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Article (Special Issue on Photocatalytic H₂ Production and CO₂ Reduction)**Bifunctional S-scheme g-C₃N₄/Bi/BiVO₄ hybrid photocatalysts toward artificial carbon cycling**Quan Xie ^{a,†}, Wanmei He ^{a,†}, Shengwei Liu ^{a,*}, Chuanhao Li ^{a,#}, Jinfeng Zhang ^{b,\$}, Po Keung Wong ^{c,d}^a School of Environmental Science and Engineering, Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, Sun Yat-sen University, Guangzhou 510006, Guangdong, China^b College of Physics and Electronic Information, Huaibei Normal University, Huaibei 235000, Anhui, China^c School of Life Sciences, The Chinese University of Hong Kong, Shatin, NT, Hong Kong, China^d Institute of Environmental Health and Pollution Control, School of Environmental Science & Engineering, Guangdong University of Technology, Guangzhou 510006, Guangdong, China

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ABSTRACT

Although both the aerobic photocatalytic oxidation of organic pollutants into CO₂ and the anaerobic photocatalytic reduction of CO₂ into solar fuels have been intensively studied, few efforts have been devoted to combining these carbon-involved photocatalytic oxidation-reduction processes together, by which an artificial photocatalytic carbon cycling process can be established. The key challenge lies in the exploitation of efficient bifunctional photocatalysts, capable of triggering both aerobic oxidation and anaerobic reduction reactions. In this work, a bifunctional ternary g-C₃N₄/Bi/BiVO₄ hybrid photocatalyst is successfully constructed, which not only demonstrates superior aerobic photocatalytic oxidation performance in degrading an organic pollutant (using the dye, Rhodamine B as a model), but also exhibits impressive photocatalytic CO₂ reduction performance under anaerobic conditions. Moreover, a direct conversion of Rhodamine B to solar fuels in a one-pot anaerobic reactor can be achieved with the as-prepared ternary g-C₃N₄/Bi/BiVO₄ hybrid photocatalyst. The excellent bifunctional photocatalytic performance of the g-C₃N₄/Bi/BiVO₄ photocatalyst is associated with the formation of efficient S-scheme hybrid junctions, which contribute to promoting the appropriate charge dynamics, and sustaining favorable charge potentials. The formation of the S-scheme heterojunction is supported by scavenger studies and density functional theory calculations. Moreover, the *in-situ* formed plasmonic metallic Bi nanoparticles in the S-scheme hybrid g-C₃N₄/Bi/BiVO₄ photocatalyst enhances vectorial interfacial electron transfer. This novel bifunctional S-scheme g-C₃N₄/Bi/BiVO₄ hybrid photocatalyst system provides new insights for the further development of an integrated aerobic-anaerobic reaction system for photocatalytic carbon cycling.

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1. Introduction

For a long time, the natural carbon cycling between the land, atmosphere, and oceans has sustained the carbon balance. Presently, because of intensive human activities and industrial developments, carbon-based fuels, chemicals, and materials are widely used in a variety of fields; thus, the carbon balance has been severely broken, and carbon-based environmental pollution has become a major problem. In particular, the excessive emission of some persistent organic pollutants and volatile organic compounds into environmental media threatens human health and the ecological balance. A variety of advanced environmental techniques, such as microbial decomposition, have been developed to remove these carbon-based pollutants from air and water, which attempt to convert toxic and harmful organic compounds into innocuous CO_2 [1–6]. Nevertheless, CO_2 itself is the major greenhouse gas in the atmosphere, and increasing emissions of CO_2 overloads the self-purification capacity of the environment based on natural carbon cycling [7–9]. Ideally, the CO_2 produced from the treatment of organic pollutants should be further converted into valuable organic chemicals (such as solar fuels) to establish an artificial carbon cycling (Fig. 1). Natural photosynthesis is one of the most important processes in natural carbon cycling, which is key to reducing the CO_2 concentration in the atmosphere. Natural photosynthesis has inspired scientists to develop artificial photosynthesis to achieve CO_2 resourcing. In principle, artificial photosynthesis is mainly based on semiconductor-mediated photocatalytic processes. Fortunately, the photocatalytic processes are versatile in establishing carbon cycling. Normally, CO_2 can be converted to hydrocarbon solar fuels by anaerobic photocatalytic reduction processes [10–14], while organic pollutants can be also mineralized to nontoxic CO_2 by aerobic photocatalytic oxidation processes [15]. Although both these reactions have been intensively studied, only few studies have combined both [16–21]. As illustrated in Fig. 1, by combining these carbon-involved photocatalytic oxidation-reduction processes, an artificial photocatalytic carbon cycling process can be established. Such photocatalytic carbon cycling processes can use abundant solar energy to simultaneously solve environmental problems and produce sustainable energy. The difficulty lies in that the specific mechanisms for the aerobic oxidation of organic pollutants and the anaerobic reduction of CO_2 are

quite different. Therefore, the development of efficient bifunctional photocatalyst(s) capable of triggering both aerobic oxidation and anaerobic reduction reactions is the key challenge.

Recently, graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) has attracted a great deal of attention as one of the most promising metal-free visible light-responsive photocatalysts, owing to its earth-abundant C- and N-based components; fascinating layered crystal structures; and high thermal, chemical, and photochemical stability [22,23]. More significantly, $\text{g-C}_3\text{N}_4$ possesses a bandgap of ca. 2.7 eV, with the conduction band (CB) and valence band (VB) positions at ca. -1.1 and $+1.6$ eV, respectively, versus a normal hydrogen electrode (NHE). Such band structures of $\text{g-C}_3\text{N}_4$ enable it to be a visible-light-active photocatalyst, capable of triggering a variety of photocatalytic reactions [24–26]. Nevertheless, one of the major obstacles hindering the charge transfer dynamics and impairing the apparent photocatalytic quantum efficiency is the relatively weak oxidation ability of the holes in the VB of $\text{g-C}_3\text{N}_4$, which is not strong enough to trigger one-hole-mediated activation of surface-adsorbed water. The retarded hole transfer and utilization efficiency in the $\text{g-C}_3\text{N}_4$ photocatalyst do not only impair the overall photocatalytic activity, but also induce hole-mediated self-etching. Combining two suitable semiconductors with matched band alignment is a promising strategy to enhance photocatalytic activity by promoting spatial charge separation [27–37]. Conventional heterojunctions (such as p-n junction, type-II heterojunctions) typically result in unfavorable losses of the redox ability of the photogenerated electrons and holes, the Z-scheme hybrid photocatalyst system that mimics natural photosynthesis can maximally maintain both the high reductive and oxidative powers of the photogenerated charge carriers [38,39]. Recently, in order to overcome the shortcomings of conventional heterojunctions (Type-II), while combining previous work on Z-scheme photocatalysts [40–45], Yu et al. [29] proposed a new step-scheme (S-scheme) heterojunction concept. The S-scheme heterojunction photocatalyst mainly comprises two n-type semiconductor photocatalysts. The driving force of the charge transfer is mainly the internal electric field between the two photocatalysts. The charge transfer in the S-scheme heterojunction is more like a “step” (macroscopic viewpoint) or “N” (microscopic viewpoint) type. As a consequence, the electrons and holes are separated in space, located in the CB of the reduction photocatalyst and the VB of the oxidation photocatalyst, respectively. Finally, the photocatalytic oxidation and reduction reactions are initiated by these holes and electrons, respectively. Therefore, efficient S-scheme hybrid photocatalyst systems are highly desirable, which not only largely promote the desired charge dynamics, but also substantially sustain favorable charge potentials. Because of the unique layered structure and tunable surface affinity of $\text{g-C}_3\text{N}_4$, it can be easily manipulated to form an excellent 2D host matrix with outstanding compatibility to various inorganic/organic moieties, which is favorable for hybridizing $\text{g-C}_3\text{N}_4$ with diverse functional components. A variety of $\text{g-C}_3\text{N}_4$ -based S-scheme photocatalyst systems have been fabricated for enhancing the photocatalytic activity of single $\text{g-C}_3\text{N}_4$ [27–35,46–48]. In particular, BiVO_4 , as a chemically stable visible-light photocatalyst

Fig. 1. Photocatalytic carbon cycling, which combines the aerobic oxidation of organic pollutants into CO_2 and the anaerobic reduction of CO_2 into hydrocarbon-based solar fuels. BSP = bifunctional S-scheme photocatalyst, $h\nu$ = solar energy.

with a bandgap energy of 2.40 eV, has attracted much interest for its superior photocatalytic oxidation performance, due to its proper VB edge located at ca. 2.7 eV vs. NHE [49–54]. The major limitations of the BiVO₄ photocatalyst are the slow electron transfer dynamics and weak reduction potentials of the CB electrons (CB energy levels of ca. 0.3 eV vs. NHE), which not only hinder the charge dynamics and photocatalytic performances, but also restrict the application of the BiVO₄ photocatalyst for photocatalytic reduction reactions. To overcome the respective drawbacks of the g-C₃N₄ and BiVO₄ photocatalyst, their S-scheme coupling is highly desirable by deliberately sacrificing the holes in g-C₃N₄ and the electrons in BiVO₄ with poor redox ability, and spatially separating the electrons in g-C₃N₄ and the holes in BiVO₄ with strong redox ability. Based on this consideration, many attempts have been made to construct an efficient S-scheme g-C₃N₄/BiVO₄ hybrid photocatalyst system [55–62].

It is assumed that the photoexcited electrons from the CB of BiVO₄ may favorably combine with the holes in the VB of g-C₃N₄ in those S-scheme g-C₃N₄/BiVO₄ hybrid photocatalyst systems. However, such interparticle electron transfer across the g-C₃N₄/BiVO₄ interface is usually the rate-limiting process. Because of the difficulty in electron transfer across the interface between the coupled photocatalyst [63–68], most reported g-C₃N₄/BiVO₄ composites continue to suffer from a high recombination rate of the photogenerated electrons and holes and limited photocatalytic efficiency [49–60,63–65]. Some ionic redox couples, such as Fe³⁺/Fe²⁺ and IO₃[−]/I[−], as well as noble metal nanoparticles or nanocarbon materials with good conductivity, have been successfully introduced to facilitate the interfacial charge transfer in a Z-scheme hybrid photocatalyst system [63–69]. In this regard, exploiting a cheap, earth-abundant, and efficient electron mediator is indispensable to achieve a practical S-scheme hybrid photocatalyst system. Metallic bismuth (Bi) is an ideal candidate, owing to the unique advantages of low price, nontoxicity, electrical conductivity, and a surface plasmon resonance (SPR) effect. It is reported that the charge transfer rate in a variety of photocatalysts can be accelerated by coupling with Bi metal nanoparticles [70–73]. However, the possible role of Bi nanoparticles as a solid-state electron mediator in S-scheme hybrid photocatalysts still requires further investigation. In this work, binary g-C₃N₄/BiVO₄ hybrids are first fabricated by preformed g-C₃N₄ nanosheet-mediated chemical deposition of BiVO₄ nanoparticles. Then, the g-C₃N₄/BiVO₄ hybrids are partially reduced to form the final ternary g-C₃N₄/Bi/BiVO₄ hybrid photocatalyst. During the reduction process, plasmonic metallic Bi nanoparticles form *in-situ* and uniformly decorate the g-C₃N₄/BiVO₄ hybrids. The as-prepared g-C₃N₄/Bi/BiVO₄ is demonstrated as an efficient visible-light S-scheme hybrid photocatalytic system, which not only shows enhanced photocatalytic oxidation performance in degrading organic pollutants under aerobic conditions, but also exhibits impressive photocatalytic reduction performance in CO₂ valorization under anaerobic conditions. Such a bifunctional S-scheme g-C₃N₄/Bi/BiVO₄ hybrid photocatalyst system can pave the way for further development of an integrated aerobic-anaerobic reaction system for photocatalytic

carbon cycling.

2. Experimental

2.1. Preparation of photocatalysts

g-C₃N₄ nanosheets. All chemicals used in this study were of analytical grade and used without further purification. Typically, the bulk g-C₃N₄ was obtained by direct heating of 10 g melamine at 550 °C for 4 h with a ramping rate of 5 °C/min in a semi-closed alumina crucible with a cover. After cooling to room temperature, the bulk g-C₃N₄ was ground into yellow powder and reannealed at 550 °C in air for a further 2 h to transform the bulk g-C₃N₄ into g-C₃N₄ nanosheets, involving thermal oxidation etching. The obtained g-C₃N₄ nanosheet products are denoted as **C** for simplicity.

Binary g-C₃N₄/BiVO₄ nanocomposites. The g-C₃N₄/BiVO₄ composite photocatalysts with different loading amounts of BiVO₄ nanoparticles were synthesized by a simple substrate-directed liquid phase deposition method. The preformed g-C₃N₄ nanosheets (sample C) were used as the substrate to direct the deposition of the BiVO₄ nanoparticles. Firstly, 0.5 g of g-C₃N₄ nanosheets was suspended into 100 mL deionized water under sonication for 30 min. Subsequently, bismuth(III) nitrate pentahydrate (Bi(NO₃)₃·5H₂O) and ammonium metavanadate (NH₄VO₃), with a mole ratio of 1:1, were added to the above suspension under violent stirring, and the optimized initial mass percentage of BiVO₄ to g-C₃N₄ was 15%. The mixed suspension was violently stirred for another 30 min. After this, the precipitate was centrifuged and washed with deionized water several times to remove impurities. The collected precipitate was dried overnight in a drying oven at 80 °C. Finally, the dried powders were ground and heated in a muffle furnace at 400 °C for 2 h with a heating rate of 5 °C/min to enhance the interfacial interactions between the g-C₃N₄ nanosheets and BiVO₄ nanoparticles. The as-obtained binary g-C₃N₄/BiVO₄ nanocomposite photocatalysts are named CB. For comparison, a pure BiVO₄ photocatalyst was also prepared under identical conditions and procedures but in the absence of the g-C₃N₄ nanosheets; the obtained sample is denoted as B.

Ternary g-C₃N₄/Bi/BiVO₄ nanocomposites. The ternary g-C₃N₄/Bi/BiVO₄ nanocomposites were prepared by a simple sodium borohydride (NaBH₄)-induced *in-situ* reduction method, using the above-prepared binary g-C₃N₄/BiVO₄ nanocomposites with the best photocatalytic performances (that is, sample CB) as the substrate. For a typical synthesis, 0.2 g of sample CB was first dispersed into 50 mL deionized water under magnetic stirring for 10 min. Then, 50 mL of dilute NaBH₄ solution was added dropwise into the above suspension; the optimized initial molar ratio of NaBH₄ to BiVO₄ was 0.4. After 10 min, the products were collected and washed with deionized water three times and dried at 50 °C for 12 h in a vacuum drying oven. The obtained sample is denoted as CBB.

2.2. Characterization

The as-synthesized samples were investigated by powder

X-ray diffraction (XRD), the patterns of which were recorded with a Bruker D8 Advance X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). Field emission scanning electron microscopy (FE-SEM) images were obtained using a Hitachi S-4800 scanning electron microscope. Transmission electron microscopy (TEM) images, high-resolution TEM (HRTEM) images, high-angle annular dark field (HAADF) scanning TEM (STEM) image, and energy-dispersive X-ray spectroscopy (EDS) elemental mappings were obtained using a JEM-2100F transmission electron microscope at 200 kV. UV-visible diffuse reflectance spectra (UV-vis DRS) were obtained using a Shimadzu UV-2600 spectrophotometer equipped with an integrating sphere attachment, using BaSO_4 as the background. An X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Physical Electronics PHI 1600 ESCA system operating with an Al $K\alpha$ X-ray source ($E = 1486.6 \text{ eV}$), and all the binding energies were calibrated using the C1s peak at 284.6 eV. Nitrogen sorption isotherms and CO_2 adsorption curves were measured on a TriStar II 3020 gas adsorption apparatus (Micromeritics, USA). All the samples were degassed at 180°C for 12 h prior to measurements. The Brunauer-Emmett-Teller (BET) surface area (S_{BET}) was determined using adsorption data in a relative pressure (P/P_0) range of 0.05–0.3 by a multipoint BET method. Furthermore, the pore-size distribution was determined using the desorption data via the Barrett-Joyner-Halenda (BJH) method. The volume of nitrogen desorbed at $P/P_0 = 0.99$ was used to determine the pore volume (V_p) and the average pore size (d_p). The photoelectrochemical measurements, including the transient photocurrent response and electrochemical impedance spectra (EIS), of the samples were conducted on a CHI760E electrochemical workstation (CH Instrument Corporation, Shanghai). All the photoelectrochemical measurements were performed in a three-electrode cell. The film electrode of each synthesized sample on FTO conductive glass served as the working electrode, while an Ag/AgCl electrode and platinum foil were employed as the reference electrode and counter electrode, respectively. Moreover, a 300-W Xenon lamp with a UV-cutoff filter ($> 420 \text{ nm}$) was used as the visible light source, and 0.1 M Na_2SO_4 aqueous solution was used as the electrolyte.

2.3. Evaluation of photocatalytic performance

The bifunctional photocatalytic performances of the as-prepared ternary $\text{g-C}_3\text{N}_4/\text{Bi}/\text{BiVO}_4$ nanocomposite and other control samples were evaluated in terms of the aerobic photocatalytic degradation of Rhodamine B (RhB) and anaerobic photocatalytic reduction of CO_2 . For the former, a 350-W Xenon lamp (Changzhou Siyu, China) equipped with a 420-nm UV-cutoff filter was used as the visible light source. The distance between the lamp and reactor remained at a constant height of 15 cm. Before light illumination, 50 mg of each photocatalyst was suspended in a 50 mL 10 mg/L aqueous RhB solution under vigorous stirring. The suspensions were continuously stirred for another 30 min in the dark to reach an adsorption-desorption equilibrium between the photocatalysts and RhB molecules prior to light irradiation. During light irradiation, 3 mL of the suspensions were extracted at regular time

intervals and centrifuged to remove the photocatalysts. The residual concentration of RhB was monitored by a UV-2550 UV-visible spectrophotometer (Shimadzu, Japan). To determine the dominant reactive oxidative species (ROSs), 2-propanol (IPA) and 4-hydroxy-2,2,6,6-tetramethylpiperidine-N-oxyl (Tempol) were introduced as scavengers for hydroxyl radicals ($\bullet\text{OH}$) and superoxide radicals ($\bullet\text{O}_2^-$), respectively, during the aerobic photocatalytic RhB degradation reaction under otherwise identical conditions.

For the anaerobic photocatalytic reduction of CO_2 , all the measurements were carried out at ambient temperature and atmospheric pressure in a 200-mL homemade two-neck Pyrex top-irradiation reactor. The two necks of the reactor were sealed with silicone rubber septums to form a closed system. A 300-W Xenon lamp (PerfectLight, PLS-SXE300, China) with a 420-nm UV-cutoff filter was used as the light source and was positioned ca. 15 cm above the reactor. As a typical photocatalytic experiment, 100 mg of the photocatalyst was uniformly deposited onto the bottom of the reactor. Prior to the light irradiation, the reactor was sealed and purged by blowing nitrogen for 45 min to ensure the anaerobic conditions of the reaction system. In each testing experiment, CO_2 and H_2O vapor were *in-situ* produced by the reaction of NaHCO_3 powder and aqueous H_2SO_4 solution inside a specially designed groove in one neck of the reactor. The NaHCO_3 powder (0.084 g) was put into the groove before sealing, while the aqueous H_2SO_4 solution (2 M, 0.3 mL) was injected into the groove by a syringe before light irradiation. After 1 h of light irradiation, the gas products extracted from the reactor were analyzed using gas chromatography (GC-7890B, Agilent) equipped with two flame-ionized detectors and a thermal conductivity detector. High-purity helium was used as the carrier gas in the gas chromatography. The retention time and yield of each detected gas product were determined and calibrated with a standard gas mixture.

The anaerobic photocatalytic degradation of the aqueous RhB solution over sample CBB was conducted in the above anaerobic reaction system under identical conditions, except that the 50 mL aqueous RhB solution (10 mg/L) was introduced, instead of the NaHCO_3 powder and aqueous H_2SO_4 solution to produce CO_2 and H_2O vapor. The gas products and concentration change of the aqueous RhB solution were analyzed by gas chromatography (GC-7890B, Agilent) and UV-visible spectrophotometry (UV-2550, Shimadzu), respectively.

3. Results and discussion

3.1. Phase structures and chemical compositions

The XRD patterns were used to identify the phase structures of the various as-prepared samples, as shown in Fig. 2. Obviously, the phase structure of BiVO_4 in sample B comprised both the monoclinic scheelite (m-BiVO_4) (JCPDS No. 14-0688) and tetragonal zircon structure (t-BiVO_4) (JCPDS No. 14-0133) [49–53]. The phase structure is usually of great importance for the photocatalytic activity, as it largely determines the band structures and surface properties. Moreover, it is well-documented that photocatalysts with mixed phase struc-

Fig. 2. XRD patterns of C (a), CB (b), CBB (c), and B (d) samples. The XRD peaks labeled with “#” correspond to g-C₃N₄, those labeled with “*” correspond to tetragonal BiVO₄, and the others labeled with Miller indices (h, k, l) correspond to monoclinic BiVO₄.

tures could form phase junctions to enhance the separation of the photogenerated electrons and holes [49]. For sample C, two typical diffraction peaks at 12.9° and 27.6° were recorded, which can be indexed to the {100} and {002} planes of g-C₃N₄, corresponding to the in-plane structural packing motif and interlayer stacking of aromatic systems, respectively. The XRD patterns for samples CB and CBB were rather similar to that for sample B. Comparing with the XRD pattern for sample C, the typical peak at 12.9° for g-C₃N₄ phase in sample CB and CBB was almost invisible, while the typical peak at 27.6° for the g-C₃N₄ phase in samples CB and CBB was largely weakened. There may be several possible reasons for this decrease in peak in-

tensity. For example, a decrease in the planar size of the g-C₃N₄ nanosheets may occur by etching during the liquid phase deposition process, followed by the thermally induced crystallization process of the BiVO₄ nanoparticles. Additionally, the coverage of the g-C₃N₄ nanosheets with highly crystalline BiVO₄ nanoparticles may shield, to some extent, the XRD signals for the g-C₃N₄ phase. It is worth noting that no obvious shift in the peak position was observed in the binary (CB) and ternary (CBB) nanocomposites, suggesting no lattice doping occurred during the synthesis processes. It is noted that because of the tiny amount of reduced metallic Bi nanoparticles, no characteristic XRD signal for metallic Bi was observed in sample CBB.

XPS was conducted to further determine the detailed surface elemental compositions and their chemical states, and to unveil the strong interactions between distinct phases in sample CBB. The XPS survey spectrum for sample CBB is displayed in Fig. 3(a), in which the XPS peaks for the C, N, Bi, V, and O elements can be well resolved. The high-resolution XPS spectra of Bi 4f before and after Ar⁺ etching are shown in Fig. 3(b). Because of the instability of metallic Bi upon oxidation in air, only the XPS peaks centered at 158.82 and 164.13 eV were recorded before Ar⁺ etching, which are typically ascribed to the Bi–O bonds of elemental Bi [70–73]. Furthermore, it is common that a thin bismuth oxide layer will easily form on the surface of the metallic Bi upon exposure to air [70–73]. After Ar⁺ etching of sample CBB, the characteristic XPS peaks corresponding to Bi–Bi bonding significantly appeared at around 156.74 and 161.90 eV. This result certified the existence of metallic Bi in sample CBB. Figs. 3(c)–(f) show the high-resolution XPS spectra of C 1s, N 1s, V 2p, and O 1s in sample CBB, respectively. The C 1s XPS peaks (Fig. 3(c)) at 284.64 and 288.17 eV are ascribed to the adventitious hydrocarbon from the XPS instrument itself

Fig. 3. (a) XPS survey spectrum (a) and high resolution XPS spectra for Bi 4f (b), C 1s (c), N 1s (d), V 2p (e), and O 1s (f), respectively, in sample CBB. In (b), the XPS spectra of Bi 4f before and after Ar⁺ etching indicate the partial oxidation of metallic Bi upon exposure to air.

and the defect-containing sp^2 -hybridized carbon atoms in the graphitic domains, respectively. The latter is possibly assigned to the N=C=N coordination in g-C₃N₄ [27–35]. The fitted four peaks of the high-resolution N 1s XPS spectrum (Fig. 3(d)), centered at around 398.67, 399.86, 401.17, and 404.85 eV, can be assigned to the sp^2 -hybridized nitrogen involved in the triazine rings (C–N=C), tertiary nitrogen N–(C)₃ groups, amino functional groups having a hydrogen atom (C–N–H), and π excitations, respectively, in g-C₃N₄ [27–35]. Importantly, the dominant peaks of C 1s and N 1s in sample CBB shifted to higher binding energies relative to the reference [27–35]. From the high-resolution XPS spectrum of V 2p in Fig. 3(e), the binding energies at 516.51 and 523.81 eV are assigned to V 2p_{3/2} and V 2p_{1/2}, respectively. For the high-resolution XPS spectrum of O 1s in Fig. 3(f), the peak with binding energy at 529.54 eV was attributed to crystal lattice oxygen of BiVO₄ in the form of Bi₂O₂²⁺, while the peak at 531.45 eV was ascribed to the hydroxyl groups on the surface [49–53]. It is worth noting that the shifts of the C 1s and N 1s peaks towards higher binding energies were accompanied with the shifts of the Bi 4f, V 2p and O 1s peaks towards lower binding energies in sample CBB. This result indicates the decrease in the electron density on the C and N moieties, the simultaneous increase in the electron density on the Bi, V, and O moieties, and that a built-in electric field formed at the g-C₃N₄/BiVO₄ interface. In combination, it was manifested that a strong interaction existed between the g-C₃N₄ phase and the BiVO₄ phase in the nanocomposite (sample CBB), rather than a simple physical mixture. Moreover, it was supposed that upon light irradiation, electron transfer from BiVO₄ to g-C₃N₄ would be favored due to the electrostatic effects of the built-in electric field, suggesting an S-scheme junction across the interface in sample CBB.

3.2. Morphology and porous structures

The morphology of the samples was firstly investigated by the SEM images (Fig. S1). A sheet-like uniform morphology was observed for pure g-C₃N₄ (sample C, Fig. S1(a)), whereas, concave cube-like larger microcrystals were observed for pure BiVO₄ (sample B, Fig. S1(b)). The overall morphologies of the binary (sample CB, Fig. S1(c)) and the ternary (sample CBB, Fig. S1(d)) nanocomposites were quite similar, comparable to that of pure g-C₃N₄. Interestingly, in both samples CB and CBB, no bulk BiVO₄ microcrystals were observed, while most evolved into nanoflakes, nanorods, or irregular nanoparticles, which were mainly attached to the g-C₃N₄ host. Such an observation was further confirmed by the corresponding TEM image for sample CBB (Fig. 4(a)). Many nanoparticles in the form of nanoflakes, nanorods, or of irregular shape were deposited on the surface of the transparent g-C₃N₄ nanosheets. The inset of Fig. 4(a) corresponds to the SAED patterns of sample CBB, indicating the polycrystalline features of the multicomponent nanocomposites. The corresponding HRTEM image (Fig. 4(b)) revealed that highly crystalline monoclinic BiVO₄ (m-BiVO₄), surrounded by some amorphous Bi nanoparticles, were deposited on the surface of the g-C₃N₄ nanosheets. The clear lattice fringe spacing of 0.31 nm corresponded to the (121) crystal

Fig. 4. TEM (a), HRTEM (b), and HAADF-STEM (c) images and the corresponding EDS elemental mappings (d–i) for the typical sample CBB. The inset of (a) is the corresponding SAED pattern.

plane of monoclinic BiVO₄ [49–53]. Considering the abundant sheet-like morphology of monoclinic BiVO₄ in the nanocomposites, it was supposed that these monoclinic BiVO₄ nanosheets were largely attached to the g-C₃N₄ nanosheets via the m-BiVO₄(001)/g-C₃N₄(001) interface. To further clearly demonstrate the elemental distribution in the nanocomposites (sample CBB), the EDS elemental mappings of C, N, Bi, V, and O (Figs. 4(d)–(i)) of sample CBB were obtained on the corresponding HAADF-STEM image, shown in Fig. 4(c), which was the same observation zone in Fig. 4(a). The C and N distribution profiles correspond to the transparent underlayer in Fig. 4(a), while the Bi, V, and O distribution profiles correspond well to the overall appearance of the surface-deposited nanoparticles in Figs. 4(a) and (c). Combining the above XRD, XPS, SEM, TEM, and EDS results, it was clear that binary g-C₃N₄/BiVO₄ and ternary g-C₃N₄/Bi/BiVO₄ nanocomposites were successfully constructed with a well-contacted interface.

The porous structures of samples B, C, CB, and CBB were investigated by nitrogen adsorption-desorption isotherms, as shown in Fig. S2(a). All the samples had isotherms of type IV, according to the Brunauer-Deming-Deming-Teller classification, indicating the presence of mesopores (2–50 nm). The sorption isotherms of samples C, CB, and CBB were very similar, suggesting their comparable porous structures. The introduction of BiVO₄ and the Bi nanoparticles to couple with the g-C₃N₄ nanosheets had a tiny influence on the microstructures. The sorption isotherms of sample B were otherwise very different, having almost no adsorption in the wide relative pressure (P/P_0) range, and only a minor hysteresis loop at high

P/P_0 , suggesting there were much less mesopores in sample B, in good agreement with the corresponding pore size distribution. In fact, as shown in Table S1, the specific surface area of sample B was only $19 \text{ m}^2/\text{g}$, much smaller than that of samples C, CB, and CBB ($>50 \text{ m}^2/\text{g}$). The hysteresis loops for samples C, CB, and CBB covered a considerably wide range of relative pressures, suggesting their wide bimodal mesopore size distributions, as confirmed by the corresponding broad BJH pore-size distributions (Fig. S2(b)). Typically, they had two main mesopore peaks centered at around 4 and 45 nm. Moreover, the isotherms for samples C, CB, and CBB showed high adsorption at high P/P_0 approaching 1.0, implying the existence of large mesopores and macropores. The formation of various mesopores and macropores is due to the intra- and inter-agglomeration [10–11].

It is well known that CO_2 adsorption on the surface of a photocatalyst is key to initiating the photocatalytic CO_2 reduction reaction. Furthermore, the CO_2 adsorption capacity is a significant factor influencing the photocatalytic CO_2 reduction efficiency [10–11]. As shown in Fig. S3, all the samples showed an almost linear relationship between the CO_2 adsorption capacity and the relative pressure (P/P_0) in the higher P/P_0 range of 0.3–1.0. Such a characteristic indicates a dominant physical interaction between CO_2 and the various samples; thus, the specific surface area was found to be the most important influencing factor. In particular, with the increasing S_{BET} from sample B to samples C and CB, the CO_2 adsorption capacity steadily increased. Meanwhile, in the lower P/P_0 range of 0–0.3, a relatively faster increase in CO_2 uptake was recorded for all the samples, particularly for sample CBB, indicating the occurrence of the chemical adsorption of CO_2 . The chemical adsorption of CO_2 on sample B is minor, suggesting that the chemical interaction between CO_2 and BiVO_4 is weak. However, samples C, CB, and CBB have much stronger chemical adsorption. This is probably due to the stronger interaction of the $\text{g-C}_3\text{N}_4$ moieties, which have abundant amino functional groups (XPS results), with the CO_2 molecules. In particular, the *in-situ* reduction step to fabricate sample CBB might lead to further surface functionalization of $\text{g-C}_3\text{N}_4$ to enhance the chemical adsorption of CO_2 .

3.3. Optical properties and band structures

The band structures of the photocatalysts could be revealed by combined optical and electrochemical analyses. Specifically, the bandgap energies can be estimated by analyzing the optical absorption spectrum. The UV-vis DRS spectra were measured to study the optical properties and electronic structures of the as-prepared samples (Fig. 5). All the four samples have good absorption in the visible light region. The optical absorption edges of samples C and B were approximately estimated to be 450 and 525 nm, respectively (Fig. 5(a)). The absorption curves for samples CB and CBB are located between those of samples B and C (Fig. 5(a)). In particular, because of the SPR effects of the *in-situ* generated Bi nanoparticles [61,70], sample CBB exhibited a slight promotion in visible light absorption above 500 nm, compared with sample CB. The bandgap energy (E_g) values of samples B and C can be evaluated using the following equation: $\alpha h\nu = B(h\nu - E_g)^{n/2}$ where α is the absorption coefficient, ν is the frequency of the light, h is Planck's constant, B is the absorption constant, and $n = 1$ or 4 depending on the nature of the semiconductor (direct or indirect bandgap, respectively) [60]. Both $\text{g-C}_3\text{N}_4$ and BiVO_4 are direct bandgap semiconductors, consequently, E_g can be estimated from a plot of $(\alpha h\nu)^2$ versus $(h\nu)$. The interception of the tangent to the x-axis would give a good approximation of E_g of the samples. As the absorbance (A) is proportional to the absorption coefficient (α), the value of A was used as a substitute of α in the present study, as in Fig. 5(b). Here, the E_g values of samples B and C were estimated to be 2.40 and 2.83 eV, respectively, which agree well with the reported values [49]. Moreover, the conduction band energy (E_{CB}) of a photocatalyst can be calculated according to the following equation (Mulliken electronegativity theory): $E_{\text{CB}} = \chi - E^e - 0.5E_g$, where χ is the absolute electronegativity of the semiconductor photocatalyst, E^e is the energy of the free electron in the hydrogen scale (approximately 4.5 eV), and E_g is the bandgap energy [60]. The χ values for BiVO_4 and $\text{g-C}_3\text{N}_4$ are 6.04 and 4.66 eV, respectively [60], so the calculated CB potentials for samples B and C were approximately 0.34 and -1.26 V , respectively. Combined with the value of E_g , the VB potentials

Fig. 5. (a) UV-Vis diffuse reflectance spectra of samples B, C, CB, and CBB; (b) Plots of $(\alpha h\nu)^2$ vs. $h\nu$ of samples B and C.

of samples B and C were, thus, calculated to be 2.74 and 1.57 V vs. NHE, respectively. The band structures of the BiVO_4 (sample B) and $\text{g-C}_3\text{N}_4$ (sample C) photocatalysts are illustrated in Fig. S4.

3.4. Photoelectrochemical measurements and charge dynamics

As the charge separation and transfer efficiency play a critical role in the final photocatalytic performance, we combined the transient photocurrent and EIS analyses to clarify the charge dynamic process in the different photocatalysts (Fig. 6). The transient photocurrent responses were recorded at a bias potential of 0.4 V for several on-off cycles under visible light irradiation. As shown in Fig. 6(a), for all the samples, the photocurrent reached a constant value when the light was on, and decreased to zero when the light was off. The photocurrents of both samples B and C were obviously lower than those of the other two composite samples. It was suggested that the interfacial hybridization of $\text{g-C}_3\text{N}_4$ and BiVO_4 in sample CB was beneficial for the charge separation. Moreover, after introducing a certain amount of Bi nanoparticles in sample CBB, the photocurrent was further increased, relative to sample CB. It was supposed that a portion of Bi nanoparticles located at the interface of $\text{g-C}_3\text{N}_4$ and BiVO_4 acted as an electron bridge, promoting the interfacial charge transfer. EIS analysis is a powerful tool to study the electrochemical charge transfer behavior at high frequency [3,11]. Fig. 6(b) shows the EIS spectra in the Nyquist mode in the frequency range of 100 kHz – 1 kHz for the electrodes made from samples B, C, CB, and CBB. The Nyquist plot can be interpreted in terms of the equivalent circuit, as displayed in the inset. In the equivalent circuit, R_s is the solution resistance, CPE is the constant phase element for the electrolyte/electrode interface, and R_{ct} is the charge transfer resistance across the interface of the electrode/electrolyte [3,11]. The arcs in the Nyquist plot are related to the charge transfer at the photoelectrode/electrolyte interface. The fitted R_{ct} values were 46.8, 42.0, 38.2, and 34.4 Ω for the electrodes made from samples B, C, CB, and CBB, respectively. Sample CBB, with the lowest R_{ct} , presented the best charge transfer efficiency. Over-

all, it can be concluded that the charge transfer rate in sample CB can be improved because of the reduced charge recombination by forming a heterojunction, compared to those in samples B and C. By introducing a portion of Bi nanoparticles at the interface of $\text{g-C}_3\text{N}_4$ and BiVO_4 acting as an electron bridge, the charge transfer rate in sample CBB could be further enhanced.

3.5. Photocatalytic activity

In this study, Rhodamine B (RhB) was chosen as the target pollutant to evaluate the aerobic photocatalytic oxidation activity of the as-prepared samples under visible light irradiation (> 420 nm). As presented in Fig. 7(a), sample CBB shows the best aerobic photocatalytic oxidation activity in the degradation of the RhB molecules. The temporal changes in the absorption spectra of the RhB aqueous solution (10 mg/L) upon visible light irradiation over sample C are illustrated in Fig. 7(b). It is noted that the maximum absorption band (wavelength corresponding to the maximal absorbance, λ_{max}) of the reaction solution gradually shifted from 554 to 495 nm during the photocatalytic degradation of RhB. This hypsochromic shift in λ_{max} of the RhB solution corresponds to the step-by-step de-ethylation of RhB to give N,N,N'-triethyl rhodamine (TER, 539 nm), N,N'-diethyl rhodamine (DER, 522 nm), N-ethyl rhodamine (MER, 510 nm), and rhodamine at 495 nm [50]. As shown in Fig. 7(c), the degree of de-ethylation can be represented by the blue shift in the wavelength of the maximum absorption: $\Delta\lambda_{\text{max}} = 554 - \lambda_{\text{max}}$ [50]. Importantly, as for all the samples, de-ethylation occurred dominantly in the early stage; at the end of this stage, there was a leap in $\Delta\lambda_{\text{max}}$, then, $\Delta\lambda_{\text{max}}$ was very limited (Fig. 7(c)), indicating that the de-ethylation process was almost terminated and the mineralization process of rhodamine (decomposition of the conjugated structure of rhodamine to small molecules) was initiated [50]. In this regard, there are two distinctive stages of the aerobic photocatalytic RhB oxidation process: de-ethylation and mineralization. Generally, the rate of de-ethylation is higher than that of the following mineralization process, and very limited changes in the spectral intensity are recorded at the maximal absorption during miner-

Fig. 6. Transient photocurrent response (a) and EIS spectra (b) of photoelectrode made from samples B, C, CB, and CBB in 0.1 M Na_2SO_4 electrolyte under visible light illumination (> 420 nm) at a bias potential of 0.4 V. The solid line in (b) can be well-fitted using the proposed equivalent circuit in the inset.

Fig. 7. Aerobic photocatalytic oxidation activity over the various as-prepared photocatalysts under visible light illumination ($\lambda \geq 420$ nm) using RhB as the target pollutant. (a) Photocatalytic degradation efficiency; (b) Temporal UV-Vis spectral changes of aqueous RhB solution over typical sample C (c) Degree of de-ethylation reflected by the blue shift in $\Delta\lambda_{\max}$; (d) Pseudo first order reaction kinetics.

alization. The photocatalytic oxidation rate of RhB can be approximately calculated based on the de-ethylation process of RhB. The photocatalytic degradation kinetics of RhB during de-ethylation can be described using a pseudo first order reaction model, expressed by the following: $-\ln(C/C_0) = kt$, where C_0 and C are the initial and final RhB concentrations, respectively; k is the pseudo first order rate constant; and t represents the light irradiation time. The k values can be estimated from the $\ln(A_0/A)$ vs. t plot, as shown in Fig. 7(d). Sample CBB had the highest k value of 0.067 min^{-1} , much higher than that of samples B (0.005 min^{-1}), C (0.033 min^{-1}), and CB (0.051 min^{-1}). The aerobic photocatalytic oxidation activity of sample CBB is obviously better than that of some previously reported similar materials [52–60].

It is worth noting that, during the aerobic photocatalytic oxidation processes, RhB could be usually degraded completely into CO_2 , which is generally regarded as the ideal harmless product for organic pollution control. However, in terms of carbon cycling, CO_2 is not an ideal product because it is a typical greenhouse gas; thus, it is highly desirable to reduce the above-generated CO_2 into other value-added chemicals or fuels. In this study, the possibility of the anaerobic photocatalytic reduction of CO_2 into valuable chemicals using the various as-prepared samples was also evaluated in the presence of

water vapor under visible light irradiation ($\lambda \geq 420$ nm). The anaerobic photocatalytic reduction of CO_2 involves a series of complicated processes, i.e., charge generation and transfer, C–O bond breaking, and C–H and O–H bond formation [12]. The main reactions during photocatalytic CO_2 reduction with H_2O are as follows [12].

The anaerobic photocatalytic gaseous reduction of CO_2 in the presence of water vapor was performed under visible light irradiation for 1 h at atmospheric pressure. As shown in Fig. 8, the evolution of CO was recorded as the main product for all the samples, while some other reduction products such as H_2 , CH_4 , and CH_3OH could also be detected for the binary and ternary composites. As CH_3OH , CH_4 , and H_2 are important industrial chemicals and fuels, their selective production over samples CB and CBB suggests the significance of the construction of a composite photocatalyst. More specifically, owing to the formation of the heterojunction between g- C_3N_4 and BiVO_4 , a trace amount of CH_4 and a small amount of H_2 were detected for sample CB, but the yield of CO considerably decreased. In contrast, for sample CBB, while much more multi-electron reduc-

Fig. 8. (a) H₂, CH₃OH, CH₄, and CO yield over samples B, C, CB, and CBB by anaerobic photocatalytic gaseous reduction of CO₂ with water vapor under visible light irradiation ($\lambda \geq 420$ nm); (b) CO yield (left) and RhB removal (right) over sample CBB by anaerobic photocatalytic degradation of aqueous RhB solution under visible light irradiation ($\lambda \geq 420$ nm).

tion products (CH₄ and CH₃OH) were generated, the yields of the two-electron reduction products (CO and H₂) also significantly increased. The efficient charge transfer and surface enrichment in composite photocatalysts would favor the generation of multi-electron reduction products.

The above separated aerobic photocatalytic oxidation and anaerobic photocatalytic reduction experiments clearly demonstrate the dual functionality of the designed composite photocatalyst. As illustrated in Fig. 1, these results imply the possibility of achieving photocatalytic carbon cycling by the integration of the aerobic oxidation and anaerobic reduction processes. However, the two-pot reaction systems, involving RhB to CO₂ followed by CO₂ to solar fuels, will be complicated in operation. Under this consideration, the direct conversion of RhB to solar fuels under anaerobic conditions in one-pot was also studied over the as-prepared ternary g-C₃N₄/Bi/BiVO₄ hybrid photocatalysts. The anaerobic photocatalytic degradation of the aqueous RhB solution over sample CBB was also performed in the anaerobic reaction system under identical conditions, except that 50-mL aqueous RhB solution (10 mg/L) was introduced instead of CO₂ and H₂O vapor. The one-pot anaerobic photocatalytic result is shown in Fig. 8(b). The RhB degradation efficiency was approximately 30% in 1 h, which was much lower than that conducted under aerobic conditions. This result suggests that oxygen was important for enhancing the photocatalytic RhB removal process. Interestingly, CO, as the major gas product, was indeed detected. The yield (0.63 μmol/(g·h)) was much lower than that obtained from the photocatalytic CO₂ reduction with H₂O vapor. More complex reaction processes are involved in the one-pot anaerobic reaction system, while the overall photocatalytic conversion efficiency can be further improved by promoting the anaerobic RhB oxidation efficiency, which would compete with the water splitting process that is crucial for CO hydrogenation.

3.6. Photocatalytic mechanism

As shown above, the photocatalytic activities of samples CB and CBB were tremendously enhanced because of the formation of the heterojunction; thus, it is essential to understand

the synergetic mechanism in the binary and ternary composite system. Combining the XPS analyses of sample CBB (Fig. 2) with the band structure analyses of the g-C₃N₄ and BiVO₄ photocatalyst (Fig. 8), the formation of the S-scheme junction at the interface of the BiVO₄/g-C₃N₄ composite photocatalyst probably accounts for the promotion of the charge dynamics (Fig. S2) and photocatalytic efficiency. Such an assumption was further confirmed by the following results of the density functional theory (DFT) calculation and scavenger studies [30,65–68].

The calculations were conducted using the CASTEP mode of Materials Studio according to DFT [74–77]. The Perdew-Burke-Ernzerhof form exchange-correlation functional was used within the generalized gradient approximation. The geometry optimization and electrostatic potential calculations were completed with the cutoff energy of 380 eV and Monkhorst-Pack grids of 2 × 5 × 1 for the monoclinic BiVO₄ (001) crystal plane, and 3 × 3 × 1 for the monolayer g-C₃N₄. The convergence thresholds for the geometry optimization were set as: energy of 5.0 × 10⁻⁶ eV/atom, maximum force of 0.01 eV/Å, and maximum stress of 0.02 GPa. The optimized models and calculated average potential profiles of the monoclinic BiVO₄ (001) crystal plane and monolayer g-C₃N₄ are shown in Fig. 9.

The Fermi energy of the semiconductor is one important parameter for estimating the charge transfer between the interfaces of two semiconductor materials, and can be calculated by:

$$\Phi = E_{\text{vac}} - E_{\text{F}}$$

where E_{vac} and E_{F} are the electrostatic potential of the vacuum energy and Fermi energy, respectively [74–77]. The calculated work functions of the monoclinic BiVO₄ (001) facet and monolayer g-C₃N₄ were 6.92 and 4.23 eV, respectively. The Fermi energy of the g-C₃N₄ was higher than that of the monoclinic BiVO₄ (001) facet. Upon the interfacial contact between the monoclinic BiVO₄ (001) facet and monolayer g-C₃N₄, electrons will transfer from g-C₃N₄ to the monoclinic BiVO₄ (001) facet until their Fermi energies reach the same level. As a consequence, this leads to the decrease of electron density of g-C₃N₄ and an increase in BiVO₄, implying the formation of a built-in electric field at the BiVO₄ and g-C₃N₄ interface (Fig. S5). It is worth noting that the direction of the abovementioned

Fig. 9. Optimized crystal structures (a, c) and calculated electrostatic potentials (b, d) of monoclinic BiVO_4 (001) crystal plane (a, b) and monolayer $\text{g-C}_3\text{N}_4$ (c, d). The yellow red, green, purple, blue, and gray spheres correspond to the O, V, Bi, N, and C atoms, respectively.

built-in electric field is from the $\text{g-C}_3\text{N}_4$ surface to the BiVO_4 surface, which is beneficial to the vectorial interfacial transfer of the photogenerated charge carriers from the CB of BiVO_4 to the VB of $\text{g-C}_3\text{N}_4$ during the photocatalytic reaction processes (Fig. S5). Overall, the DFT calculation suggests the formation of an S-scheme junction at the interface of the $\text{BiVO}_4/\text{g-C}_3\text{N}_4$ composite photocatalyst [74–77].

By a simple comparison of the $\text{OH}^\bullet/\cdot\text{OH}$ and $\text{O}_2/\cdot\text{O}_2^-$ redox potentials versus the CB and VB potentials of $\text{g-C}_3\text{N}_4$ and BiVO_4 (Fig. S4), it is clear that $\cdot\text{OH}$ radicals cannot be generated over pure $\text{g-C}_3\text{N}_4$, but can be generated over pure BiVO_4 . On the contrary, $\cdot\text{O}_2^-$ radicals cannot be generated over pure BiVO_4 , but can be generated over pure $\text{g-C}_3\text{N}_4$. Such assumptions have been well confirmed by the scavenger studies. IPA as the $\cdot\text{OH}$ scavenger and Tempol as the $\cdot\text{O}_2^-$ scavenger were introduced in the respective reaction system for the aerobic photocatalytic RhB degradation to determine the involved main ROSs over each photocatalyst (Fig. 10). Importantly, in the sample B-based photocatalytic system, the degradation efficiency was obviously inhibited after introduction of IPA as the scavenger of $\cdot\text{OH}$, suggesting the weak reductive ability of the photogenerated electrons in BiVO_4 , while the main ROS were h^+ -derived oxidative species ($\cdot\text{OH}$). In contrast, the degradation efficiency of the sample C-based photocatalytic system was inhibited after introduction of Tempol as the scavenger of $\cdot\text{O}_2^-$, suggesting the weak oxidative ability of the photogenerated holes in BiVO_4 , while the main ROS were e^- -derived oxidative species ($\cdot\text{O}_2^-$). After the formation of the heterostructure between $\text{g-C}_3\text{N}_4$ and BiVO_4 , both $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ significantly contributed to the aerobic photocatalytic RhB degradation over samples CB and CBB. This result suggests that in the $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ binary nanocom-

Fig. 10. Scavenger studies on the main reactive oxidative species during the aerobic photocatalytic RhB degradation processes over photocatalyst samples B, C, CB, and CBB.

posites, both the photoexcited holes with strong oxidative ability from the VB of BiVO_4 and the photoexcited electrons with strong reductive ability from the CB of $\text{g-C}_3\text{N}_4$ were retained, and an S-scheme hybrid photocatalyst system was established. Moreover, after introduction of the Bi nanoparticles, the synergistic photocatalytic mechanism did not vary, sustaining the S-scheme interfacial charge transfer in the $\text{g-C}_3\text{N}_4/\text{Bi}/\text{BiVO}_4$ ternary nanocomposites. In fact, metallic Bi nanoparticles, as an important component of CBB ternary photocatalysts, may have three basic functions [67]. First, the plasmonic effects of Bi nanoparticles enhance the visible light absorption ability (Fig. 5(a)). Second, the field effects of plasmonic Bi nanoparticles enhance the charge separation efficiency (Fig. 6). Third, a portion of metallic Bi nanoparticles located at the interface of the S-scheme of $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ may promote the interfacial charge transfer by acting as an S-scheme electron mediator (Fig. 6), similar to the roles of the Au nanoparticles in the $\text{Au}/\text{CdS}/\text{TiO}_2$ hybrid system [66].

The complex photocatalytic mechanism of the S-scheme $\text{g-C}_3\text{N}_4/\text{Bi}/\text{BiVO}_4$ hybrid photocatalyst is demonstrated in Fig. 11. First, for the light harvesting process, there are three active visible light absorption centers, being the $\text{g-C}_3\text{N}_4$ nanosheets, BiVO_4 , and surface-decorated metallic Bi nanoparticles. In particular, due to the SPR effects, the metallic Bi nanoparticles enhanced the visible light absorption capacity. Second, for the charge transfer processes, due to the formation of a built-in electric field at the $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ interface, S-scheme interfacial charge transfer, that is the transfer of photogenerated electrons from the CB of BiVO_4 toward the VB of $\text{g-C}_3\text{N}_4$, dominated upon light irradiation. Moreover, the metallic Bi nanoparticles acted as an S-scheme electron mediator to promote the interfacial charge transfer in the ternary S-scheme $\text{g-C}_3\text{N}_4/\text{Bi}/\text{BiVO}_4$ hybrid system. Incidentally, the photoexcited hot electrons from the metallic Bi nanoparticles transferred to the CB of the BiVO_4 moiety, then toward the VB of $\text{g-C}_3\text{N}_4$, inhibiting the charge recombination. As a consequence, the holes in $\text{g-C}_3\text{N}_4$ and the electrons in BiVO_4 with poor redox ability were sacrificed, and the electrons in $\text{g-C}_3\text{N}_4$ and the holes in BiVO_4 with strong redox ability remained and were spatially separated, which together modulate the charge potentials and dynamics to suit the

Fig. 11. Illustration of the enhanced photocatalytic carbon cycling over the bifunctional ternary S-scheme g-C₃N₄/Bi/BiVO₄ hybrid photocatalyst under visible light irradiation.

requirement of dual functionality for both the aerobic photocatalytic oxidation and the anaerobic photocatalytic reduction reactions. Finally, the surface photocatalytic reaction mechanisms are dependent on the reaction atmospheres. The holes in the VB of BiVO₄ activated H₂O, either for the generation of •OH favoring the RhB oxidation under aerobic conditions, or splitting water to promote CO₂ hydrogenation under anaerobic conditions. Relatively, the electron-initiated reactions are much more complicated. Under aerobic conditions, O₂ was activated by the electrons in the CB of g-C₃N₄ to generate •O₂⁻; therefore, RhB was effectively oxidized by the cooperative effects of •O₂⁻ and •OH. Under anaerobic conditions, the generation of •O₂⁻ by electron activation was retarded, and the RhB removal efficiency largely decreased. Instead, the photogenerated electrons in the CB of g-C₃N₄ dominantly promoted the reduction of CO₂ and H₂O to produce CO, CH₄, CH₃OH, and H₂.

4. Conclusions

A ternary g-C₃N₄/Bi/BiVO₄ hybrid photocatalyst was fabricated and employed to establish artificial CO₂ cycling. The as-prepared g-C₃N₄/Bi/BiVO₄ hybrid photocatalyst was demonstrated to be an efficient bifunctional photocatalyst system, which not only showed enhanced aerobic photocatalytic oxidation performance in degrading organic pollutants, but also exhibited impressive anaerobic photocatalytic reduction performance in CO₂ valorization. Such a bifunctional g-C₃N₄/Bi/BiVO₄ hybrid photocatalyst system will pave the way for further development of integrated aerobic-anaerobic reaction systems for photocatalytic carbon cycling. Based on combined XPS analyses, scavenger studies, and DFT calculations, it is suggested that the excellent bifunctional photocatalytic performance of the g-C₃N₄/Bi/BiVO₄ hybrid photocatalyst is associated with the formation of efficient S-scheme hybrid junctions, which not only largely promote suitable charge dynamics, but also sustain favorable charge potentials. Furthermore, the introduction of metallic Bi nanoparticles not only

enhanced the visible light absorption by SPR effects, but also promoted the interfacial charge transfer by S-scheme bridging effects. Further studies would be devoted to the construction of an integrated aerobic-anaerobic reaction system and the application of the bifunctional S-scheme hybrid photocatalyst for simultaneous environmental protection and energy production based on artificial CO₂ cycling processes.

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Graphical Abstract

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Bifunctional S-scheme g-C₃N₄/Bi/BiVO₄ hybrid photocatalysts toward artificial carbon cycling

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Bifunctional S-scheme g-C₃N₄/Bi/BiVO₄ hybrid photocatalysts demonstrate both superior aerobic photocatalytic organic pollutant oxidation performance and impressive anaerobic photocatalytic CO₂ reduction ability, enabling the integrated aerobic-anaerobic reaction system for photocatalytic carbon cycling.

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双功能S-型g-C₃N₄/Bi/BiVO₄复合光催化剂驱动人工碳循环

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摘要: 长期以来, 陆地、大气和海洋之间的碳循环维持了大自然碳平衡。随着密集人类活动和高度工业发展, 碳燃料、碳化学品和碳材料广泛应用于各个领域, 导致碳排放过量, 碳平衡已被严重破坏, 碳污染已成为一个严峻问题。例如, 持久性有机污染物和挥发性有机化合物过量排放到环境中, 威胁着人类的健康和生态平衡。人们陆续开发出各种先进的环境技术, 如微生物分解, 去除空气和水中的碳基污染物, 将有毒有害的有机化合物转化为无害CO₂。但是, CO₂本身是大气中的主要温室气体, 它在大气中的浓度早超过了天然碳循环所能维持的环境自洁净能力。基于先进催化技术建立人工碳循环, 将有机污染物矿化生成的CO₂进一步转化为有价值的有机化学品(如太阳能燃料)是一种理想的低碳方法。光合作用是自然碳循环中核心过程之一, 是降低大气中CO₂浓度的关键。受到光合作用启发, 科学家们积极开发人工光合成技术推动CO₂资源化。人工光合成技术本质上基于半导体光催化过程。半导体光催化过程具有双重作用。一方面, 基于有氧光催化氧化过程, 有机污染物可以矿化生成无毒CO₂。另一方面, 基于缺氧光催化还原过程, CO₂可以转化为碳氢化合物太阳能燃料。理论上, 结合上述两个过程, 为建立人工碳循环奠定基础, 但是, 至今很少有人成功建立有氧氧化-无氧还原串联光催化工艺, 实现人工碳循环。难点在于有机污染物的有氧氧化反应和CO₂的无氧还原反应的操作条件与反应机制是完全不同的, 目前缺乏同时适用于上述两种反应的双功能光催化剂。本文成功构建了具有双功能的g-C₃N₄/Bi/BiVO₄三元复合光催化剂, 它不仅在降解有机污染物方面表现出优异的有氧光催化氧化性能(以降解染料罗丹明B为例), 而且还表现出优异的缺氧CO₂光催化还原性能。此外, 基于“一锅法”厌氧耦合氧化-还原反应, g-C₃N₄/Bi/BiVO₄三元复合光催化剂成功实现同步罗丹明B降解与太阳能燃料生成, 构建了从毒害有机污染物到高品质太阳燃料的碳循环。结合牺牲剂实验分析与密度泛函理论理论计算, 作者提出g-C₃N₄/Bi/BiVO₄复合光催化剂的双功能性与g-C₃N₄与BiVO₄界面内建S-型复合异质结有关。S-型复合异质结既促进界面电荷转移与分离, 又维持了最佳电荷氧化还原电位。此外, S型g-C₃N₄/Bi/BiVO₄复合光催化剂中原位生成的具有等离子体效应的Bi纳米颗粒具有双重作用, 既促进界面电荷定向转移, 又促进可见光吸收。本文开发的新型双功能S-型g-C₃N₄/Bi/BiVO₄复合光催化剂系统为进一步开发集成式有氧-缺氧光催化碳循环反应系统奠定基础。

关键词: S型; 等离子体Bi纳米颗粒; 光催化CO₂还原; 光催化降解有机污染物; 碳循环

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