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Reduced-graphene-oxide-wrapped BiOI-AgI heterostructured nanocomposite as a high-performance photocatalyst for dye degradation under solar light irradiation

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ABSTRACT

Solar photocatalytic water treatment has emerged as a promising way to provide clean water. However, most traditional photocatalysts (TiO_2, ZnO, etc.) are active only under ultraviolet light and have high recombination rates of photoinduced electron-hole pairs; therefore, they are not sufficient to fulfill all of the demands of practical applications. This problem could be overcome by developing highly solar-light-active and durable heterostructured photocatalysts. In this study, a new solar-light-active heterostructured reduced graphene oxide (RGO)/BiOI/AgI photocatalyst was successfully fabricated through a simple precipitation method. The resultant heterostructured RGO/BiOI/AgI nanocomposite exhibited extraordinary photocatalytic performance in the degradation of rhodamine B (RhB) under simulated sunlight irradiation. The measured rate constant of the RGO/BiOI/AgI nanocomposite was six times higher than that of bare BiOI nanostructures. Its extraordinary capacity for harvesting full-spectrum light and long-term stability makes the RGO/BiOI/AgI nanocomposite a potential photocatalyst for environmental remediation.

1. Introduction

The conversion and utilization of sustainable clean solar energy for the remediation of detrimental water pollutants is a global challenge for the research community [1,2]. Photocatalysis techniques using active semiconductor nanostructures are useful proven green techniques to solve the above problems [3]. However, most traditional photocatalysts (TiO_2, ZnO, etc.) are active only under ultraviolet light and have high recombination rates of photoinduced electron-hole pairs, rendering them unsuitable for practical applications [4,5]. To overcome these limitations, visible-light-active hybrid heterostructure photocatalysts, composed of two or more active components, are promising potential novel semiconductor photocatalysts with reduced band gaps, which improve their response to vastly abundant solar energy toward enhancing photocatalytic performance [6,7].

Recently, researchers have paid tremendous attention to the use of photocatalysts based on bismuth oxyhalides (BiOX) for environmental remediation [8,9]. BiOX have tetragonal layered structures containing $[Bi_2O_2]^{2+}$ slabs that are interleaved by double slabs of halogen atoms. This particular structural arrangement produces an internal electrostatic field perpendicular to each layer, which reduces the recombination rate of the photogenerated electron-hole pairs, enhancing photocatalytic performance [10,11]. Among the BiOX (X = Cl, Br, I), BiOI is the most promising visible-light-harvesting photocatalyst, because of its narrow band gap and efficient sunlight-harvesting nature [6]. In addition, shape, morphology, and facet control strategies have been employed for the effective utilization of BiOI as a solar-light-active photocatalyst [12–14]. For instance, Ye et al. [12] showed that symmetrical BiOI single-crystal nanosheets with dominant (001) facets exhibited greater photocatalytic performance than irregular BiOI in the degradation of RhB dye. Pan et al. [13] demonstrated that BiOI (110) nanosheet-assembled microspheres showed better photocatalytic efficiency than those with (001) facets. Huang et al. [14] designed three-dimensional (3D) hierarchical graphene-BiOI micro-flowers like nanoarchitectures assembled on the graphene surface, which exhibited improved photocatalytic performance under visible light irradiation. Thus, BiOI-based photocatalysts are promising for the

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effective utilization of enormous amounts of solar energy, though the electrons and holes of single-component BiOI recombine very rapidly.

Recently, widespread research efforts have been directed toward the development of photocatalysts based on silver halides (AgX, X = Cl, Br, I) [15,16]. They have shown enhanced photocatalytic activity in water splitting and organic pollutant photodegradation. Among these photocatalysts, silver iodide (AgI) has shown promising efficiency in the degradation of organic pollutants using solar light irradiation [16,17]. However, the stability of this photocatalyst is insufficient for extended reuse, since the AgI photocatalysts are completely converted into metallic silver (Ag^0) upon reuse [18]. This unacceptable durability is the main obstacle to the wide application of AgI as a highly efficient photocatalyst. To overcome this, the current trend is to develop heterostructured nanocomposite photocatalysts with AgI and supporting semiconductor nanostructures, so that the electrons migrate from AgI to the supporting semiconductor nanostructures, and this has improved the stability of AgI nanostructures and enhanced their photocatalytic activity [19–21]. Very recently, graphene, a two-dimensional aromatic monolayer of carbon atoms forming a honeycomb crystal lattice structure, was discovered, and has attracted enormous attention from researchers because of its remarkably high electron mobility and fast electron transfer ability [22,23]. In addition, graphene and its derivatives, reduced graphene oxide (RGO), have ultrahigh surface areas, which facilitate the effective separation of electron-hole pairs in heterostructured nanocomposites. Many studies have been conducted to improve the photocatalytic activity of photocatalysts by coupling with RGO [24,25].

Considering the importance of BiOI, AgI, and RGO, herein, for the first time, we report the systematic study of an RGO/BiOI/AgI nanocomposite photocatalyst prepared via a green solution process method. Structural and microstructural analyses revealed that the RGO/BiOI/AgI nanocomposite was successfully fabricated with high purity and crystallinity. Optical studies indicated that the as-synthesized nanocomposite harvested sunlight efficiently. Photocatalysis experiments indicated that the as-synthesized novel heterostructured nanocomposite showed good performance and high stability in dye degradation under solar light irradiation. Finally, we strongly believe that the work presented here will be useful in the design and construction of novel sunlight-active photocatalysts with enhanced performance and stability.

2. Experimental

All of the chemicals and reagents such as bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$), potassium iodide (KI), silver nitrate ($AgNO_3$), and ethylene glycol (EG) were purchased from Daejung Chemicals, South Korea, and of analytical grade, and were used without further purification. Deionized (DI) water was used throughout the experiments. Graphene oxide (GO) was prepared from natural graphite flakes according to a modification of the Hummers method, similarly to our previous studies [26,27].

2.1. Preparation of BiOI, BiOI/AgI, and RGO/BiOI/AgI nanocomposites

In a typical synthesis, different amounts of the as-prepared GO were ultrasonically dispersed in 20 mL of EG containing 1 mmol of $Bi(NO_3)_3 \cdot 5H_2O$. Afterwards, 1 mmol of KI was dissolved in 20 mL of DI water and then this solution was added dropwise into the above GO and $Bi(NO_3)_3 \cdot 5H_2O$ suspension under strong magnetic stirring. Then, the suspension was stirred for 1 h at room temperature. Finally, 0.5 mmol of $AgNO_3$ was dissolved in 20 mL of DI water and this solution was added to the above suspension dropwise under magnetic stirring; subsequently, the solution was stirred for 2 h at room temperature. The precipitate, RGO/BiOI/AgI, was then separated, washed with DI water several times, and then dried at 80 °C for 8 h. Similarly, BiOI/AgI photocatalysts were synthesized without dispersing GO, and pure BiOI was synthesized under the same conditions except for the additions of GO and $AgNO_3$. Bare AgI was synthesized with 1:1 M ratio of KI and $AgNO_3$, without dispersing GO.

2.2. Characterization of the photocatalysts

The surface morphologies and elemental compositions were evaluated using a Hitachi S-4800 field emission scanning electron microscope equipped with an energy-dispersive spectrometer (Inca 400, Oxford Instruments). The crystal structures of these samples were examined by X-ray diffraction (XRD) spectroscopy using a Bruker D8 Advanced X-ray diffractometer with Cu Kα radiation as the X-ray source. The diffuse reflectance spectrum (DRS) was recorded with an ultraviolet–visible (UV–Vis) spectrometer (UV-1800 Shimadzu).

2.3. Photocatalytic experiments

The photocatalytic activities of the different photocatalysts, such as BiOI, BiOI/AgI, and the RGO/BiOI/AgI nanocomposite, were explored via the degradation of RhB (10 mg/L) in aqueous solution under a solar simulator (Model 10500 Low Cost Solar Simulator with a Model 10513 90° Uniform Illumination Accessory) equipped with an AM 1.5G filter and 150 W Xe lamp as the light source (Abet Technologies). In a 150 mL Pyrex conical flask, 100 mg of photocatalyst was dispersed in 100 mL of RhB solution. Before irradiation, the photocatalyst suspension was magnetically stirred at room temperature in the dark to attain adsorption-desorption equilibrium. After adsorption-desorption equilibrium was achieved, the solar simulator was turned on. During irradiation, 2.0 mL of the suspension was withdrawn at regular 10 min time intervals and centrifuged to remove the photocatalyst, and then the dye concentration was measured at the characteristic maximum absorption wavelength of RhB of 553.8 nm with a UV–Vis spectrophotometer (UV–1650PC, Shimadzu, Japan) at room temperature. Similarly, in the photocatalytic process, ethylenediaminetetraacetic acid (EDTA), benzoquinone (BQ), and *t*-butyl alcohol (TBA) were added to the photocatalyst suspension to examine the effects of reactive species such as holes (h^+), $\cdot O_2^-$, and $\cdot OH$ radicals, respectively. For the recycling experiment, previously used RGO/BiOI/AgI photocatalyst was separated from the solution through centrifugation, dried for 8 h at 80 °C, and then reused for the degradation of RhB at the same concentration.

3. Results and discussion

3.1. Morphology of the as-synthesized photocatalysts

The morphologies of as-prepared BiOI, BiOI/AgI, and RGO/BiOI/AgI were examined using field emission scanning electron microscopy (FESEM). In Fig. 1a, BiOI shows a 3D hierarchical flower-like microsphere structure consisting of numerous smooth two-dimensional (2D) nanosheets. The nanosheets were connected to one another at their centers to form 2–3 μm microspheres [28]. In Fig. 1b, it is clear that AgI nanoparticles are uniformly anchored onto the BiOI nanosheets [24]. In addition, as shown in Fig. 1c, the BiOI/AgI nanoflower-like shapes are wrapped by RGO nanosheets and interconnected within the hierarchical structure. Furthermore, energy-dispersive spectroscopy (EDS) was carried out on the RGO/BiOI/AgI nanocomposite and the peaks belonging to Bi, O,