Iodine doped Z-scheme $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$ photocatalysts: facile synthesis, efficient visible light photocatalysis, and photocatalytic mechanism

Zhuomin Qiang ^a, Ximeng Liu ^a, Feng Li ^{ab}, Taihai Li ^{ab*}, Meng Zhang ^{c*},
Harishchandra Singh ^b, Marko Huttula ^b and Wei Cao ^b

a. College of Chemistry, Key Lab of Environment Friendly Chemistry and Application in Ministry of Education, Xiangtan University, Xiangtan, 411105, China.

b. Nano and Molecular Materials Research Unit, Faculty of Science, University of Oulu, P.O. Box 3000, FIN-90014, Finland.

c. Department of Physics, East China University of Science and Technology, Shanghai, 200237, China.

* Correspondence Author. Tel.: +86-731-58292202; fax: +86-731-8292251;

E-mail address: hnlth@xtu.edu.cn (T. Li); mzhang@ecust.edu.cn (M. Zhang).

Abstract

The Bi-based hierarchical multi-component photocatalytic system is an important player in energy and environmental catalysis due to its full-spectrum light absorption and stable separation of photo-generated charges. In this study, a novel family of iodine doped $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$ heterojunctions was successfully developed by a facile ionic liquid assisted solvothermal method. A visible light photocatalytic H_2 production rate of $664.5 \mu\text{mol g}^{-1} \text{h}^{-1}$ (0.3I- $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$ with 3% Pt) has been durably obtained, much higher than those of pristine and undoped counterparts. The photocatalysts are also capable for persistent pollutant and dye degradation. Through electrochemical and spectroscopic tests and density functional theory calculation, the enhanced photocatalytic activity is attributed to formation of the Z-scheme photocatalyst. Therein, the lowered and indirect bandgap and heterojunctional band alignment spontaneously benefit visible light harvesting, electron-hole pair separation, and proton reduction. Besides a facile synthesis for effective photocatalysis, the Z-scheme mechanism is hoped to facilitate the design and realization of similar systems for photocatalytic H_2 evolution and organic hazards decontamination.

Keywords: photocatalytic; I-doped $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$; solvothermal; Z-scheme; density functional theory calculation.

1. Introduction

As one of the most promising routes for H₂ production and water purification, semiconductor photocatalysis shoulders the mission of harvesting solar energy onto photocatalytic H₂ evolution and decomposing hazardous organics discharged in the industrial wastewater [1,2]. The Bi-based photocatalysts are photocatalytically active under visible light radiation owing to their unique band structure and resistance to photocorrosion [3,4]. Among various bismuth compounds, the Bi₂WO₆ has received the most attentions due to its high visible light photocatalytic property and good stability [5-7]. However, as a single semiconductive compound, the Bi₂WO₆ is lack of effective charge separation after photoexcitation, yet demanding further treatments to improve the photocatalytic efficiency in practical uses [8-11].

The Z-scheme can separate electrons and holes effectively. Various materials engineering has been performed for further treatments of the Bi₂WO₆, including doped with noble metals [12-16], carbon quantum dot [17-19], carbon nitride [20-22], and joint with other bismuth semiconductors such Bi₂O₃ [23,24] or Bi₂O₂CO₃ [25,26]. Significant improvements have been reached by using these activated Bi₂WO₆. The latest reports on the Bi-based catalysts for different photocatalytic applications are summarized in Table S1. In addition, the final photocatalytic properties of the materials are affected by the specific morphologies subjected to the synthesis process. For example, the Bi₂WO₆ microspheres self-assembled from ultra-thin nanoslice owns better catalytic abilities than the flake or block counterparts [27,28]. The nanoplate form is not exclusively owned by the Bi₂WO₆. The Bi₂O₂CO₃ has similar two-dimensional sheet structures, ensuring a possible formation of a heterojunction to the Bi₂WO₆. This can be seen in the previous studies where the Bi₂WO₆/Bi₂O₂CO₃

heterojunctions are formed via hydrothermal methods [29,30]. Though showing enhanced photocatalytic activities for rhodamine B (RhB) degradation, these heterojunctions suffer from side products of organic hazards in the synthesis or irregular product morphologies deviated from nanoslices. Moreover, these heterojunctions can not split water to production H_2 . Furthermore, the wide bandgap of $Bi_2O_2CO_3$ (~3.2 eV) hinders sunlight absorption [31-33], and it needs to be lowered by other methods.

Ionic liquids (IL) can provide more heteroatoms to change the structure of the electrocatalysts or photocatalysts, which attribute to their excellent ionic conductivity and so on [34]. In addition, ionic liquids are used for doping ions into materials and improve their conductivity. Inspired by the aforementioned considerations, the iodine doped $Bi_2O_2CO_3/Bi_2WO_6$ composites were prepared by solvothermal method under the auxiliary action of ionic liquids in this work. The as-prepared doped $Bi_2O_2CO_3/Bi_2WO_6$ microspheres are well crystalized and uniformly assembled by large amount of nanosheets. The composite photocatalyst shows excellent catalytic performance to split water and degrade the tetracycline (TC) and RhB. The photocatalytic mechanism is also revealed based on free radical capture experiments and electronic structures given by density functional theory calculations.

2. Experimental section

2.1 I-doped $Bi_2O_2CO_3/Bi_2WO_6$ composite photocatalyst synthesis

Chemical reagents of analytical grade were used without further purification. Firstly, 0.912 g $Bi(NO_3)_3 \cdot 5H_2O$ was ultrasonically dispersed in 30 ml anhydrous methanol for 10 min, then stirred for 10 min to form a homogeneous suspension. The iodized 1-butyl-3-methidazole ionic liquid (0.160 g) and $Na_2WO_4 \cdot 2H_2O$ (0.660 g)

were dissolved in 30 mL distilled water to form a colorless solution. Under the stirring conditions, the anion solution was dropped continuously into the $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ suspension to form a pale yellow-orange red suspension, which underwent another 30 min stirring. Then, the suspension was moved to a 100 mL Teflon-lined stainless steel autoclave. The autoclave was heated at 160 °C for 24 h, and a light-yellow precipitation was obtained. The powders were washed with distilled water and anhydrous ethanol for three times, respectively. Then, powders were dried in vacuum at 70 °C for 12 h. This powder was named S5 (0.3:1 I-BCW). By varying the amount of ionic liquid and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, the I/W ratios in the reactants can be tuned to 0:1, 0.05:1, 0.1:1, 0.2:1, 0.3:1, 0.5:1 and 1:1, respectively. The products were labelled as S1 (BW), S2 (0.05 I-BCW), S3 (0.1 I-BCW), S4 (0.2 I-BCW), S5 (0.3 I-BCW), S6 (0.5 I-BCW), and S7 (1.0 I-BCW), respectively. In addition, the pure I-doped $\text{Bi}_2\text{O}_2\text{CO}_3$ was prepared separately in the same method and labeled as S8. For comparison, pure $\text{Bi}_2\text{O}_2\text{CO}_3$ (S9) and 0 I-BCW (S10) were also prepared according to the method reported by Umar [35].

2.2 Materials characterization

The microstructural determination was performed via X-ray powder diffraction (XPRD) on a D8 X-ray diffractometer of Brook, Germany (wavelength = 0.154056 nm, Cu K alpha radiation) with the scanning range of 5~80°. The scanning electron microscopy (SEM) carried on a JEOL JSM-6710LV electron microscope was employed to characterize basic morphology and microstructure of the samples. The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed on a JEOL JEM-2010. The energy dispersive spectroscopy (EDS) was also

applied along with the TEM. The x-ray photoelectron spectra (XPS) and ultraviolet photoelectron spectroscopy (UPS) were measured by the multifunctional X-ray photoelectron spectroscopy, ESCALAB 250Xi spectrometer from Thermo Electron Corporation. Optical absorption properties were determined through analyzing the ultraviolet visible diffuse reflectance spectra (UV-Vis-DRS) which were collected on a SHIMADZU UV2550 spectrometer. A TRISTAR II pore analyser from Micromeritics Instrument Corp was used to determine specific surface area and pore size distribution, while the photoluminescence (PL) spectra of powders were carried out by LS55 with 320 nm as excitation wavelength. The absorbance of the photocatalytic reaction solution was determined by the Agilent Co Cary 60 ultraviolet visible spectrophotometer. The electron spin resonance (ESR) signals of samples were performance on a Bruker ESR JES-FA200 spectrometer.

2.3 Photocatalytic evaluation

The photocatalytic hydrogen evolution experiments of samples were carried out. Before the light irradiation, 25 mg sample was dispersed to a 50 mL aqueous solution (10 vol% methanol, as the sacrifice agent) and stirred for 30 min. Hydrogen was quantified by a gas chromatograph (GC-6890A) under a 300 W Xe arc lamp with a cut-off filter ($\lambda \geq 420$ nm). The apparent quantum efficiency (AQE) was calculated based on the following equation:

$$\text{AQE(\%)} = 2N_{\text{H}_2}/N_p$$

Where N_{H_2} is the number of generated H_2 molecules and N_p is the number of emitted Photons [36-38].

The photocatalytic activity of powders was tested via photodegradation of TC and RhB aqueous solutions under ambient conditions. In detail, 50 mg of the sample

powder was added in 50 ml TC aqueous solutions in a 100 mL self-designed quartz photochemical reactor. A high concentration of 20 mg L^{-1} was selected to test the photocatalytic abilities of heterojunctions. The suspension was hold in dark for 30 min to reach an adsorption-desorption equilibrium before incident light irradiation. The photocatalytic reaction was conducted under a 500 W xenon lamp ($380 \text{ nm} < \lambda < 780 \text{ nm}$). At given time intervals, 1.5 mL solution was taken out every 10 min and centrifuged. The pollutant concentration at the time was analyzed by the UV-visible absorption spectra. An Agilent Cary 60 (USA) spectrophotometer was employed to record spectra at a scan range of 200-800 nm. Steps for photocatalytic degradation of RhB were the same as these for TC removal. A concentration of 10 mg L^{-1} was selected initially and the time interval fixed to 20 min.

2.4 Electrochemical measurements

5 mg photocatalyst was dispersed in 1 mL ethanol containing a small amount of nafion solution to prepare working electrode. An FTO glass electrode was coated with 10 μL of dispersion to reach an area of $1 \times 1 \text{ cm}^2$. All electrochemical measurements were performed on an electrochemical workstation. The CHI660E (CH Instruments Inc, Shanghai) workstation is equipped with a three-electrode mode and operated at an electrolyte solution of 0.5 M Na_2SO_4 . Transient photocurrent response was conducted under the circumstance of open-circuit potential. The Nyquist plots of impedance spectroscopy measurements (EIS) were measured at 0 V vs Ag/AgCl with the frequency range being modulated between 100 kHz to 0.1 Hz at amplitude frequency 10 mV under sun light generated by a 300 W Xe arc lamp with a 420 nm cut-off filter.

2.5 Theoretical calculations

Geometric optimization and band structure were carried out by employing the density functional theory (DFT) code implanted in the Cambridge Serial Total Energy Package (CASTEP) package [39]. A generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE) functional was implemented to treat the exchange-correlation [40]. Spin polarization was chosen during the geometry optimization at the SCF convergence threshold of 10^{-6} eV atom⁻¹. 380 eV was used as an actual value of cut-off energy to expand the plane waves included in the basis set. The Brillouin Zone integrations were carried out on a 3×3×1 Monkhorst-Pack k-points grid for geometry optimization, and a 6×6×1 k-points grid with 0.005 Å⁻¹ k-point separation for band structure calculations. The band structures were calculated along the special lines which connect the high-symmetry points of G (0, 0, 0), Z (0, 0, 0.5), T (-0.5, 0, 0.5), Y (-0.5, 0, 0), S (-0.5, 0.5, 0), X (0, 0.5, 0), U (0, 0.5, 0.5) and R (-0.5, 0.5, .5) in the k-space.

3. Results and Discussion

3.1 Microstructure, morphology and chemical state

As shown in Fig. 1, the XRD peaks at angles of 28.3, 32.9, 47.2, 56.0, 58.5, 76.1, 78.5, and 87.7° were indexed to (1 3 1), (0 0 2), (2 0 2), (1 3 3), (2 6 2), (2 10 2), (2 0 4) and (2 10 3) planes of Bi₂WO₆, respectively (JCPDS card No.39-0256). The diffraction peaks of all the products are very complete and sharp, denoting the high crystallinities of the samples prepared in the solvothermal method. Below 30% I/W molar ratio, the diffraction peaks of the products are typical tungsten bismuth types corresponding to the standard card of Bi₂WO₆ (JCPDS card No. 39-0256). With the increasing of the I/W molar ratio, diffraction peaks of the Bi₂O₂CO₃ turned out, in corresponding to the standard Bi₂O₂CO₃ card (JCPDS card No. 41-1488). The peak

intensities gradually increase with the I/W molar ratio. Two $\text{Bi}_2\text{O}_2\text{CO}_3$ phases were detected along with the Bi_2WO_6 matrix. No impurity peaks are found in the XRD spectra of the products, denoting the high purity of the synthesized samples. The diffraction peaks of S9 sample, as a contrast, can be easily indexed to $\text{Bi}_2\text{O}_2\text{CO}_3$ (JCPDS card No. 41-148) in Fig. S1a. For S10 sample, distinct diffraction peaks appear at around 28.3, and 58.5°, which can be matched with those of Bi_2WO_6 (JCPDS card No. 39-0256). Moreover, as shown in Fig. 1b, the (0 1 1) peak of $\text{Bi}_2\text{O}_2\text{CO}_3$ obviously shift to higher angle, which indicates that the iodine was doped into the lattice of $\text{Bi}_2\text{O}_2\text{CO}_3$. And the (1 3 1) peak of Bi_2WO_6 was slightly shifted to lower angle (Fig. 1c), which can be attributed to I's coordination with the $(\text{Bi}_2\text{O}_2)^{2+}$ layers in Bi_2WO_6 matrix [39].

A simulative refinement of XRD for Bi_2WO_6 was carried out to determine the local coordination structure of I-doped $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$. The shown XRD data in Fig. 1d and Fig. S1 sign Bi_2WO_6 as the main phase. While the iodine incorporating with the $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$ matrix, following changes have been observed based on four representative Bragg diffractions of the Bi_2WO_6 i.e. (1 3 1), (0 0 2), (2 0 2) and (1 3 3). The atomic arrangements of crystal unit cell, cell size and shape, and crystalline order are determined through peak position, intensity, and full width at half maximum (FWHM), respectively. An overall linear decrease in the Bragg peak position of selected diffraction has been observed for all the studied samples (Fig. 1d). Such systematic reduction in 2θ values of these reflections indicate the modification of unit cell size and shape as a function of iodine's incorporation as compared to Bi_2WO_6 . Such a decrease in the 2θ results in the higher interplanar spacing of the crystal unit cell with possible change in exact unit cell dimensions and the unit cell

volume. Change in Bragg peak position and intensity denotes a systematic crystal structural evolution for these selected reflections of studied samples in Fig. S1b. However, the pattern in the change is different below and above $I/W = 10\%$. Taking Bi_2WO_6 as the reference, the intensity goes up until $I/W = 10\%$ and then down beyond that. A similar trend has also been noticed in Bragg peak position. The intensity variation indicates a possible refinement in the local atomic arrangement towards better crystallinity until $I/W = 20\%$ and then for poor crystallinity above that. The FWHM usually shows a complementary change than that of intensity, however, the same is little complex in the present case. The FWHMs of the selected reflections are depicted in Fig. S1c. The change for the reflection (0 0 2) is much smaller than that of rest of the three selected diffractions of (1 3 1), (2 0 2) and (1 3 3). The FWHM value of Bi_2WO_6 for reflection (0 0 2) is larger while the same shows intermediate value for rest of the selected reflections. One of the possible reasons is the difference of the structural symmetry under different level of iodine incorporation to the heterojunctional matrix [41].

Fig. 1

Fig. 2 presents the SEM images of all samples. Different from irregular self-assembled Bi_2WO_6 spheres synthesized without ionic liquids (Fig. 2a), all products are microspheres composing various regular nanoplates. The S5 owns a large number of self-assembled microspheres with many sparsely distributed nanoplates. When the molar ratio of the ionic liquid increases gradually (Fig. 2a-g), the surface of the microspheres become denser and rougher, which is attributed to the phase formation of $\text{Bi}_2\text{O}_2\text{CO}_3$ and the load of $\text{Bi}_2\text{O}_2\text{CO}_3$ nanosheet or nanoparticles in the main structure of Bi_2WO_6 . As shown in Fig. 2, the thickness of the nanosheet is about

20 nm. The formation of $\text{Bi}_2\text{O}_2\text{CO}_3$ and Bi_2WO_6 with two-dimensional structures is significantly related to ionic liquids. $[\text{BMIM}]^+$ organic cation in ionic liquids inhibits the growth in perpendicular direction of the crystal surface. Thus, only the in-plane growth is allowed.

Fig. 2

The lattice orientations and heterojunction interfaces were further studied. The TEM and HRTEM results of the 30% I-BCW (S5) sample are depicted in Fig. 3. In Fig. 3a, the nanosheets are rectangle. The partial zoomed nanoslice edge was depicted in Fig. 3b and Fig. S2. By the HRTEM picture of S5, lattice spacings of 0.273 nm and 0.272 nm are from the (2 0 0) and (0 0 2) planes of Bi_2WO_6 , respectively. The selected area electron diffraction (SAED) of a region in the figure was calibrated after fast Fourier transformation (FFT) (Fig. 3e). The corresponding plane is indexed to the (0 2 0) and (2 0 0) crystal plane of the orthorhombic Bi_2WO_6 . The corresponding crystal structure overlook diagram is shown in Fig. 3g-h. In addition, the other region of the selected sample was amplified, as shown in Fig. 3c, the lattice fringes of 0.193 nm, 0.273 nm belonged to the lattice plane of $\text{Bi}_2\text{O}_2\text{CO}_3$ (JCPDS card No. 41-1488) (0 2 0) and (1 1 0). The crystal surface of the plane corresponds to the (0 0 2) surface of $\text{Bi}_2\text{O}_2\text{CO}_3$, and the corresponding crystal structure overlook diagram is shown in Fig. 3i. Some large $\text{Bi}_2\text{O}_2\text{CO}_3$ phases were clearly observed on the Bi_2WO_6 nanosheet in Fig. 3d. The 0.193 nm spacing belongs to the (2 6 0) Bi_2WO_6 crystal plane. Furthermore, the 0.372 nm spacing can be indexed to the (0 1 1) planes of the $\text{Bi}_2\text{O}_2\text{CO}_3$. The element mapping of the selected area is also carried out in the TEM mode. Fig. S3 a-f show the Bi, W, O, C and I elements disperse on the nanosheet. The content of I element is less than that of the other elements but slightly more abundant

next to W-O interfaces at a gross glance. This indicates the iodine was dilute doped in the photocatalyst and preferably sit next to the heterojunctional interface. The I-doped $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$ heterojunctions have been prepared successfully.

Fig. 3

The XPS was employed to determine chemical states of the involved elements in the heterojunctions. Fig. 4a shows that the S5 powder contains four elements, including Bi, W, O, C and I. This is consistent with the element mapping results. The C owns two chemical states which are identified by the peaks at 284.89 eV and 288.78 eV, respectively. The former is from the adventitious carbon and employed as reference for energy calibration, while the latter is attributed to the C-O bond in $[\text{CO}_3]^{2-}$ [29]. Two Bi peaks at 159.1 eV and 164.5 eV (Fig. 4c) are attributed to Bi 4f_{7/2} and Bi 4f_{5/2} from Bi^{3+} ions in the $[\text{Bi}_2\text{O}_2]^{2+}$ [42,43]. In Fig. 4d, the W 4f_{7/2} and W 4f_{5/2} peaks locate at 35.28 eV and 37.48 eV respectively, indicating the W^{6+} in the $[\text{WO}_4]^{2-}$ [44,45]. The O 1s peak could be fitted into two main peaks at 530.24 eV and 531.59 eV (Fig. 4e), which were related to the oxygen in $[\text{Bi}_2\text{O}_2]^{2+}$, $[\text{WO}_4]^{2-}$ and $[\text{CO}_3]^{2-}$ in the composite catalyst and the oxygen adsorbed on the surface of materials (e.g., in the form of the OH^- and H_2O), respectively [29,43]. Finally, the XPS spectrum of the I 3d has two peaks at 619.17 eV and 630.78 eV, which can correspond to I 3d_{5/2} and 3d_{3/2} respectively. The value sits between these from the iodine and iodate, showing a cathodic form [46]. To sum up, the results from XPS determinations are consistent with other characterizations. Chemical states of the iodine changed after being doped into the $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$ composite.

Fig. 4

The specific surface area and size distribution of pores will affect the catalytic properties of materials. The large specific surface area brings many active sites into the materials [46]. Fig. S4a shows the isotherm for all samples, which exhibits a type IV with a H3 hysteresis loop according to the IUPAC classification, reflecting the presence of a mesoporous structure of the composites. As shown in Fig. S4b, the pore-size distributions are also estimated using the Barrett-Joyner-Halenda (BJH) method from the desorption branch of the isotherm, which indicated that the size of mesopores is not uniform ranging from 2 to 50 nm. Sample S5 has the maximum specific surface area ($27.73 \text{ m}^2 \text{ g}^{-1}$). Such a porous structure may contribute to high absorptivity and catalytic activity. The specific surface area, pore volume and pore size distribution of different samples are summarized in Table S2.

The optical absorption property of the materials is characterized by UV-Vis-DRS. A rough assessment towards the absorbances shows that photoionization cross sections do not vary much, denoting comparable light adsorption abilities among the samples. The Bi_2WO_6 and $\text{Bi}_2\text{O}_2\text{CO}_3$ absorbance edges are estimated to be 450 nm and 380 nm, respectively (Fig. S5), which is consistent with the literature [7-9,28-32,44]. Among them, the predominant visible light absorption of Bi_2WO_6 is ascribed to the doping. The band gap of Bi_2WO_6 and $\text{Bi}_2\text{O}_2\text{CO}_3$ can be calculated by:

$$\alpha h\nu = A(h\nu - E_g)^{n/2}$$

Where A represents a constant, and α , ν and E_g represent the adsorption coefficient, optical frequency, and bandgap, respectively [47-49]. For the value of n , it depends on the type of optical transition of semiconductors ($n = 1$ for direct transition and $n = 4$ for indirect transition). As previous literatures reported, Bi_2WO_6 and $\text{Bi}_2\text{O}_2\text{CO}_3$ were indirect band gap semiconductor and their values of n is 4 [50,51]. The result was

shown in Fig. S5b. Bandgap energies are calculated to 2.75 eV and 3.26 eV respectively for pure Bi_2WO_6 and $\text{Bi}_2\text{O}_2\text{CO}_3$, and further decreased in the doped sample S5.

3.2 Photocatalytic activity

To evaluate the photocatalytic properties of the Z-scheme heterojunction, the photocatalytic hydrogen evolution of SN ($N = 1-8$) were carried out (Fig. 5a). All of the I-doped $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$ samples exhibit an enhanced photocatalytic H_2 production activity compared to the pure Bi_2WO_6 , which can't produce H_2 . This is attributed to the conduction band potential of pure Bi_2WO_6 is hardly to produce hydrogen from splitting water. Moreover, with the increase of ionic liquids, the photocatalytic hydrogen production activity of the sample increased firstly and then decreased. The S5 sample owns the best photocatalytic hydrogen production performance ($186.22 \mu\text{mol g}^{-1} \text{h}^{-1}$). The result implied that iodine dopant effect played an important role in enhancing catalytic properties of the samples. Introducing iodine into the system can further narrow the band gap of heterojunction by lowering the conduction band position and meanwhile generating impurity level in the valence band, which could facilitate efficiently photo-generated electron-holes separation and migration. Nevertheless, As the I/W ratios increases from 0.5 to 1, the efficiency of hydrogen production is decreased due to the high indirect recombination ability of photo-generated charge carriers, which may be caused by the recombination level produced from too much iodine doping in the bandgap. Moreover, the proper deposition of Pt presents superior performance due to a suitable Fermi level for accepting photogenerated electrons and a low overpotential for hydrogen production. Insufficient Pt deposition could weaken the migration of photogenerated electrons,

while the aggregation of the excess Pt, leading to reduce the photocatalytic performance. According to literature reports [52], 3% Pt co-catalyst was selected as cocatalyst in this work, the photocatalytic hydrogen production efficiency of S5 reached $664.54 \mu\text{mol g}^{-1} \text{h}^{-1}$ with the apparent quantum efficiency of 14.9%. Although the efficiency is lower than the recently reported $11192 \mu\text{mol g}^{-1} \text{h}^{-1}$ of nanomaterial black phosphorus/CdS [53], it could be much higher than the most Bi-based photocatalysts reported (Table S1). For comparison, the hydrogen evolution of pure $\text{Bi}_2\text{O}_2\text{CO}_3$ (S9) and 0% I-BCW (S10) were both lower than that of S5 composite under the same condition (Fig. S6). The stability tests of S5 were evaluated by the cycling H_2 evolution experiment, and the results are depicted in Fig. 5b. It is clearly observed that S5 photocatalyst do not have obvious decrease for H_2 generation after five cycles, indicating that I-doped $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$ composite exhibits excellent stability.

Fig. 5

Photocatalytic degradation of the antibiotics was studied. The TC is selected as the typical antibiotic and experiment performed under light irradiation. As observed from Fig. 6a, samples showed different adsorption abilities towards the TC in dark. The pure $\text{Bi}_2\text{O}_2\text{CO}_3$ shows slightly photocatalytic degradation efficiencies of approximately 5%. The Bi_2WO_6 and their composite exhibit the higher degradation properties of TC. TC degradation rate peaked at 80% after 60 min under visible light irradiation when S5 was used as the catalyst. Fig. S7a shows the change process of TC characteristic absorption curve with time. It can be seen from the diagram that the sample has a strong adsorption to TC. After the establishing of an adsorption-desorption equilibrium for 30 min, the height of the characteristic

absorption peak of TC (356 nm) fell by more than half. TC is rapidly degraded in the first 10 min after light irradiation, then the degradation rate gradually decreased, and finally reached a limit at 60 min, which may be due to the existence of a strong conjugated structure in TC and the radical potential excited by the material cannot reach its oxidation potential so couldn't completely destroy it.

The photocatalytic degradation of RhB was also carried out under simulant sunlight irradiation. Fig. 6b displays the photocatalytic properties of the products. Concentration ratio curves show the pure Bi_2WO_6 and $\text{Bi}_2\text{O}_2\text{CO}_3$ have rather poor adsorption and degradation properties. With the increase of mole ratio of I ionic liquid in reactants, the degradation efficiency of RhB first increases and then decreases. The degradation removal yield of S1-S8 samples is 73.5%, 72.3%, 83.6%, 98.3%, 99.9%, 98.2%, 96% and 10.9%, respectively. It's worth noting that S5 illustrated the higher adsorption efficiency of 88.7% for RhB because of its mesoporous materials with largest specific surface area. To explore the adsorption capacity of S5 sample, the adsorption-desorption experiments were carried out for RhB dye under the dark and results are shown in Fig. S8. It is clearly seen that, the adsorption-desorption of RhB molecules for S5 sample reached equilibrium after 30 min and the desorption efficiency was found to be 72.6%, indicating that remarkable synergistic contributions from adsorption and photocatalytic degradation, leading to high removal efficiency of RhB. Degradation efficiency of RhB is significantly improved compared with pure Bi_2WO_6 or $\text{Bi}_2\text{O}_2\text{CO}_3$, but the best dye removal rate can be obtained only at certain I/W ratio. We employed the first order kinetics of degradation to study photocatalytic dynamics. The first-order rate constant k was calculated through

$$kt = \ln (C_0/C)$$

In the equation, C_0 and C denote RhB concentrations at the times 0 and t , and the slope k refers to the apparent reaction rate constant. The corresponding pseudo-first-order rate constants of S1-S8 are calculated to be 0.0089 min^{-1} , 0.0107 min^{-1} , 0.0131 min^{-1} , 0.0230 min^{-1} , 0.0075 min^{-1} , 0.0228 min^{-1} , 0.0164 min^{-1} and 0.0005 min^{-1} , respectively (Fig. 6c and Fig. S7c).

Recovery and reuse of photocatalysts are important to assess the quality of the catalysts, because they directly affect the practical application of the catalyst. The reusability of the S5 composite was investigated by repeatedly photodegrading RhB (Fig. 6d and Fig. S7d). It can be seen that the sample still maintain a high removal rate after 4 cycles. The above results indicated that the S5 composite has good stability and recycling.

Fig. 6

The charge separation and transfer properties were investigated via PL spectra. Fig. S9 shows the PL spectrum of the Bi_2WO_6 and sample S5 in the range of 350-600 nm with excitation wavelength of 320 nm. It can be seen from the diagram that the samples show strong luminescence intensity at the wavelength around 420 nm. The singlet form of the spectra further denotes main electron-hole recombination mainly involves charges next to conduction band minimum (CBM) and valance band minimum (VBM) but not relies on incident photon energy [Pankratov 2016]. Hence, electron-hole recombination of intermediates during the system relaxation [Tuomela 2020] is not predominant since no other peaks are detectable in the PL. Obviously, the emission intensity of the S5 is lower than S1, which indicates electron-hole recombination in S5 composite is inhibited [54-56]. Therefore, more free electrons

and holes will be converted into free radicals to degrade organic pollutants, improving the photocatalytic properties.

To verify the efficient charge transfer of Bi_2WO_6 composites, the photocurrent and EIS characterizations of samples were investigated and shown in Fig. 7 and Fig. S10. The S1 sample exhibits a low photocurrent attributing to heavily charge recombination. However, the photocurrent performance of S5 was about 16 times higher than S1, which demonstrates that the S5 can separate electron-hole pairs more effectively. Moreover, The EIS Nyquist plot of S5 exhibited the smallest radius compared with S1 and S8 (Fig. 7b), which implied that S5 exhibited remarkable improvement in inhibiting the charge recombination [57]. Furthermore, the PL, photocurrent and EIS results show the S5 has high photogenerated electrons and holes separation. PL, photocurrent and EIS are well consistent with the result of photocatalytic degradation experiment.

Fig. 7

The charge transfer of Z-scheme I-doped $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$ heterojunctions is further investigated by Mott-Schottky (M-S) method. The charge carrier density N_D is calculated according to the following equation:

$$N_D = \frac{2}{e_0 \varepsilon \varepsilon_0 k}$$

Here, e_0 is the elementary electron charge, ε_0 the permittivity of free space, ε the permittivity of the Bi_2WO_6 electrode, and k the slope of the M-S plot [34]. The slope of the Mott-Schottky curve is closely related to the charge carrier density. As displayed in Fig. S11, the M-S plots of Bi_2WO_6 and S5 are 5.4 and 4.2, and the N_D value of S5 is 1.28 times higher than Bi_2WO_6 , which means the S5 has excellent charge carrier transportation.

3.3 Theoretical exploration

To explore the mechanism enabling I-doped $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$ as a highly efficient catalyst in H_2 production, we have conducted a series of theoretical investigations based on DFT calculations. The heterostructure of I-doped $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$ was constructed between an orthogonal Bi_2WO_6 and an orthogonal $\text{Bi}_2\text{O}_2\text{CO}_3$ as shown in Fig. 8. The unit cell parameters for pristine Bi_2WO_6 and $\text{Bi}_2\text{O}_2\text{CO}_3$ were firstly optimize. The lattice constants were calculated to $a = 5.498 \text{ \AA}$, $b = 5.558 \text{ \AA}$, $c = 16.701 \text{ \AA}$ for the Bi_2WO_6 and $a = 5.529 \text{ \AA}$, $b = 5.650 \text{ \AA}$, $c = 14.323 \text{ \AA}$ for the $\text{Bi}_2\text{O}_2\text{CO}_3$, respectively. Values are in good agreement with experimental and other theoretical results [58-60]. The heterojunctional structure composed of $\text{Bi}_2\text{O}_2\text{CO}_3$ (001) and Bi_2WO_6 (010) planes was built based on results given by the HRTEM determination and the above optimization. It is found that the interface model with fully O-O bonding (four O atoms) near both sides of Bi-O part of $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$ is energetically more favorable as shown in Fig. 8. Finally, the iodine atoms were introduced into the heterojunction through doping in the caves and atom substitution with Bi and W sites in both Bi_2WO_6 and $\text{Bi}_2\text{O}_2\text{CO}_3$ sides. The nanosheet contains 68 atoms including 1 I atom, 4 W atoms, 4 C atoms, 15 Bi atoms, and 44 O atoms. A vacuum region of $10 \text{ \AA}$ was selected in the z-direction to prevent interactions between top and bottom atoms in the periodic slab images.

The new layered structures of heterojunctions were re-optimized after doping iodine atoms with a full structural relaxation including a unit cell volume change. According to the calculation, the iodine preferably substitutes the Bi atom at the Bi_2WO_6 side and bonds with oxygen atoms in the most thermodynamically stable structure. Correspondingly, the iodine is positively charged due to lower

electronegativity compared to the oxygen. Bader charge analysis shows that the iodine dopant donates approximately 1.10 electrons to adjacent oxygen atoms in the heterojunctions, which is close to the result of Mulliken population analysis of 0.76 electrons. The xy-plane lattice constant of I-doped $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$ heterojunction is $a = 5.511 \text{ \AA}$, $b = 5.599 \text{ \AA}$. Compared the pristine Bi_2WO_6 and $\text{Bi}_2\text{O}_2\text{CO}_3$, the lattice parameters of the Bi_2WO_6 are slightly larger, while the values of $\text{Bi}_2\text{O}_2\text{CO}_3$ decreased after the formation of the I-doped heterojunction to accommodate the lattice constant difference. In our theoretical calculation, we have performed several different concentrations of iodine, such as 0.8%, 1.5%, and 3.0%. These different concentrations yielded essentially the similar result. Here, we adopt the results of 1.5% concentrations of iodine throughout the present work.

Our theoretical calculations are consistent with the experimental results. The XRD spectra of Bi_2WO_6 were slightly shifted to lower angle, indicating the lattice length becomes slightly larger in heterojunction according to Bragg's law. Another possible reason is that some iodine dopants are actually incorporated into the crystalline lattice of Bi_2WO_6 and enlarge the unit cell parameters. On the other hand, the lattice length of the $\text{Bi}_2\text{O}_2\text{CO}_3$ decreased after the interfacing in according with the XRD spectra of $\text{Bi}_2\text{O}_2\text{CO}_3$ with shifting to higher angle. The positively charged iodine here in line with the XPS determination of the chemical state (Fig. 4) and its abundance distribution atom next to the interface in according to the element mapping in Fig. S3.

The calculated electronic band structures for the crystal Bi_2WO_6 , $\text{Bi}_2\text{O}_2\text{CO}_3$, pure and iodine doped $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$ heterojunction are depicted at the bottom sides of the Fig. S12 and Fig. 8b-c respectively. The high-symmetry points were selected as

these for the bulk Bi_2WO_6 . The band gaps are 2.19 and 1.99 eV for the Bi_2WO_6 and $\text{Bi}_2\text{O}_2\text{CO}_3$ bulks, as given in Fig. S12. The computed bandgap energies are in good agreements with previous theoretical results. However, a systematically lower trend is noticed when compared to the experimental results, owing to the well-known underestimation of the band gap in DFT calculations [59-62]. Compared to the bulk Bi_2WO_6 and $\text{Bi}_2\text{O}_2\text{CO}_3$, the undoped $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$ heterojunction effectively lowers the band gap energy to 0.61 eV in Fig. 8b. The bandgap was also switched from the indirect to the direct after heterojunction construction. Additional bands turned out next to the Fermi level and induced the newly formed valence band maximum (VBM) and conduction band minimum (CBM) points within the I-free heterojunctional system (red line). At the hetero sites, the original VBM and CBM of bulk Bi_2WO_6 (green line) and $\text{Bi}_2\text{O}_2\text{CO}_3$ (magenta line) shift upward and downward respectively.

The electronic structures of the heterojunction underwent subtle changes after iodine doping. The CB of the I-doped heterojunction still mainly involves bands arising from the interface of the heterojunction. However, it is interesting to notice that an impurity level composed of the halogen dopant was generated near the Fermi level (brown lines in Fig. 8c). To clearly analyze the contribution of I orbitals for the CB and VB, the electronic partial density of states (PDOS) of the pure and iodine doped $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$ heterojunction is also provided as an assistant analysis in the supporting information as Fig. S12b, which is consistent with the result of the corresponding band structure. The top of the valence band (VBM) is mainly dominated by I 5p orbitals (brown lines in Fig. S12b). As a result, doping iodine can further narrow the band gap of heterojunction (0.46 eV) by lowering the conduction

band position and meanwhile generating impurity level in VB. Such a trend is in line with the UV-Vis determinations of systems' bandgap as shown in Fig.S5. A lowered bandgap further extends absorption region of the incident photon source, which is beneficial to the photocatalytic performance. In addition, the band structures of doped heterojunction show a typically indirect feature. The CBM lies at the X point, while the VBM is near the T point as schematically shown in Fig. 8c. Noteworthily, the conduction band minimums of Bi_2WO_6 , $\text{Bi}_2\text{O}_2\text{CO}_3$, interface and I-dopant in $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$ heterojunction are aligned in the same symmetric position X point in k-space. Electrons easily migrates to the bands at the hetero-sites thanks to momentum conservation. Combining the above features, this modified band structure is beneficial to electron excitation. Recombination through indirect band would require participation from other factors to satisfy conservation of momentum in k-space leading to the very low electron-hole recombination efficiency at the doped interfacial region. Recombination between photoinduced electrons and holes will be substantially delayed. This claim is directly supported by photoluminescence determinations as discussed in Sect. 3.2.

Fig. 8

3.4 Photocatalytic mechanism

In order to determine the active species in the photocatalytic process, we have performed an electron spin resonance (ESR) technique on the S5 sample to detect the reactive species produced by the sample under simulant sunlight irradiation. As shown in Fig. 9a-b, after two minutes of light, strong ESR signal peaks of $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ were found compared to darkness, suggesting the composites can produce large amounts of $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ radicals under the simulated sunlight irradiation. The

trapping experiments with different scavengers of photodegradation TC were performed to further validate active species participated in the photocatalysis. In this study, three different quenchers, isopropanol (IPA, $\bullet\text{OH}$ scavengers), ammonium oxalate (AO, h^+ scavengers), and 1,4-benzoquinone (PBQ, $\bullet\text{O}_2^-$ scavengers) were adopted [63]. As perceived in Fig. S13, the TC decomposition process was significantly inhibited with PBQ and IPA, implying that $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ worked in the photocatalytic reaction. In contrast, little efficiency reduction with the addition of AO demonstrated that h^+ might not be the predominant active species. Thus, ESR information and the radical trapping experiments verified the important role of $\bullet\text{O}_2^-$ and $\bullet\text{OH}$, leading to the enormous photocatalytic activity improvement.

Fig. 9

In Fig. S11, the flat-band positions of Bi_2WO_6 can be determined [34,64]. The straight upward curves demonstrate that Bi_2WO_6 is a n-type semiconductor, and the CB of Bi_2WO_6 was calculated by Nernst equation. Hence, Bi_2WO_6 's CB level is ca. -0.05 V (vs. NHE) and the VB level is ca. 2.70 V (vs. NHE). It is known that the CB and VB levels of $\text{Bi}_2\text{O}_2\text{CO}_3$ are ca. -1.47 and 1.79 V (vs. NHE), respectively [45]. In order to further determine the ionization potential (equivalent to the valence band energy) of Bi_2WO_6 and $\text{Bi}_2\text{O}_2\text{CO}_3$, the UPS experiment was carried out shown in Fig. S14. The valence band energy of Bi_2WO_6 and $\text{Bi}_2\text{O}_2\text{CO}_3$ were calculated to be 7.14 and 6.23 eV by subtracting the width of the He I UPS spectra from the excitation energy (21.22 eV), which are converted to be 2.70 and 1.79 V (vs. NHE). The results are consistent with Mott-Schottky tests.

The above analysis denotes the photocatalytic mechanism in the present Z-systems is benefited from the heterojunctional structures of the doped catalysts. A

photocatalytic scheme is depicted in Scheme 1. The experimental values from the above electrochemical determinations were adopted here. Under the simulated solar light excitation, the electrons in the valence band of the Bi_2WO_6 and $\text{Bi}_2\text{O}_2\text{CO}_3$ are photoexcited to their conduction bands, leaving holes at the respective valence bands. The electrons on the Bi_2WO_6 conduction band are not combined with the holes on the valence band immediately but transferred to the valence band of $\text{Bi}_2\text{O}_2\text{CO}_3$ through the interface and recombined with the hole at the $\text{Bi}_2\text{O}_2\text{CO}_3$ valence band. This is mainly due to two reasons: First, the valence band position of $\text{Bi}_2\text{O}_2\text{CO}_3$ is lower than that of Bi_2WO_6 , making its electron drop path shorter. Secondly, a regular two-dimensional heterojunction structure is formed between Bi_2WO_6 and $\text{Bi}_2\text{O}_2\text{CO}_3$ composites, owing to the similar cell parameters of Bi_2WO_6 and $\text{Bi}_2\text{O}_2\text{CO}_3$. Heterojunctions is linked by chemical bonds, which leads to the easier transfer of electrons from Bi_2WO_6 conduction band to $\text{Bi}_2\text{O}_2\text{CO}_3$ valence band. In the valence band of the $\text{Bi}_2\text{O}_2\text{CO}_3$, the electrons from the Bi_2WO_6 phase are continuously obtained, and then transferred to the conduction band of $\text{Bi}_2\text{O}_2\text{CO}_3$ under light excitation, and then reduced H_2O to H_2 . In addition, the photogenerated electrons and holes will remain on the conduction band of $\text{Bi}_2\text{O}_2\text{CO}_3$ (-1.47 V) and valence band of Bi_2WO_6 (2.70 V), where the electrons own enough reducibility to meet the requirement of $\cdot\text{O}_2^-$ generation, and the holes with strong oxidizability can react with H_2O to produce $\cdot\text{OH}$. Subsequently, these formed active species of $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ will participate in the reaction to degrade the TC and RhB molecules. Hence, the Z-Scheme photocatalytic system similar to photosynthesis is formed, which is more favorable to the separation of photogenerated electrons and holes than the ordinary heterojunction.

Scheme 1

The above proposition is explicated with the computational results. First, the photoexcitation of electrons is more favoured in the undoped and doped heterojunctional $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$ systems compared to the individual hetero components. The bandgap is lowered due to presence of the impurity bands from the interface alloys (red lines in Fig. 8b) and further reduced due to iodine orbits in the doped heterojunction (Fig. 8c). As a result, a wider range in the incident photon spectrum will be covered during the photoabsorption process. Second, the indirect bandgap feature of the I-doped system inhibits electron-hole recombination by requesting additional moment compensation e.g., through a phonon. Instead of recombination in forms of emerging luminescence in the direct-band typed semiconductor [Mak 2010], charges tend to migrate within the present indirect bandgap heterojunctions. Additionally, migrations of excited electrons become gradually easier in the present heterojunction and doping strategy. This is because of i) the aligned band minimums next to the X point and ii) intensified band density with the existence of iodine. The electrons transfer straightforwardly between the hetero sites [Shi 2018, Small 14: 1704526] and contribute to an electron reservoir where proton reduction happens [65]. As a result, the hydrogen evolution is substantially promoted in the I-doped $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$.

4. Conclusions

To summarize, an I-doped $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$ Z-scheme photocatalytic system was successfully prepared via a facile ionic liquid assisted solvothermal method. Compared with pure Bi_2WO_6 , $\text{Bi}_2\text{O}_2\text{CO}_3$ and the undoped photocatalysts, the photocatalytic activity of I-doped $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$ composite was greatly enhanced

for durable hydrogen evolution under simulated sunlight irradiation. The S5 photocatalyst showed the highest H₂ evolution rate of 664.5 $\mu\text{mol g}^{-1} \text{h}^{-1}$. A photocatalytic mechanism was proposed based on PL, ESR test and density functional theory calculations. It is found that the band structure and alignment in the doped heterojunction simultaneously facilitate visible light harvesting, charge separation, and proton reduction. Besides providing a new insight to the quick synthesis and design of novel 3D multi-function heterojunction, the catalytic mechanism unveiled here is hoped to bring new design principles for the future photocatalysts for environmental and energy applications.

Notes

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List of Figure Captions

Fig. 1 XRD spectra of SN (N = 1-7) samples (a). The peak shift of (0 1 1) for $\text{Bi}_2\text{O}_2\text{CO}_3$ (b) and (1 3 1) for Bi_2WO_6 (c). The Bragg peak position spectra of (1 3 1), (0 0 2), (2 0 2), (1 3 3) for Bi_2WO_6 (d).

Fig. 2 SEM images of S1 (a), S2 (b), S3 (c), S4 (d), S5 (e), S6 (f), S7 (g), S8 (h) samples and Local magnification of S5 sample (i).

Fig. 3 TEM (a), HRTEM (b, c, d) images, SAED patterns (e, f) and corresponding crystal structures (g-i) for S5 sample.

Fig. 4 XPS survey spectra (a), C 1s (b), Bi 4f (c), W 4f (d), O 1s (e) and I 3d (f) for S5 sample .

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Fig. 7 Transient photocurrent response (a) and EIS Nyquist plots (b) of S1, S5 and S8 samples.

Fig. 8 DFT results of the I-doped $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$ heterojunction. (a) Supercells of the pristine Bi_2WO_6 and $\text{Bi}_2\text{O}_2\text{CO}_3$, and $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$ heterojunction. (b, c) The band structures of the $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$, and I-doped $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$ heterojunction, respectively. Note that the graphic interface use thicker stick model with bgcolor in Fig. 8a, and O, C, Bi, W and I atoms are marked by red, grey, purple, blue and brown atoms represent, respectively. In Fig. 8b-c, the green, magenta, red and brown lines indicate the nearest bands next to VBM and CBM from Bi_2WO_6 , $\text{Bi}_2\text{O}_2\text{CO}_3$, $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$, and I-doped $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{WO}_6$ heterojunction, respectively. Horizontal dashed lines represent Fermi levels.

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