Charge Separation



A Facet-Dependent Schottky-Junction Electron Shuttle in a BiVO₄{010}–Au–Cu₂O Z-Scheme Photocatalyst for Efficient Charge Separation

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Interfacial charge separation and transfer are the main challenges of efficient semiconductor-based Z-scheme photocatalytic systems. Here, it is discovered that a Schottky junction at the interface between the BiVO₄ {010} facet and Au is an efficient electron-transfer route useful for constructing a high-performance BiVO₄{010}–Au–Cu₂O Z-scheme photocatalyst. Spectroscopic and computational studies reveal that hot electrons in BiVO₄ {010} more easily cross the Schottky barrier to expedite the migration from BiVO₄ {010} to Au and are subsequently captured by the excited holes in Cu₂O. This crystal-facet-dependent electron shuttle allows the long-lived holes and electrons to stay in the valence band of BiVO₄ and conduction band of Cu₂O, respectively, contributing to improved light-driven CO₂ reduction. This unique semiconductor crystal-facet sandwich structure will provide an innovative strategy for rational design of advanced Z-scheme photocatalysts.

1. Introduction

Artificial photosynthetic techniques to convert carbon dioxide into carbon-based fuels have attracted attention as economical and renewable strategies to meet ever-growing global energy demands and solve associated environmental issues.^[1,2] To

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DOI: 10.1002/adfm.201801214

mimic natural photosynthesis, a twophoton pathway, called a Z-scheme photocatalytic system, was created with a double-component photosystem and was expected to easily achieve a high quantum efficiency. The Z-scheme system successfully eliminates the inherent bandgap engineering contradiction of single-component photosystems, i.e., the trade-off between an extended light-harvesting range and degraded redox capacity.^[3,4] Typically, a Z-scheme photocatalytic system consists of an electron-transfer mediator that connects two semiconductors, which are called photosystem I (PS I) and II (PS II). If PS I and II have a more positive valence band (VB) level and more negative conduction band (CB) level, respectively,

the light-excited electrons in the VBs of PS I and II moving into their CBs will make the VB of PS I a strong electron acceptor and the CB of PS II a strong electron donor when an electrontransfer mediator is used to deliver electrons in the CB of PS I into the VB of PS II. Therefore, both an excellent redox ability and spatial separation of photogenerated charges can be created in a Z-scheme photocatalytic system by combining two narrowbandgap semiconductors, and these properties are beneficial for sufficient light harvesting.

In a Z-scheme system, electron migration between the two photocatalysts is the rate-determining process.^[5,6] Ionic redox couples, such as Fe^{3+}/Fe^{2+} and IO^{3-}/I^{-} , have been shown to be effective in shuttling electrons in Z-scheme systems.^[3,4] Unfortunately, the effectiveness of ionic redox couples depends on the reaction environment and is probably weakened by back reactions. Alternatively, a series of solid-state electron mediators with noble-metal nanoparticles (Au, Ag, Pt, etc.) or metal-free conductive materials (carbon layer, reduced graphene oxide, etc.) may be more favorable to ensure a continuous flow of electrons between the two photosystems.^[6-9] Great efforts have been devoted to improve intrinsic conductive properties and structural modifications. An Au layer or carbon film has been used as an electrical connection between Mo-doped BiVO₄ and (La, Rh)-codoped SrTiO₃^[8,9] to achieve highly efficient overall water splitting. However, studies on the available semiconductor-conductor contact interface, which plays a crucial role in manipulating the interfacial charge transfer determined by the interface energetics, are lacking.

Theoretically, when the work function of a metal is greater than that of an n-type semiconductor, a Schottky junction can be established after their close contact to effectively hinder the back transfer of photoexcited hot electrons trapped by the metal.^[4,10-12] Different atomic coordination environments on different facets induce significant distinctions in work functions.^[12,13] Thus, the formation of a Schottky junction depends on whether the facets on a semiconductor have an applicable work function to establish a Schottky junction with a metal. Recently, facet engineering was used to produce a reduction facet for electron accumulation and an oxidation facet for hole accumulation based on different surface work functions, which led to different surface band bending.^[12,14–19] Typically, obvious work function differences are observed on adjacent facets, such as {100} and {111} of Cu₂O,^[12] {110} and {010} of BiVO₄,^[14,15] {001} and {110} of SrTiO₃,^[16] {100} and {111} of CeO₂,^[17] and [001] and [101] of TiO₂,^[18,19] effectively inducing spatial charge separation. Evidently, forming a Schottky junction on the reduction facet of a semiconductor by anchoring a metal is beneficial for enhancing hot-electron injection into the metal because of the high density of hot electrons on a reduction facet and the enhanced surface electric states on a semiconductor due to metal modification, which accelerates electron transfer to metal.^[20] In addition, the Schottky barrier offers a unidirectional electrontransfer route from the semiconductor to the metal, enhancing efficient charge separation. Thus, manipulating the metal contact with a specific facet of a semiconductor will result in a pronounced effect on the variable interface charge kinetics.^[14,16] Therefore, selectively assembling a metallic electron mediator with a specific facet of a semiconductor in a Z-scheme photocatalytic system is an effective strategy to swiftly transfer electrons and effectively suppress reverse electron transfer, enhancing the spatial charge separation in the two photosystems.

Here, for the first time, we constructed an efficient electronmigration pathway in a ternary BiVO₄-Au-Cu₂O heterostructure by anchoring an Au-Cu2O composite configuration onto the $\{010\}$ facet of a BiVO₄ truncated octahedron through a step-by-step synthetic route. The synthesized BiVO₄{010}-Au-Cu₂O allows inert BiVO₄ and Cu₂O to be activated and exhibits increased CO₂ reduction activity, i.e., three and five times greater than that of BiVO₄{110}-Au-Cu₂O and BiVO₄{010}-Cu₂O, respectively. BiVO₄{010}-Au-Cu₂O simultaneously shows excellent stability under prolonged irradiation due to inhibited photocorrosion in Cu₂O. Single-particle and time-resolved photoluminescence (PL) spectroscopy analyses and theoretical calculations revealed that a desirable Schottky junction forms at the interface between the BiVO4 {010} facet and Au. The photoexcited electrons in the BiVO₄ {010} facet can tunnel through the Schottky barrier and directionally recombine with photogenerated holes in Cu₂O, leaving long-lived holes in the VB of BiVO₄ and longlived electrons in the CB of Cu₂O to increase photocatalysis.

2. Results and Discussion

2.1. Synthesis and Characterization of the Z-Scheme Photocatalysts

The facet-dependent Z-scheme $BiVO_4\mbox{-}Au\mbox{-}Cu_2O$ heterostructures were synthesized as illustrated schematically in Figure 1a

and described in detail in the Experimental Section. Briefly, $BiVO_4$ truncated octahedron with coexposed {010} and {110} facets was prepared via a solid-liquid state reaction.^[21] Au nanoparticles were selectively deposited on the surfaces of {010} BiVO₄ through a photoreduction method using HAuCl₄·4H₂O as a precursor because photogenerated electrons mostly accumulate on the $\{010\}$ surface of BiVO₄. To obtain BiVO₄ $\{110\}$ -Au, Au⁴⁺ was reduced into Au particles on the electron-deficient $BiVO_4$ {110} facets because the $BiVO_4$ {010} facets were coated by a polyvinyl pyrrolidone (PVP) insulating layer to hinder the reduction of Au4+. A hemispherical Cu2O shell layer was subsequently coated on the Au nanoparticles by a facile aqueous solution approach.^[22,23] The X-ray diffraction (XRD) patterns of these as-prepared BiVO4-based samples exhibited all the identified peaks of BiVO4 crystals, which were indexed to single-phase, monoclinic BiVO₄ (JCPDS NO.14-0688). A visible diffraction peak with $2\theta = 38.2^{\circ}$ was observed for both BiVO₄-Au and BiVO₄-Au-Cu₂O materials, indicating that Au particles were successfully deposited on the BiVO₄ surfaces. The weak diffraction peak of Cu₂O was apparent (JCPDS NO.65-3288), indicating Cu₂O was effectively coated onto the BiVO₄ and BiVO₄-Au crystals (Figure 1b).

The microstructures and morphologies of the as-prepared samples were examined by field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) observations. As shown in Figure 1c-e and Figure S1 (Supporting Information), truncated octahedron-shaped BiVO₄ crystals with a length of $\approx 1 \ \mu m$ and a smooth surface are symmetrically enclosed by the {010} and {110} facets. After photoreduction Au deposition, Au particles (30-60 nm) were evenly distributed on the $\{010\}$ facets of BiVO₄, and the $\{110\}$ facets remained clear, implying that the electrons mostly accumulate on the {010} facet under irradiation. In contrast, Au particles with similar sizes were mainly deposited on the {110} facet when PVP surfactant was preadsorbed on the {010} facet, resulting in Au4+ ions being captured only by electrons from the {110} facets. Figure 1f,g shows that epitaxial Cu₂O prefers to anchor on the Au surface to establish hemispherical, core-shell Au-Cu₂O on the BiVO₄ {010} and {110} facets, respectively. Further observations by TEM indicated that the Cu₂O shell with a thickness of \approx 200 nm is tightly coated on the Au particle surface. In addition, the high-resolution TEM (HRTEM) images show that the lattice fringe spacing of the shell is 0.290 nm, which can be assigned to the lattice pitch of the Cu₂O (110) atomic plane (Figure 1h).^[24] Figure 1i shows the elemental mapping for the Au-Cu₂O core-shell structure, further revealing the spatial distribution of Bi, Au, Cu, and O in BiVO₄-Au-Cu₂O. As a reference, the BiVO₄{010}-Cu₂O heterostructure (Figure S2, Supporting Information) and Cu₂O particles were also synthesized through a photoreduction route using CuCl₂ as the precursor. The compositions of various BiVO₄-based samples were further confirmed by X-ray photoelectron spectroscopy (XPS) analyses (Figure S3, Supporting Information). UV-vis absorption measurements (Figure S4, Supporting Information) showed that the similar visible-light absorption of BiVO₄{010}-Au and BiVO₄{110}-Au was broader relative to that of the pristine BiVO₄ crystal, which was ascribed to localized surface plasmon resonance absorption from the Au particles.^[5,25] Moreover, the absorption spectrum of BiVO₄





Figure 1. a) Schematic illustration of the synthetic process for the BiVO₄-based heterostructures. b) XRD patterns of the as-prepared samples. SEM images of the as-synthesized c) BiVO₄ truncated octahedron, d) BiVO₄{010}–Au, e) BiVO₄{110}–Au, f) BiVO₄{010}–Au₋Cu₂O, and g) BiVO₄{110}–Au₋Cu₂O. h) TEM and i) elemental mapping images of the Au₋Cu₂O core-shell heterostructure, and the corresponding HRTEM image is shown in the inset of (h).

{010}–Cu₂O improved after the deposition of Cu₂O on the BiVO₄ surface, which was due to the characteristic absorption of Cu₂O. Obviously, the surface plasmon resonance absorption of Au particles and the hybrid absorption of Cu₂O and BiVO₄ were incorporated into absorption spectrum of the BiVO₄–Au–Cu₂O composite. A visible absorption peak at 750 nm in the UV–vis absorption spectrum of Cu₂O results from the narrowband gap absorption of CuO.^[26] An XPS analysis (Figure S5, Supporting Information) showed that a Cu⁺ oxidation state with a binding energy of 952.3 eV for Cu 2p1/2 existed on the surface of Cu₂O, which indicated that a small amount of amorphous CuO formed on the Cu₂O due to inevitable surface oxidation.

2.2. Photocatalytic CO₂ Reduction

According to the valence band XPS and UV–vis diffuse reflectance spectra (Figure S6, Supporting Information), the CB and VB positions in $BiVO_4$ and Cu_2O were estimated to be -0.1 and 2.43 eV and -1.65 and 0.35 eV, respectively. This result suggested the weak electron reduction ability of the $BiVO_4$ CB and

the weak hole oxidation ability of the Cu₂O VB, which result in the inert photocatalytic activities of BiVO₄ and Cu₂O even when their surfaces are modified with Au particles.^[6,8,9,27] The photocatalytic activities of these as-synthesized BiVO₄-based samples were then investigated for CO₂ photoreduction under visiblelight illumination ($\lambda \ge 420$ nm). As seen in **Table 1**, BiVO₄, Cu₂O, BiVO₄[010]–Au, and BiVO₄[110]–Au exhibited no or slight photocatalytic activities for CO₂ reduction. CH₄ and CO evolved over the Cu₂O catalyst, which was in good agreement with a previous report on the generation of various products over Cu-based catalysts.^[27] The heterostructure BiVO₄[010]– Cu₂O composite created by coating Cu₂O on the BiVO₄[010] facet obviously had a significant enhancement in CH₄ and CO evolution.

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Under irradiation, if the BiVO₄{010}–Cu₂O composites conform to traditional type-II heterojunction band alignment (**Figure 2**a), the photoinduced holes in the VB of BiVO₄ will transfer to the VB of Cu₂O, and electrons will flow through their CBs in the reverse direction, leading to poor photocatalytic performance of the heterostructures because the accumulated electron reduction level in the CB of BiVO₄ is insufficient for CO₂ photoreduction. However, the significant increase in CH₄

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Entry ^{a)}	PS I	Electron mediator	PS II	Activity [µmol h¹ g⁻¹]		AQE ^{b)}
				CH ₄	СО	
1	BiVO ₄	-	_	-	_	-
2	-	-	Cu ₂ O	0.03	0.02	-
3	BiVO ₄ {010}	Au	_	0.04	_	-
4	BiVO ₄ {110}	Au	_	0.04	_	-
5	BiVO ₄ {110}	Au	Cu ₂ O	1.22	1.12	0.38
6	BiVO ₄ {010}	Au	Cu ₂ O	3.14	2.02	0.43
7	BiVO ₄ {010}	-	Cu ₂ O	0.59	0.45	0.32
8	BiVO₄{010}	Au	Cu ₂ O–Au	3.15	2.08	0.44

Table 1. Photocatalytic CO₂ reduction tests of the BiVO₄-based Z-scheme photocatalysis systems under visible-light irradiation.

^{a)}Conditions: photocatalyst (0.1 g); light source, 300 W Xe lamp with a cut-off filter ($\lambda \ge 420$ nm); top-irradiation cell with a Pyrex window; ^{b)}Apparent quantum efficiency (AQE) for the BiVO₄-based heterostructures irradiated under 500 nm monochromatic light.

and CO generation implied that the charge-transfer process between Cu₂O and BiVO₄ is not a type-II heterojunction band alignment. A reasonable Z-scheme charge-transfer route is that the photogenerated electrons in the CB of BiVO₄ transfer to the contact interface and recombine with holes in the VB of Cu₂O (Figure 2b), leading to long-lived holes and electrons in the VB of BiVO₄ and CB of Cu₂O, respectively. This charge-transfer process is beneficial for both enhancing the charge-separation efficiency and maintaining the strong redox ability of the photocatalysts. The CO₂ reduction experiment performed in the dark or in the absence of a photocatalyst resulted in no detected products, which indicated that the CO₂ reduction process with the photocatalyst is driven by light. Both CH₄ and CO were detected over the Cu₂O or Cu₂O-containing composite catalysts, which may imply that CO₂ reduction occurs on the surface of Cu₂O.

The CH₄ and CO generation rates over BiVO₄[010]–Au– Cu₂O were \approx 5.3 and 4.5 times higher, respectively, than those over BiVO₄[010]–Cu₂O, demonstrating that Au particles offer effective channels as electron shuttles to promote high-mobility directional electron migration between BiVO₄ and Cu₂O (entries 6 and 7 in Table 1). To further prove the Z-scheme transfer mechanisms, the oxidation and reduction activities of holes and electrons in the BiVO₄–Au–Cu₂O heterostructures were investigated by PL detection with the assistance of scavengers. Using terephthalic acid as a probe molecule, a single-particle PL technique can effectively detect •OH in solution since •OH easily reacts with terephthalic acid to produce 2-hydroxyterephthalic acid, a fluorescent product with a PL peak at 425 nm.^[28,29] In aqueous solutions, •OH, the primary oxidant, is generated via direct hole oxidation^[30] or photogenerated electron-induced multistep reduction of O_2 (O_2 + $e^- \rightarrow \bullet O_2, \ \bullet O_2 + e^- + 2H^+ \rightarrow H_2O_2, \ H_2O_2 + e^- \rightarrow \bullet OH + OH^-).^{[31]}$ As seen in Figure S7a,b (Supporting Information), when Ethylenediaminetetraacetic acid disodium salt (EDTA-Na₂) was used as an efficient hole scavenger, no •OH formed on BiVO₄, implying that •OH cannot be generated by a multistep reduction of O₂ because the CB potential of BiVO₄ is probably more positive than that of the $O_2/\bullet O_2^-$ couple (-0.046 V vs NHE).^[32] However, in the presence of EDTA-Na₂, PL signals were detected at 425 nm for Cu₂O, BiVO₄{010}-Cu₂O and BiVO₄{010}–Au–Cu₂O, and the PL intensity followed the order of $BiVO_4\{010\}$ -Au-Cu₂O > $BiVO_4\{010\}$ -Cu₂O > Cu₂O. This result shows that the electron potential of the Cu₂O CB is sufficiently negative to reduce O_2 into O_2^- , generating OH by a multistep reduction of O₂. Similarly, when *p*-benzoquinone was used as an electron scavenger, Cu₂O did not exhibit a PL



Figure 2. A scheme to describe the possible charge-transfer mechanism between BiVO₄ and Cu₂O. a) Type-II heterojunction and b) Z-scheme system.

signal since the VB potential of Cu₂O is more negative than the E° of the •OH /H₂O couple (2.38 V vs NHE).^[32] The PL peak intensity followed the order of BiVO₄{010}–Au–Cu₂O > BiVO₄{010}–Cu₂O > BiVO₄ (Figure S7c,d, Supporting Information), confirming efficient charge separation by Au and that the holes on the BiVO₄ VB are positive enough to oxidize H₂O into •OH. These results indicated that Au acts as a carrier mediator to promote electron migration between BiVO₄ and Cu₂O via the Z-scheme mechanism. Indeed, BiVO₄{010}–Au–Cu₂O possessed the highest photoreduced activity (entries 5 and 6 in Table 1), which is 2.6 and 1.8 times higher for CH₄ and CO, respectively, than those of BiVO₄{110}–Au-Cu₂O. Thus, deliberately coating Au–Cu₂O onto the different facets of BiVO₄ may potentially be responsible for the unusual enhancement in the photocatalytic performance of BiVO₄ {010}–Au–Cu₂O.

The amount of CO₂ physically adsorbed on BiVO₄{010}-Au-Cu2O, BiVO4{110}-Au-Cu2O, BiVO4{010}-Cu2O, and BiVO₄ was evaluated by the Brunauer-Emmett-Teller (BET) method to be 1.35, 1.18, 1.02, and 0.91 mg g^{-1} , respectively. The amounts of CO₂ adsorbed on these samples were normalized by the specific surface areas to be 0.41-0.43 mg m⁻². Thus, the CO₂ adsorption, which was nearly the same for all samples, did not induce the difference in the CO₂ photoreduction activity (Figures S8 and S9 and Table S1, Supporting Information). Transient photocurrent response measurements showed that the current density on the BiVO₄{010}-Au-Cu₂O electrode was obviously higher than that on the BiVO₄{110}-Au-Cu₂O or $BiVO_4{010}-Cu_2O$ electrode, implying a higher separation efficiency of photoexcited electron-hole pairs in the BiVO₄{010}-Au-Cu₂O sample (Figure S10, Supporting Information). The CO₂ photoreduction apparent quantum efficiency (AQE) was measured with monochromatic light at 500 nm and calculated according to the following equation (1):

$$AQE = \frac{8 \times \text{number of } CH_4 \text{ molecules} + 2 \times \text{number of CO molecules}}{\text{numeber of incident photons}} \times 100\%$$
(1)

The AQE of Z-scheme heterostructure BiVO₄[010]–Au–Cu₂O, BiVO₄[110]–Au–Cu₂O, and BiVO₄[010]–Cu₂O was 0.43, 0.38, and 0.32, respectively, at 500 nm. The same trend of the AQE and photocatalytic activities suggested that the CO₂ reduction reaction was a result of the light-driven catalytic reaction. BiVO₄[010]–Au–Cu₂O exhibited superior photoreduction activities, indicating that preferentially coating Au–Cu₂O onto the BiVO₄ {010} crystal facet may have a strong positive association with its excellent interparticle charge-transfer ability.

2.3. Experimental Evidence for Electron Transfer by Schottky Junction

To investigate the interface-related dynamics of charge carriers, a single-particle PL technique was employed to study PL intensity changes on BiVO₄ crystal facets coated with Au, Cu₂O, or Au–Cu₂O. As shown in **Figure 3**a, a broad PL band (550–800 nm) with a peak at 680 nm was observed on BiVO₄ and can be assigned to radiative recombination of photogenerated charges trapped by crystal defects.^[33] The similar, quenched characteristic PL peaks suggested that all the BiVO₄-based composite

catalysts exhibited the same radiative PL processes. The PL intensity followed the order of $BiVO_4 > BiVO_4 \{010\}-Cu_2O >$ $BiVO_{4}{011}-Au > BiVO_{4}{010}-Au > BiVO_{4}{110}-Au-Cu_{2}O >$ BiVO₄{010}-Au-Cu₂O, confirming that Au and/or Cu₂O modification enhanced the charge-separation efficiency. Direct observation of the change in the PL intensity on BiVO₄ crystal facets (see squares enclosed by broken lines in Figure 3b-h) was carried out to further understand the charge behavior. Figure 3b shows a typical PL image of a BiVO₄ decahedron under irradiation from a 488 nm laser. The slightly inhomogeneous distribution of the PL intensity on the crystal indicated the spatial variation of the emission sites, which was ascribed to the intrinsic anisotropic distribution of charges on the BiVO₄ crystal facets. When Au particles were selectively deposited on {010} or {110} facets, apparent fluorescence quenching phenomena were observed (Figure 3c,d) under the same experimental conditions, revealing that the PL intensity of the BiVO₄ {110} facet on the BiVO₄{010}-Au catalyst is weaker than that of the BiVO₄ {010} facet on the BiVO₄{110}-Au catalyst. The decreased PL intensities can be ascribed to the injection of photogenerated electrons from BiVO₄ to Au particles prior to electron-hole pair capture by trapping sites, effectively suppressing radiative charge recombination. By coating Cu₂O on the Au particles, the PL intensities of the BiVO₄ {110} facet on BiVO₄{010}-Au-Cu₂O and the BiVO₄ {010} facet on BiVO₄{110}-Au-Cu₂O further decreased but retained the order of $BiVO_4{110} > BiVO_4{010}$ (Figure 3f,g). No distinct fluorescence signals were found in the PL image of Cu₂O particles, indicating that the detected PL signals were all from BiVO₄ (Figure 3e). These results demonstrated that electrons migrating to the Au surface were instantly consumed by the holes from Cu2O, which reduced their chance of returning to the BiVO₄ trapping sites. On the other hand, the PL intensity of the BiVO₄{110} facet on BiVO₄{010}-Cu₂O showed only a small decline, suggesting that the embedded Au particles primarily contribute to charge transfer at the interface between BiVO₄ and Cu₂O (Figure 3h). Given the significant distinction in PL quenching between {110} and {010} facets, the electrontransfer efficiency from BiVO4 to Au heavily relies on variation of the contact interfaces.

To acquire more information about this optical response, we measured the PL decay profiles of various BiVO₄-based photocatalysts. As seen in Figure 3i, the PL decay curves of these samples were mathematically fitted by a biexponential model (see the Supporting Information for details). In the inset table in Figure 3i, the short-lifetime component (τ_1) is attributed to nonradiative recombination of free-excitons with surface defects, and the long-lifetime component (τ_2) is assigned to the radiative pathway from photogenerated electron and hole recombination.^[5,34] Relative to that of pristine BiVO₄ $(\tau_2 = 0.43 \text{ ns})$, the transient PL decay traces of BiVO₄{010}-Cu₂O and BiVO₄[010]–Au revealed the PL lifetimes (τ_2) increased to ≈0.65 ns and ≈0.87 ns, respectively, suggesting that the photogenerated electrons in the CB of BiVO4 more easily transferred to Au than directly transferring to Cu₂O. Additionally, the PL lifetime (τ_2) of BiVO₄{010}–Au–Cu₂O further increased to ≈ 1.0 ns, indicating that electrons from BiVO₄ depleting Cu₂O holes limits charge recombination opportunities and results in a longer electron survival time in BiVO₄.



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Figure 3. a) Steady-state photoluminescence spectra of the as-prepared samples determined for individual BiVO₄ crystals under 488 nm laser irradiation. Single-particle fluorescence imaging on b) BiVO₄ single-crystal particles, c) BiVO₄ {010}–Au, d) BiVO₄ {110}–Au, e) Cu₂O, f) BiVO₄ {010}–Au–Cu₂O, g) BiVO₄ {100}–Au–Cu₂O, and h) BiVO₄ {010}–Cu₂O. Scale bars are 1 μ m. i) PL decay traces of the as-prepared samples and their corresponding fluorescence lifetimes are shown in the inset of Figure 2i (BiVO₄, Au and Cu₂O are denoted as B, A, and C, respectively).

The lifetime component (τ_2) for the BiVO₄[010] interfacerelated heterostructures modified with Au and Au–Cu₂O is 0.87 and 1.0 ns, respectively. These lifetimes are both longer than those for the corresponding configurations established on the BiVO₄[110] crystal facet, which implies that the fabricated BiVO₄[010]–Au interface may accelerate photoexcited electron transfer from BiVO₄ to Au, prolonging the carrier lifetime. Electrochemical impedance spectroscopy (EIS) measurements under irradiation showed an obvious decrease in the semicircle diameters of BiVO₄[010]–Au and BiVO₄[010]–Au–Cu₂O compared with those of BiVO₄[110]–Au and BiVO₄[110]–Au–Cu₂O (Figure S11, Supporting Information), suggesting that the BiVO₄[010]–Au interface has better electrical conductivity.

The surface band alignment of a semiconductor-metalsemiconductor hybrid structure is the dominant factor that determines the interfacial dynamic behavior of photogenerated carriers across the heterointerface. To acquire insight into this issue, slab models of BiVO₄ {010} and {110} surfaces were constructed, and their electronic structures were calculated by firstprinciples simulations (Figure S12, Supporting Information). As shown in Figure S13 (Supporting Information), the surface potential analysis shows that the work functions of the {110} and {010} surfaces are ≈5.51 and 4.24 eV, respectively, which can be ascribed to their inherent variation in atomic coordination. Given that the Fermi level position of bulk BiVO4, an n-type semiconductor, is near the CB, the surface band naturally bends upward for thermodynamic equilibrium. The band bending of the {110} facet is obviously higher than that of the {010} facet owing to its high work function; i.e., a more pronounced built-in electric field exists beneath the {110} facet and drives the accumulation of spatial holes and electrons on the {110} and {010} surfaces, respectively. This result agrees with previous reports using surface photovoltage or photodeposition investigations.^[14,15] Upon understanding the facet-preferential



Figure 4. Electrostatic potentials for a) $BiVO_4$ [010]–Au and b) $BiVO_4$ [110]–Au interfaces obtained from first-principles calculations. Time course of c) CH₄ and d) CO evolution over $BiVO_4$ -based heterostructures ($BiVO_4$, Au, and Cu_2O are denoted as B, A, and C, respectively) under irradiation from a 300 W Xe lamp with a cut-off filter ($\lambda \ge 420$ nm). e) Cu 2p XPS spectra of $BiVO_4$ -based heterostructures after illumination for 20 h. f) Schematic diagrams illustrating the surface potential positions of $BiVO_4$ [010] and [110] and the Fermi level position of Au.

migration of electrons in BiVO₄, i.e., from the bulk to the surface, we further evaluated the effect of the BiVO₄–Au contact interface on the subsequent transfer of electrons from the BiVO₄ surface to a noble metal. According to the potentials (Figure 4a,b), the potential of Au is ~1.07 eV lower than that of BiVO₄ {010}, which means that a Schottky junction can be constructed at the BiVO₄{010}–Au interface to accelerate photogenerated electron capture and effectively hinder the back transfer of photoexcited, hot electrons trapped by metal. In contrast, an electron diffusion layer rather than a Schottky junction may form at the BiVO₄{110}–Au interface because of the similar work functions of Au and BiVO₄ {110}, resulting in reduced electron migration at this interface.

Eventually, we assessed the electron transport behavior from Au to Cu₂O. Considering that the work function of Cu₂O (4.8 eV) is close to that of Au (5.1 eV),^[12,35] concentration diffusion may be the driving force for electrons in Au recombining with the holes in Cu₂O because the band alignment is relatively flat and does not have the effect of a Schottky junction (Figure S14, Supporting Information). In fact, when equal amounts of Au particles were photodeposited on BiVO₄[010]– Au–Cu₂O (denoted BiVO₄[010]–Au–Cu₂O–Au), the evolution rates of the reduced products only slight increased compared to those of BiVO₄[010]–Au–Cu₂O (entry 8 in Table 1), suggesting that the Au–Cu₂O interface does not have a significant impact on the electron migration. **Figure 4**c,d shows the time course of CO₂ reduction over various samples for 20 h with an evacuation after every 5 h of irradiation. The photocatalytic activity (CO₂ to CH₄ and CO) of BiVO₄[010]–Au–Cu₂O remains almost unchanged after four cycles, whereas BiVO₄[110]–Au–Cu₂O and BiVO₄[010]–Cu₂O only maintain 70% and 52%, respectively, of their initial performance after the fourth cycle.

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XPS analysis was employed to further investigate the surface chemical states of BiVO4 (010)-Cu2O, BiVO4 (010)-Au-Cu₂O, and BiVO₄{110}-Au-Cu₂O after the photoreduction reaction. As shown in Figure 4e, the Cu 2p core-level spectrum exhibited two main peaks, 2p3/2 at 932.6 eV and 2p1/2 at 952.3 eV, suggesting the characteristic +1 oxidation state. Two additional peaks with higher binding energies at 934.6 and 954.5 eV can be ascribed to a higher valence state, i.e., Cu²⁺.^[27,36] Notably, the Cu²⁺ 2p3/2 and 2p1/2 peaks observed for BiVO₄{010}-Au-Cu₂O are obviously weaker than those of BiVO₄{110}-Au-Cu₂O and especially BiVO₄{010}-Cu₂O, implying that the self-oxidization of Cu⁺ to Cu²⁺ was effectively suppressed in BiVO₄{010}-Au-Cu₂O during the photoreduction process. Based on the above results, we concluded that the difficulty of the photoexcited electrons on BiVO₄ crossing the BiVO₄-Au interfaces determines the charge-separation efficiency in Cu₂O and controls the photoreduction activity of the entire Z-scheme system. In BiVO₄{010}-Au-Cu₂O, an efficient electron-transfer channel at the BiVO₄{010}-Au interface was constructed to expedite the electron migration from BiVO₄ to Cu₂O, resulting in a large number of holes in Cu₂O that can be consumed by BiVO₄ electrons. Consequently, the self-oxidation







Scheme 1. Scheme to describe the carrier migration behavior from $BiVO_4$ to Cu_2O with and without Au particles deposited on the different facets of $BiVO_4$.

process (Cu⁺ + h⁺ \rightarrow Cu²⁺) and photogenerated charge recombination are simultaneously suppressed, producing an enhanced stability and better photocatalytic activity. The inferior performances of both BiVO₄{110}–Au–Cu₂O and BiVO₄{010}–Cu₂O illustrate that an available Schottky junction plays a critical role in achieving fast electron migration across an interface in a Z-scheme system (Figure 4f and Scheme 1).

3. Conclusions

In summary, a fantastic crystal-facet-dependent Z-scheme system with BiVO₄{010}-Au-Cu₂O was successfully constructed by directionally anchoring an Au-Cu₂O cell-shell layer onto the $\{010\}$ facet of a BiVO₄ truncated octahedron for the first time, and the system exhibited a significant improvement in CO₂ photoreduction with long-lived activity. The single-particle PL analysis results and theoretical simulations suggested that the formation of a Schottky junction in the BiVO₄{010}-Au interface facilitates the extraction of photogenerated electrons from BiVO4 to Cu2O, which is beneficial for prolonging the survival times of electrons in the CB of Cu₂O and holes in the VB of BiVO₄. This work combines the advantages of surface-induced charge directional distribution and an optimal metal-semiconductor contacted interface to provide a fast electron-transfer channel with activated photocatalytic activity and may provide a new strategy for developing more efficient Z-scheme photocatalysts.

4. Experimental Section

Preparation of BiVO₄ Truncated Octahedron: In a typical synthesis procedure,^[21,37] BiVO₄ truncated octahedron with coexposed {010} and {110} crystal facets was prepared via a simple solid–liquid state reaction. Typically, Bi₂O₃ powder (5 mmol) and V₂O₅ powder (5 mmol) were added to a HNO₃ solution (50 mL, 0.5 M). After ultrasonic dispersion, the mixture was stirred for 96 h at room temperature. The obtained vivid yellow powder was rinsed with deionized water thoroughly and dried at 60 °C for 12 h.

Preparation of $BiVO_4$ {010}-Au, $BiVO_4$ {110}-Au, and $BiVO_4$ {010}- Cu_2O Samples: A photoreduction method was employed to deposit Au

or Cu₂O on the surface of BiVO₄. To synthesize BiVO₄{010}–Au, the as-prepared BiVO₄ powder (0.1 g) and Au precursor (HAuCl₄) with a 3 wt% weight ratio of products to BiVO₄ were mixed in deionized water to obtain 100 mL of a suspension. The suspension was irradiated by a 300 W Xe lamp ($\lambda \ge 420$ nm) with magnetic stirring for 7 h. The obtained products were filtered, washed with deionized water several times, and dried at 60 °C overnight. Using a similar irradiation procedure, BiVO₄{010}–Cu₂O was obtained using an aqueous solution containing BiVO₄ (0.1 g, 100 mL) and CuCl₂ (1.5 mL, 0.1 M). To synthesize BiVO₄{110}–Au, polyvinyl pyrrolidone (PVP) (0.1 g) and BiVO₄ powder (0.1 g) were mixed in deionized water (100 mL). Then, an HAuCl₄ aqueous solution (3 wt%, weight ratio of Au to BiVO₄) was added. The resulting suspension was irradiated by a 300 W Xe lamp with a 420 nm filter for 7 h. The obtained product was filtered, washed with deionized water several times, and dried at 60 °C overnight.

Preparation of BiVO₄[010]-Au-Cu₂O and BiVO₄[110]-Au-Cu₂O Samples: The synthesis of BiVO₄[010]-Au-Cu₂O and BiVO₄[110]-Au-Cu₂O follows the same procedure. Typically, a CuCl₂ aqueous solution (1.5 mL, 0.1 m), sodium dodecyl sulfate (SDS) surfactant (1 g), and BiVO₄[010]-Au or BiVO₄[110]-Au powder (0.05 g) were mixed in deionized water (90 mL). After magnetic stirring for 1 h, a hydroxylamine hydrochloride (NH₂OH·HCl) solution (2.5 mL, 0.2 m) was slowly dropped into the above suspension. After 4 h of stirring, the color of the suspension changed from blue to light brown. The light-brown product was collected by suction filtration, washed with distilled water, and dried at 50 °C under vacuum.

Sample Characterizations: The crystallographic structure of the as-synthesized samples was confirmed with XRD (Rigaku Ultima III) using Cu K α radiation at 40 kV and 40 mA. The morphology and distribution of elements in the products were observed by SEM (Nova NanoSEM 230FEI Co.), TEM (JEM-200CX) and energy-dispersive X-ray spectroscopy (EDS) techniques. Ultraviolet-visible (UV-vis) diffuse reflectance spectra were recorded by a UV-vis spectrophotometer (UV-2550, Shimadzu), and the corresponding absorption spectra were calculated by a Kubelka-Munk equation. The BET surface area was obtained by using a surface area analyzer (Micromeritics Tristar-3000, USA) at the temperature of liquid nitrogen (77 K). The amounts of CO₂ physisorbed on the synthesized samples were evaluated by BET method at the temperature of ice water (273 K). The constituents of the samples were characterized by XPS (Thermo ESCALAB 250). For the single-particle PL measurements, the photoluminescence spectra were recorded on an FLS 980 spectrometer (Edinburgh Instruments, UK). A 488 nm CW laser (Coherent, OBIS 488LS) was employed to excite BiVO₄ and Cu₂O. The emission images were recorded on an electronmultiplying charge-coupled device (EMCCD) camera (Ultra897, Andor Technology) at a rate of 20 frames s^{-1} . A dichroic mirror (Di03-R488, Semrock) and long-pass filter (BLP01-514R, Semrock) were used to



improve the signal-to-noise ratio. All experimental operations were carried out at room temperature. The data were analyzed using the open source image software ImagePro. All the photoluminescence spectra were measured in air unless otherwise noted. The time-resolved fluorescence decay curves of the as-fabricated products were estimated on an FLS 980 spectrometer (Edinburgh Instruments, UK) using a picosecond Ti:Sapphire laser (Mira HP, from Coherent) as the excitation source. The decay profiles of the synthesized products were fitted by a biexponential function of $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where I(t) is the fluorescence intensity at time t, A_1 and A_2 are the preexponential factors, and τ_1 and τ_2 are the lifetimes.

Photocatalytic CO2 Conversion Test: The photocatalytic activity of the as-synthesized samples was estimated based on the photocatalytic reduction of CO₂ under irradiation from a 300 W Xe lamp with a cut-off filter ($\lambda \ge 420$ nm). Typically, the prepared powders (0.1 g) were homogeneously dispersed on a glass reactor with an area of 4.2 cm². The volume of the reaction system was \approx 230 mL. High-purity CO₂ gas (99.999%) was introduced into the reaction system to reach ambient pressure after the system was vacuum-treated several times. Then, 0.4 mL of deionized water was injected into the reaction system as the reducing agent. During irradiation, ≈1 mL of gas was withdrawn from the reaction tank at a given interval and used for the CH₄ concentration analysis by gas chromatography (GC-2014, Shimadzu Corp, Japan). The AQE for CO₂ reduction was measured using the same experimental procedure except a monochromatic bandpass filter (Y50, 500 nm) was employed. The number of photons reaching the catalyst was measured using a spectroradiometer (LS-100, EKO Instruments Co., LTD.). Assuming that the incident photons were completely absorbed by the catalyst, the total number of incident photons at 500 nm was estimated to be 2.36×10^{21} photon h⁻¹.

Theoretical Calculations: All calculations were performed using the Cambridge Series Total Energy Pack (CASTEP) code^[38] employing the ultrasoft pseudopotential, and the exchange and correlation effects were described by PBEsol in a generalized gradient approximation (GGA).^[39] The Monkhorst–Pack scheme K-points grid sampling was set as $3 \times 3 \times 1$ or $5 \times 2 \times 1$ for the irreducible Brillouin zone. The fast Fourier transform grid was set as 36 \times 30 \times 288 or 20 \times 45 \times 540. The Kohn–Sham wave function was extended using an energy cutoff value of 380 eV. The convergence criterion was as follows: maximum force on the atom is 0.01 eV Å $^{-1}$, maximum stress on the atom is 0.02 GPa, maximum atomic displacement is 0.0004 Å, and the maximum energy change per atom is 5×10^{-6} eV. In order to improve the computational accuracy, dipole calibration was applied to all models. Finally, the electronic structure was calculated based on the optimized models. The heterostructure models possess 8 layers of BiVO₄ (96 atoms) and 12 layers of Au (96 atoms). Between the BiVO₄/Au heterostructure slabs, a 20 Å thickness vacuum layer is added to eliminate the mirror-image interaction of 3D periodic boundary conditions. Based on the optimized models, the electron density could be estimated. On the other hand, the energy eigenvalue also could be obtained in the self-consistent field calculation. According to the definition, the Fermi energy is further calculated in the present work.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported primarily by the National Basic Research Program of China (2013CB632404), the National Natural Science Foundation of China (51572121, 21603098, and 21633004), the Natural Science Foundation of Jiangsu Province (BK20151265, BK20151383, and BK20150580), the Postdoctoral Science Foundation of China (2017M611784), and the

Fundamental Research Funds for the Central Universities (021314380133 and 021314380084). The authors are grateful to the High Performance Computing Center (HPCC) of Nanjing University for doing the numerical calculations in this paper on its IBM Blade cluster system.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

charge separation, CO_2 reduction, photocatalysis, Schottky junctions, Z-scheme photocatalysts

Received: February 14, 2018 Revised: May 15, 2018 Published online:

- M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, N. S. Lewis, *Chem. Rev.* 2010, *110*, 6446.
- [2] J. L. White, M. F. Baruch, J. E. PanderIII, Y. Hu, I. C. Fortmeyer, J. E. Park, T. Zhang, K. Liao, J. Gu, Y. Yan, T. W. Shaw, E. Abelev, A. B. Bocarsly, *Chem. Rev.* 2015, *115*, 12888.
- [3] P. Zhou, J. G. Yu, M. Jaroniec, Adv. Mater. 2014, 26, 4920.
- [4] H. J. Li, Y. Zhou, W. G. Tu, J. H. Ye, Z. G. Zou, Adv. Funct. Mater. 2015, 25, 998.
- [5] H. J. Li, Y. Y. Gao, Y. Zhou, F. T. Fan, Q. T. Han, Q. F. Xu, X. Y. Wang, M. Xiao, C. Li, Z. G. Zou, *Nano Lett.* **2016**, *16*, 5547.
- [6] A. Iwase, Y. H. Ng, Y. Ishiguro, A. Kudo, R. Amal, J. Am. Chem. Soc. 2011, 133, 11054.
- [7] H. Tada, T. Mitsui, T. Kiyonaga, T. Akita, K. Tanaka, Nat. Mater. 2006, 5, 782.
- [8] Q. Wang, T. Hisatomi, Q. X. Jia, H. Tokudome, M. Zhong, C. Z. Wang, Z. H. Pan, T. Takata, M. Nakabayashi, N. Shibata, Y. B. Li, I. D. Sharp, A. Kudo, T. Yamada, K. Domen, *Nat. Mater.* 2016, 15, 611.
- [9] Q. Wang, T. Hisatomi, Y. Suzuki, Z. H. Pan, J. Seo, M. Katayama, T. Minegishi, H. Nishiyama, T. Takata, K. Seki, A. Kudo, T. Yamada, K. Domen, J. Am. Chem. Soc. 2017, 139, 1675.
- [10] S. J. Moniz, S. A. Shevlin, D. J. Martin, Z. X. Guo, J. W. Tang, Energy Environ. Sci. 2015, 8, 731.
- [11] M. R. Khan, T. W. Chuan, A. Yousuf, M. N. Chowdhury, C. K. Cheng, *Catal. Sci. Technol.* **2015**, *5*, 2522.
- [12] L. L. Wang, J. Ge, A. L. Wang, M. S. Deng, X. J. Wang, S. Bai, R. Li, J. Jiang, Q. Zhang, Y. Luo, Y. J. Xiong, *Angew. Chem.*, Int. Ed. 2014, 53, 5107.
- [13] M. G. Kibria, S. Zhao, F. A. Chowdhury, Q. Wang, H. P. T. Nguyen, M. L. Trudeau, H. Gu, Z. Mi, *Nat. Commun.* **2014**, *5*, 3825.
- [14] R. G. Li, F. X. Zhang, D. Wang, J. X. Yang, M. R. Li, J. Zhu, X. Zhou, H. X. Han, C. Li, *Nat. Commun.* **2013**, *4*, 1432.
- [15] J. Zhu, F. T. Fan, R. T. Chen, H. Y. An, Z. C. Feng, C. Li, Angew. Chem., Int. Ed. 2015, 54, 9111.
- [16] L. C. Mu, Y. Zhao, A. L. Li, S. Y. Wang, Z. L. Wang, J. X. Yang, Y. Wang, T. F. Liu, R. T. Chen, J. Zhu, F. T. Fan, R. G. Li, C. Li, *Energy Environ. Sci.* 2016, *9*, 2463.
- [17] P. Li, Y. Zhou, Z. Y. Zhao, Q. F. Xu, X. Y. Wang, M. Xiao, Z. G. Zou, J. Am. Chem. Soc. 2015, 137, 9547.
- [18] J. Yu, J. Low, W. Xiao, P. Zhou, M. Jaroniec, J. Am. Chem. Soc. 2014, 136, 8839.
- [19] X. Liu, G. Dong, S. Li, G. Lu, Y. Bi, J. Am. Chem. Soc. 2016, 138, 2917.

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- [20] A. G. Scheuermann, J. P. Lawrence, K. W. Kemp, T. Ito, A. Walsh, C. E. D. Chidsey, P. K. Hurley, P. C. McIntyre. *Nat. Mater.* 2016, 15, 99
- [21] H. L. Tan, X. M. Wen, R. Amal, Y. H. Ng, J. Phys. Chem. Lett. 2016, 7, 1400.
- [22] C. H. Kuo, T. E. Hua, M. H. Huang, J. Am. Chem. Soc. 2009, 131, 17871.
- [23] J. W. Hong, D. H. Wi, S. U. Lee, S. W. Han, J. Am. Chem. Soc. 2016, 138, 15766.
- [24] H. Q. Li, W. S. Hong, Y. M. Cui, X. Y. Hu, S. H. Fan, L. J. Zhu, Mater. Sci. Eng., B 2014, 181, 1.
- [25] S. Y. Bao, Q. F. Wu, S. Z. Chang, B. Z. Tian, J. L. Zhang, Catal. Sci. Technol. 2017, 7, 124.
- [26] Q. B. Zhang, K. L. Zhang, D. G. Xu, G. C. Yang, H. Huang, F. Nie, C. M. Liu, S. H. Yang, Prog. Mater. Sci. 2014, 60, 208.
- [27] J. C. Wang, L. Zhang, W. X. Fang, J. Ren, Y. Y. Li, H. C. Yao, J. S. Wang, Z. J. Li, ACS Appl. Mater. Interfaces 2015, 7, 8631.
- [28] S. F. Chen, Y. G. Yang, W. Liu, J. Hazard. Mater. 2011, 186, 1560.

- [29] K. Ishibashi, A. Fujishima, T. Watanabe, K. Hashimoto, *Electrochem. Commun.* 2000, 2, 207.
- [30] S. H. Yoon, J. Lee, Environ. Sci. Technol. 2005, 39, 9695.
- [31] G. G. Liu, X. Z. Li, J. C. Zhao, S. Horikoshi, H. Hidaka, J. Mol. Catal. A 2000, 153, 221.
- [32] A. J. Bard, R. Parsons, J. Jordan, Standard Potentials in Aqueous Solution, Marcel Dekker, Inc., New York 1985.
- [33] T. Tachikawa, T. Ochi, Y. Kobori, ACS Catal. 2016, 6, 2250.
- [34] A. Tanaka, K. Hashimoto, H. Kominami, J. Am. Chem. Soc. 2014, 136, 586.
- [35] G. B. Murdoch, M. Greiner, M. G. Helander, Z. B. Wang, Z. H. Lu, *Appl. Phys. Lett.* 2008, *93*, 083309.
- [36] F. Du, Q. Y. Chen, Y. H. Wang, J. Phys. Chem. Solids. 2017, 104, 139.
- [37] A. Iwase, H. Kato, A. Kudo, J. Sol. Energy Eng. 2010, 132, 021106.
- [38] S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. J. Probert, K. Refson, M. C. Payne, Z. Kristallogr. 2005, 220, 567.
- [39] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. L. Zhou, K. Burke, *Phys. Rev. Lett.* 2008, 100, 136406.