoinduced electron–hole pair separation.

Bismuth oxyhalide compounds (BiOX, X = F, Cl, Br, and I) offer remarkable chemical stability, uniquely layered structures, and highly favorable photocatalytic performance under UV–Vis illumination. Scholars have increasingly published studies of some noteworthy characteristics of BiOX, namely favorable energy gaps, high stability, and photocatalytic activity levels superior to those of other compounds [11,12]. The bandgaps of BiOF [13], $Bi_xO_yF_z$ [14], BiOCl/BiOF [15], and BiOBr/BiOF [16] have been reported to be 3.64, 3.35–3.44, 3.56 eV, and 3.85 eV, respectively. Among these compounds, BiOF has a direct bandgap of nearly 3.5 eV; therefore BiOF is a photocatalyst that is sensitive to UV radiation. The atomic structure of BiOF has layers of $[Bi_2O_2F_2]$ because $[Bi_2O_2]^{2+}$ slabs are positioned between pairs of fluorine atoms $[F_2]^{2-}$ [13,14]. The valence band of bismuth oxyiodides is mostly composed of I_{5p} and O_{2p} orbitals, whereas the Bi_{6p} orbital comprises the conduction band [17]; thus, the bandgap energy of iodine-poor BiO_mI_n is lower compared with Bi_2O_3 but higher compared with BiOI [18]. Therefore, these materials may be effective as visible-light photocatalysts. Specifically, the structure and composition of BiO_mI_n strongly affect its physicochemical characteristics such as oxidizing abilities, optical characteristics, and electronic characteristics; thus, novel photocatalysts may be developed for the effective degradation of environmental and toxic pollutants. Keller and Kramer reported on BiOX/BiOY systems (X, Y = Cl, Br, and I) that demonstrated nearly unlimited solubility [19]; since that report, scholars have published papers regarding syntheses of similar oxyhalide materials with special photocatalytic activities. Recently, the literature has grown with numerous reports of BiOX/BiOY synthesis approaches, characterizations, and assessed features.

Per the authors' review of relevant literature, no study has examined the use of visible-light irradiation for photocatalytic degradation of CV dyes with the aid of BiO_pF_q/BiO_xI_y. This study employed a template-free and controlled hydrothermal method to synthesize a series of BiO_pF_q/BiO_xI_y nanocomposites with different F/I molar ratios, pH values, and reaction temperatures; moreover, this study compared the photocatalytic activities of these compounds in terms of CV degradation in aqueous media under visible-light irradiation. This paper puts forth and explains some mechanisms that may trigger photodegradation. The present study contributes methods for synthesizing BiO_pF_q/BiO_xI_y and degrading organic compounds; in the future, these methods may be applied for the mitigation of environmental pollution.

2. Experiment

2.1. Materials

All chemicals utilized in this study were of analytic grade, with no additional purification. The following additional materials were purchased: HBA (2-hydroxybenzoic acid or salicylic acid), Bi $(NO_3)_3{\cdot}5H_2O$, KI, KF (Katayama), KCl (Shimakyu), CV dye (TCI), sodium azide (Sigma), *p*-benzoquinone (Alfa Aesar), isopropanol (Merck), and ammonium oxalate (Osaka). Reagent-grade ammonium acetate, sodium hydroxide, nitric acid, and HPLC-grade methanol were obtained from Merck.

2.2. Instruments and analytical methods

A diffractometer system (MAC Science MXP18) applying Cu–Kα radiation (40 kV and 80 mA) recorded XRD patterns. XPS was recorded with an ULVAC-PHI spectrometer. Al–Kα radiation was realized at 15 kV; a Scinco SA-13.1 spectrophotometer recorded UV–Vis-DRS data within the 300–800 nm wavelength range at room temperature. SEM-EDS was performed using a JEOL JSM-7401F microscope, with the acceleration voltage set to 15 kV. Moreover, a JEOL-2010 microscope was utilized to obtain TEM images, EDS spectra, high-resolution TEM images, and selected-area electron diffraction patterns, with the acceleration voltage being set at 200 kV. An automated system (Micromeritics Gemini) recorded the samples' BET specific surface areas (S_{BET}) at 237 °C; in this process, nitrogen gas was utilized as the adsorbate at liquid-nitrogen temperature. UV photoelectron spectroscopy data were collected with an ULVAC-PHI XPS PHI Quantera SXM, and PL data were obtained with a Hitachi F-7000. Finally, a Brüker ER200D spectrometer, with an Agilent 5310A frequency counter operating in the X band, recorded EPR spectra at 77 K.

2.3. Synthesis of BiO_pF_q/BiO_xI_y

A 50-mL flask was filled with 5 mmol Bi $(NO_3)_3{\cdot}5H_2O$, after which 5 mL 4 M HNO_3 was added. The contents of the flask were continuously stirred, with the addition of 2 M NaOH dropwise for realizing pH value adjustment. After the observation of precipitate formation, 3 M portions of KF and KI (with various KF:KI molar ratios) were added dropwise. The solution underwent 30 min of vigorous stirring, followed by transferring it to a 30 mL Teflon-lined stainless-steel autoclave; next, the autoclave was exposed to heating temperatures ranging from 100 to 250 °C for 12 h, and it was subsequently allowed to cool to room temperature. After these processes, the solid obtained was collected to filtration, washing performed using deionized water and ethanol for ionic species removal, and then overnight dried at 80 °C. A selection of BiO_pF_q/BiO_xI_y composites were prepared with controlled values of KF:KI molar ratio (1:2 or 2:1), temperature (100–250 °C), pH (1–14), and reaction times (12 h), as indicated in Table 1. The as-prepared samples were named with identifiers sequentially from BF1I2-1-100 to BF2I1-14-250.

2.4. Photocatalytic and active species experiments

In the trials of this study, we chose either CV (or HBA) as our target pollutant to evaluate photocatalytic activity. CV (or HBA) irradiation products were immersed in stirred aqueous solutions housed in flasks (100 mL); both an aqueous dispersion of 10 ppm 100 mL CV (or HBA) and 10 mg of the photocatalyst were then placed in a Pyrex flask. The suspension's pH was adjusted through the addition of sodium hydroxide or nitric acid solution addition. Following batch sorption experiments, the mixture was subjected to a centrifugation procedure conducted at 3000 rpm to determine the absorbance of CV (or HBA) at 585 (or 300) nm through HPLC-PDA. The optical system for the catalytic reaction under visible-light includes a 10 W Xe arc lamp, a reaction container and a cut-off filter ($\lambda > 420$ nm), with the light intensity fixed at 3.2 W/m^2 for irradiating the reaction vessel 30 cm away from the light source. At specified irradiation time intermissions, 5-mL aliquots were