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$Bi_2Ga_4O_9$: An undoped single-phase photocatalyst for overall water splitting under visible light

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ABSTRACT

Visible-light-driven overall water splitting via semiconductors is one of the most challenging topics in photocatalysis, because it raises harsh requirements for photocatalysts both thermodynamically and kinetically. With the rationale of combining Bi^{3+} and Ga^{3+}, we developed an oxide photocatalyst, $Bi_2Ga_4O_9$ (loaded with RuO_x), capable of overall water splitting under visible light due to its specific band structure, i.e., suitable potentials for valence and conduction bands, and most importantly its characteristic of anisotropic charge migration. Band structure engineering of Fe^{3+}-to-Ga^{3+} doping and a sol–gel synthetic method were both applied to further enhance the light-harvesting ability and eventually lead to optimal gas generation rates of 41.5 and 19.6 μmol/h/g for H_2 and O_2, respectively. The apparent quantum yield at 420 nm is 0.09%; nevertheless, it represents a successful effort to develop a single-phase visible light catalyst for overall water splitting.

1. Introduction

Economical solar energy utilization is a long-lasting goal in energy and environmental science, and visible-light-driven overall water splitting via semiconductors is one of the most challenging approaches. Thermodynamically, such a photocatalyst should possess a narrow bandgap energy (⩽3.0 eV) and appropriate conduction and valence band positions for simultaneous H_2 and O_2 evolution (⩾1.8 eV). In kinetics, a high efficiency of charge separation is needed to allow the photogenerated charges to migrate to the solid–liquid interface for the following redox reactions. Moreover, the photocatalysts should be chemically stable under the photocatalysis conditions.

With regard to the thermodynamics aspect, two successful strategies have been developed. One is to employ the *Z*-scheme dual-catalyst systems, which comprise two photocatalysts capable of H_2 and O_2 production, respectively [1–3]. However, there might exist an upper limit of apparent quantum yields (AQYs) due to the assumed low efficiency of charge transfer via electron mediators. For instance, the AQY for $(Pt/CuGaS_2)$-(rGO/TiO_2) is 1.3%@380 nm in pure water [4]; the AQY is 1.1%@420 nm for $(Ru/SrTiO_3{:}La/Rh)$-$(Ir/CoO_x/Ta_3N_5)$ in acidic aqueous solution [5]; $ZnRh_2O_4/Ag/Ag_{1-x}SbO_{3-y}$ shows an AQY of 0.04% at 420 nm [6]; a record high AQY of 6.8%@420 nm with *Z*-Scheme was achieved recently by $(Pt\text{-}MgTa_2O_{6-x}N_y/TaON)$-$I^-/IO_3^-$-$(PtO_x\text{-}WO_3)$ [7].

The other strategy is so-called band structure engineering on originally wide bandgap photocatalysts. In detail, experimenters could narrow the bandgap by lowering the conduction band (CB) or elevating the valence band (VB) potential through rational cationic or anionic substitutions. $TiO_2{:}M$ (M = Cr, Pt, Ir, Co) [8–10], $InTaO_4$:Ni [11], $BiYWO_6$ [12], $Bi_{0.5}Dy_{0.5}VO_4$ [13], and $AgTa_{0.7}Nb_{0.3}O_3$ [14] all exhibit overall water-splitting activities under visible light through the band structure engineering strategy. However, cationic substitutions behaved as charge recombination centers and the VB potential (mainly composed of O2*p* orbitals) is generally deep (~3 V). Then experimenters turn to elevating the VB by anionic substitutions of nonoxygen atoms (such as S, N, or H). This usually results in the problem of instability, which is also the exact reason that metal sulfides cannot be used for overall water splitting. Nevertheless, a few compounds did survive under photocatalysis conditions, such as $(Zn_{1+x}Ge)(N_2O_x)$, $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$, and black titania [15–17]. Researchers are still struggling to improve their stability. There is a recent achievement of $LaMg_xTa_{1-x}O_{1+3x}N_{2-3x}$ ($x \geqslant 1/3$), extending the responsive wavelength to 600 nm; however, the catalysts need to be protected by a doubled coating of amorphous oxyhydroxides $MO_{2-m}(OH)_{2m}{\cdot}xH_2O$ (M = Si, Ti) [18].

Based on these analyses, a single photocatalyst with a suitable band structure but no extrinsic substitution could be an ideal candidate. Indeed, a very few compounds have been found capable of overall water splitting under visible light, including CoO quantum

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dots (however, they are deactivated after 1 h irradiation due to aggregation) [19] and g-C_3N_4 (decorated with C-quantum dots to catalyze the H_2O_2-to-O_2 reaction) [20]. We believe oxide materials still possess the best chance because of their great structural diversity and high chemical stability, and some specific structures may exhibit the characteristic of anisotropic charge migration to overcome the kinetic problem of charge recombination, such as that in $BiVO_4$ [21].

We intend to target a compound with a relatively higher VB position. It has already been proposed that the outer *s* or *d* orbitals of Bi^{3+}, Pb^{2+}, Sn^{2+}, Cu^{+}, and Ag^{+} contribute to the top of the VB [22]. This is why a number of famous Bi^{3+}-containing compounds (such as Bi_2O_3, $BiVO_4$, Bi_2MoO_6, Bi_2WO_6, $CaBi_2O_4$) possess narrow band-gap energies [23–27], but an insufficient CB potential for water reduction. Therefore, another element that can elevate the CB potential should be recruited. In such a scenario, we turned to Ga^{3+}, which readily points to $Bi_2Ga_4O_9$ with a mullite-type structure. In this work, the bulk material $Bi_2Ga_4O_9$ prepared directly by a high-temperature solid state reaction exhibits overall water-splitting ability (loading with 0.5 wt.% RuO_x) under pure visible light ($\lambda > 400$ nm) irradiation, i.e., H_2- and O_2-generation rates of 19.3 and 9.7 μmol/h/g, respectively. Though the idea of combining appropriate elements is simple, the key to achieving overall water splitting is the appropriate electronic structure for charge separation. Theoretical calculations suggested anisotropic migration behavior for electrons and holes. In detail, electrons move much faster than holes along the *c*-axis, or in other words, photoexcited h^+ were mostly confined within the *ab*-plane.

In addition, theoretical and experimental studies both proved that the Fe^{3+}-to-Ga^{3+} substitution would enhance the light-harvesting ability, and the sample $Bi_2Ga_{3.6}Fe_{0.4}O_9$ prepared by a sol–gel method possesses elevated H_2 and O_2 generation rates of 41.5 and 19.6 μmol/h/g, respectively. The current AQY is generally low (0.09%@420 nm); nevertheless, this work provides an archetypal compound and a good platform for further modifications.

2. Materials and methods

2.1. Syntheses and general characterizations

Solid state reaction (SSR) and sol–gel (SG) methods were employed to prepare $Bi_2Ga_4O_9$ and transition-metal-doped $Bi_2Ga_4O_9$. For the preparation of SSR-$Bi_2Ga_4O_9$, stoichiometric Bi_2O_3 and Ga_2O_3 (both preheated at 500 °C for 10 h) were mixed and ground in an agate mortar. The first heating was performed at 600 °C for 10 h. After that, the resultant powder sample was reground thoroughly and pressed into a pellet with a diameter of 13 mm. The pellet was then heated at 800 °C for 10 h to obtain phase-pure SSR-$Bi_2Ga_4O_9$. Powder samples of SSR-$Bi_2Ga_{4-x}M_xO_9$ (M = Cr, Mn, Fe; $0.2 \leqslant x \leqslant 0.8$) were prepared according to the same procedure and Cr_2O_3, Fe_2O_3, and $MnCO_3$ were used as transition metal sources.

The SG method was as follows. First, a prereaction was performed to dissolve 1 mmol of Ga_2O_3 (0.1874 g) using concentrated HNO_3 aqueous solution at 180 °C for 10 h in a sealed vessel. Then the solution, together with 0.5390 g of $Bi(NO_3)_3{\cdot}5H_2O$ and an appropriate amount of citric acid, was diluted into 50 mL of water. The diluted solution was slowly evaporated by a gentle and continuous heating. The resultant gel precursor was further dried at 200, 250, and 500 °C, respectively, 10 h for each period and with the temperature increasing at 1 °C/min. The final heating was performed at 670 °C for 10 h to obtain SG-$Bi_2Ga_4O_9$. Powder samples of SG-$Bi_2Ga_{4-x}Fe_xO_9$ ($0.3 \leqslant x \leqslant 0.5$) were prepared similarly, with the addition of $Fe(NO_3)_3{\cdot}6H_2O$ as the Fe^{3+} source.

Powder X-ray diffraction (XRD) was performed on a PANalytical X'pert powder diffractometer equipped with a PIXcel 1D detector (Cu Kα radiation). The operating voltage and current were 45 kV and 40 mA, respectively. Le Bail refinements were performed with a TOPAS software package [28]. Scanning electron microscopy (SEM) images were taken using a JSM-7800F electron microscope at a voltage of 3 kV and a working distance of ~4 mm. UV–vis diffuse reflectance spectra (DRS) were recorded at room temperature using a UV–visible–near infrared spectrometer (UV–vis–NIR, Shimadzu UV-3600) equipped with an integrating sphere attachment. $BaSO_4$ was used as a reflectance standard. X-ray photoelectron spectroscopy (XPS) was carried out with a UK Kratos Axis Ultra spectrometer with an Al Kα X-ray source operated at 15 kV and 15 mA. Electron binding energies were calibrated against the C1*s* emission at $E_b = 284.8$ eV to correct the contact potential differences between the sample and the spectrometer.

2.2. Photocatalysis evaluation

We used a gas-closed circulation system equipped with a vacuum line (CEL-SPH2N system), a reaction vessel, and a gas sampling port that was directly connected to a gas chromatograph (Shanghai Techcomp-GC7900, TCD detector, molecular sieve 5A, N_2 gas carrier). In the evaluation of photocatalytic O_2 production, helium gas was used as the gas carrier.

In a typical run, 50 mg of catalyst was dispersed by a magnetic stirrer in 50 mL of 5 vol.% triethanolamine (TEOA) aqueous solution (or 50 mL of pure water) in a 150 mL Pyrex reactor with a quartz cover. The solution was kept stirred, and a 10 °C recycling water bath was applied to keep the reaction vessel cool. The UV and visible light irradiation sources were a 500 W high-pressure mercury lamp (CEL-M500, Beijing Aulight) and a 300 W Xe lamp (CEL-HXF300, Beijing Aulight), respectively. Either a bandpass or a cutoff filter was applied to the Xe lamp to obtain a monochromatic beam light ($\lambda = 420$ nm) or pure visible light ($\lambda > 400$ nm), respectively.

2.3. Co-catalyst loading by a photodeposition method

The metal or metal oxide co-catalysts were loaded via photodeposition using the photocatalysis setup described above. Typically, 0.150 g of SSR-$Bi_2Ga_4O_9$ together with 0.52 mL of $H_2PtCl_6{\cdot}6H_2O$ aqueous solution (with a Pt concentration of 1.48 mg/mL) was charged into 50 mL of methanol aqueous solution (20 vol.%). Then this suspension was irradiated by UV light for 2 h, cooled by the 10 °C water bath. After the deposition process, a powder sample was recovered and washed with deionized water extensively. Other co-catalyst loading was performed with the metal sources $Ni(NO_3)_2{\cdot}6H_2O$ and $RuCl_3$ aqueous solution. Please note that the absolute loading content of co-catalysts was not determined experimentally, but estimated from the initial loading values.

2.4. Apparent quantum yields

It is known that the photocatalytic activity depends strongly on the applied experimental conditions, including the mass of the photocatalyst, the incident beam intensity, the type of sacrificial agents, and the volume and the concentration of the starting aqueous solution. The apparent quantum yield (AQY) is commonly used to evaluate the efficiency of a particular photocatalyst. The AQY should be lower than the absolute quantum yield because not all the incident photons are absorbed by the photocatalyst.

AQY for H_2 evolution under monochromatic irradiation was calculated according to the following equation:

$$\mathrm{AQY} = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100.$$