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# Reduced graphene oxide-modified $Bi_2WO_6$/BiOI composite for the effective photocatalytic removal of organic pollutants and molecular modeling of adsorption

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## ABSTRACT

In this study, reduced graphene oxide (rGO) with unique physicochemical, optical, and electrical properties was applied in a varying content to improve the photocatalytic performance of $Bi_2WO_6$/BiOI towards the degradation of colorless organic pollutants: acetaldehyde (AcH) and chloramphenicol (CAP) under visible light. The rGO/$Bi_2WO_6$/BiOI composites were characterized by means of X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray spectroscopy, transmission electron microscopy, ultraviolet-visible spectroscopy, X-ray photoelectron spectroscopy, and nitrogen gas adsorption analysis. The prepared rGO/$Bi_2WO_6$/BiOI composite with 1 wt% rGO demonstrated a much higher photodegradation rate constant towards the degradation of AcH and CAP than its $Bi_2WO_6$/BiOI counterpart. Such enhancement can be explained by the synergistic effects of rGO in adsorbing AcH and CAP molecules, capturing photoinduced electrons, and forming an additional *p-n* heterojunction with *n*-type $Bi_2WO_6$. The adsorption affinities of AcH molecules in the gas phase and CAP molecules in aqueous solution to model rGO, BiOI (102) and $Bi_2WO_6$ (113) surfaces were studied by molecular modeling using a layer building tool that allows the generation of layered structures and interfaces. It was found that compared to $Bi_2WO_6$, rGO and BiOI show the increased adsorption of AcH and CAP+water molecules over the rGO/BiOI surface in the rGO/$Bi_2WO_6$/BiOI and rGO/BiOI composites. The enhanced photocatalytic activity demonstrated by the newly prepared rGO/$Bi_2WO_6$/BiOI composite makes it a potential candidate for use in environmental remediation processes.

## 1. Introduction

Since the Honda-Fujishima effect was first reported in 1972, semiconductor-based photocatalysis has been regarded as one of the most green and economical processes for potential application in environmental remediation due to its use of abundant solar energy [1]. Initially, most studies were heavily concentrated on developing UV-light-responsive photocatalysts that absorb only UV light, which is present in a small amount in the solar spectrum. Over the past years, to efficiently utilize solar energy, much effort has been made towards the development of various visible-light-responsive photocatalysts, including oxide ($Fe_2O_3$ [2], $BiVO_4$ [3], doped-$TiO_2$ [4], etc.), mixed anion (oxynitrides [5], oxyhalides [6], etc.) and non-oxide (sulfides [7], nitrides [8], etc.) compounds.

Bismuth-containing photocatalysts (e.g., $Bi_2O_3$, $Bi_2MO_6$ ($M =$ Cr, Mo, or W), $BiVO_4$, Bi*X* ($X =$ Cl, Br or I), $BiPO_4$, $(BiO)_2CO_3$, and pentavalent bismuthates) have attracted much attention due to their appropriate band gap for visible-light absorption, high mobility of photogenerated charge carriers resulting from the well-dispersed Bi 6 s orbital, layered structure, easily tailored morphology, and non-toxicity [9]. Among them, $Bi_2WO_6$, as one of the simplest members of the Aurivillius oxide family of layered perovskites, is structurally composed of alternating perovskite-like blocks ($BO_6$ octahedra) and fluorite-like $Bi_2O_2$ layers [10] and has an optical band gap of 2.80 eV. To enhance its

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photocatalytic performance for the removal of organic pollutants, $Bi_2WO_6$ was coupled with other semiconductors [9,11,12], metals [13,14], or clays [15,16] or doped with Pt [17], Ce [18], or N [19].

Carbon-based materials are known to have unique electrical and electronic properties, high specific surface area, and mechanical strength and have been applied to improve the photocatalytic performance of various inorganic photocatalysts due to their ability to improve the adsorption of pollutants, increase the light absorption intensity, prolong the lifetime of electron-hole pairs, and extend the light absorption range. Xu and coworkers [20] found that $TiO_2$-graphene in essence has the same effect as composite materials of other $TiO_2$-carbon allotropes (carbon nanotubes, fullerenes, and activated carbon) on the enhancement of the photocatalytic activity of $TiO_2$. Katsumata et al. [21] reported that rutile-$C_{60}$ exhibits much higher photocatalytic activity for the decolorization of methylene blue than anatase-$C_{60}$ due to the effective transfer of photogenerated electrons from $C_{60}$ to the rutile phase. $WO_3$ was composited with polymeric graphitic carbon nitride ($g$-$C_3N_4$) to improve its photocatalytic activity for the degradation of gaseous acetaldehyde under visible-light irradiation [22]. A carbon nanotube–$TiO_2$ Schottky barrier junction was demonstrated to be an effective way to increase the recombination time [23]. A remarkable 10-fold enhancement in the photoelectrochemical water splitting reaction over that of pure $BiVO_4$ was observed on a $BiVO_4$-reduced graphene oxide composite prepared using a single-step photocatalytic reaction [24].

To further improve the photocatalytic performance of the $Bi_2WO_6$/BiOI composite, it is necessary to hybridize it with a conjugated π-structured material with good electrical conductivity [25] to reduce the direct recombination of photogenerated charge carriers. Therefore, reduced graphene oxide was chosen in this study to modify the $Bi_2WO_6$/BiOI composite, and the effect of the content of reduced graphene oxide on the photocatalytic removal of colorless organic pollutants (acetaldehyde and chloramphenicol) from model contaminated air and water under visible-light irradiation was investigated. The possible mechanism for the enhanced photocatalytic activity of reduced graphene oxide/$Bi_2WO_6$/BiOI was also discussed in detail.

## 2. Experimental

### 2.1. Preparation

$Bi(NO_3)_3 \cdot 5H_2O$ (99.9%), KI (99.5%), $KMnO_4$ (99.3%), $NaNO_3$ (98.0%), sulfuric acid (95%), ethylene glycol (99.0%), graphite (98 + %), and aqueous ammonia (28%) were obtained from Wako Pure Chemical Industries, Ltd., and $Na_2WO_4 \cdot 2H_2O$ (99 + %) was purchased from Strem Chemicals, Inc. All chemical reagents were of analytical grade and used as received without further purification. Deionized water (Millipore Milli-Q Plus purification system, 18.2 MΩ·cm) was used throughout the experiments.

Graphene oxide (GO) and $Bi_2WO_6$ (BW) powders were synthesized according to previously reported synthetic procedures [11, 26]. The reduced graphene oxide/$Bi_2WO_6$/BiOI (rGO/BW/BI) composite was prepared by a hydrothermal method. First, 0.5 mmol of $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in 10 mL of ethylene glycol, and 0.5 mmol of KI was dissolved in 10 mL of deionized water. Both solutions were mixed together under vigorous stirring. Meanwhile, 0.5 mmol of the as-synthesized $Bi_2WO_6$ powder (0.3489 g) and a desired amount of GO powder (0.5, 1.0, 2.5, 5.0, or 10 wt% rGO) were separately dispersed in 10 mL of deionized water. Subsequently, the precursor solution of BiOI was mixed with the aqueous suspension of $Bi_2WO_6$ and GO powders under vigorous stirring at room temperature for 30 min. The pH of the suspension was adjusted to 7 by the dropwise addition of an aqueous ammonia solution. After vigorous stirring for another 30 min, the formed suspension was transferred into a 40 mL Teflon-lined stainless-steel autoclave, which was then sealed and maintained at 180 °C for 12 h. After the hydrothermal synthesis, the composite powders were collected by centrifugation, washed with deionized water several times and dried at 80 °C for 8 h. For comparison, BiOI, $Bi_2WO_6$/BiOI, rGO/$Bi_2WO_6$ (1 wt % rGO), and rGO/BiOI (1 wt% rGO) were also prepared by a hydrothermal method under identical synthetic conditions as those applied for the synthesis of the rGO/$Bi_2WO_6$/BiOI composite.

### 2.2. Characterization

The crystalline phases were identified by powder X-ray diffraction (XRD) using an RINT-2100 diffractometer (Rigaku) with monochromatic Cu K$\alpha$ radiation ($\lambda = 1.5405$ Å) at 40 kV and 40 mA. The powder samples were scanned at a scanning rate of $2° \cdot min^{-1}$ over the $2\theta$ range of 10–70°. The samples were also characterized by a T64000 Raman spectrometer (Horiba Jobin Yvon S.A.S.) with an Ar laser (514.5 nm) operated at 50 mW. The particle morphology and size were examined by using an S-4500 ultrahigh-resolution scanning electron microscope (SEM, Hitachi) operated at an accelerating voltage of 15 kV. The elemental composition of the sample was analyzed by energy-dispersive X-ray spectroscopy (Hitachi) attached to the SEM. Transmission electron microscopy (TEM) observations were performed with an EM-002B high-resolution electron microscope (TOPCON) operated at an accelerating voltage of 200 kV in order to distinguish the crystal structures in the composite. The ultraviolet-visible (UV–vis) diffuse reflectance spectra of the samples were recorded on a Lambda 950 UV/VIS/NIR spectrophotometer (Perkin-Elmer), equipped with an integrating sphere, with $BaSO_4$ as the reference, over the wavelength range of 200–800 nm. The surface compositions and chemical states were analyzed by X-ray photoelectron spectroscopy (XPS, JPS-9010MC, JEOL) using non-monochromatic Mg K$\alpha$ radiation (1253.6 eV). The specific surface area ($S_{BET}$) was calculated by the Brunauer-Emmett-Teller (BET) method from the linear portion of the nitrogen gas adsorption isotherm of a sample preheated at 120 °C for 4 h under vacuum and measured at 77 K using an Autosorb-3B instrument (Quantachrome).

### 2.3. Adsorption and photocatalytic activity tests

The adsorption ability and photocatalytic activity of the prepared samples were evaluated towards the adsorption and photodegradation of colorless organic pollutants under visible-light irradiation. Acetaldehyde (AcH) and chloramphenicol (CAP) were chosen as the indoor air and water pollutants, respectively.

In the AcH test, the powder sample (50 mg) was placed in a 500 mL reaction vessel made of Pyrex® glass, and the lid, inlet, and outlet were firmly closed. Pure air (Taiyo Nippon Sanso Corp.) was blown through the reaction vessel to remove any air contaminants. Then, a certain amount of AcH was introduced into the reaction vessel using a 2 mL Pressure-Lok® glass syringe until the concentration of AcH reached 250 ppm. After reaching adsorption equilibrium in the dark for 12 h, the reaction vessel was placed under FL10 W white fluorescent daylight lamps (>400 nm, Toshiba), which emitted visible light with an irradiance of ~8000 lx, as measured with an LX-101A light meter (Lutron Electronic Enterprise Co., Ltd.). To eliminate UV light, an SC42 cutoff filter (<420 nm, Fujifilm) was used. The decrease in the AcH concentration and the increase in the $CO_2$ concentration were monitored during the photocatalytic reaction using a GC-2014 gas chromatograph (Shimadzu), equipped with a 2 m Porapak-Q column, methanizer, and flame ionization detector. $N_2$ was used as the carrier gas.

In the CAP test, the powder sample (50 mg) was ultrasonically dispersed in a 50 mL aqueous solution containing 15 $mg \cdot L^{-1}$ $C_{15}H_{15}Cl_2N_2$ (Sigma Chemie GmbH) in a reaction vessel made of quartz. Prior to visible-light irradiation, the suspension was magnetically stirred in the dark for 1 h to ensure adsorption-desorption equilibrium. A 400 W halogen lamp with a 400 nm cutoff filter was used as the visible-light source. During the photocatalytic reaction, 2 mL of suspension was taken out at a given time interval and centrifuged for subsequent analysis of the CAP concentration using a U-3010 UV–vis