Unveiling the charge transfer dynamics steered by built-in electric fields in BiOBr photocatalysts

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Construction of internal electric fields (IEFs) is crucial to realize efficient charge separation for charge-induced redox reactions, such as water splitting and CO2 reduction. However, a quantitative understanding of the charge transfer dynamics modulated by IEFs remains elusive. Here, electron microscopy study unveils that the non-equilibrium photo-excited electrons are collectively steered by two contiguous IEFs within binary (001)/(200) facet junctions of BiOBr platelets, and they exhibit characteristic Gaussian distribution profiles on reduction facets by using metal co-catalysts as probes. An analytical model justifies the Gaussian curve and allows us to measure the diffusion length and drift distance of electrons. The charge separation efficiency, as well as photocatalytic performances, are maximized when the platelet size is about twice the drift distance, either by tailoring particle dimensions or tuning IEF-dependent drift distances. The work offers great flexibility for precisely constructing high-performance particulate photocatalysts by understanding charge transfer dynamics.
Solar-driven photocatalytic reactions offer great promises for environmental remediation and renewable energy generation by converting inexhaustible solar energy into clean and environmentally benign fuels. Generally, three major steps are involved in photocatalytic reactions: (1) excitation of electron-hole pairs within a particulate semiconductor; (2) migration of charge carriers to the catalyst surface; and (3) surface redox reactions. Photocatalytic systems often suffer from poor solar energy conversion efficiency because of the intrinsically strong propensity of charge carrier recombination in the second step. Therefore, it is imperative to develop strategies to manipulate carrier migration with great controllability to inhibit carrier recombination. The construction of internal electric field (IEF) by surface tailoring and interface engineering approaches, including co-catalyst loading, phase junctions, and facet junctions, could precisely manipulate the migration of photo-generated electrons (e\textsuperscript{-}) and holes (h\textsuperscript{+}) to spatially separated reductive and oxidative sites, thereby enhancing the photocatalytic performance.

Knowledge of the charge migration properties, including the diffusion length and the IEF-dictated drift distance of non-equilibrium charge carriers, guides the rational design of particulate photocatalysts. Charge transport behavior in semiconductors is typically characterized by transient absorption, photoluminescence-quenching measurements, and electrical characterization, where the diffusion constants and lifetimes of photogenerated charge carriers could be determined. However, these measurements were only applicable to thin-film electrodes with external electric fields, which differs from the carrier diffusion dynamics modulated by IEF produced at the semiconductor-liquid interface for power photocatalysts in the solvent. A comprehensive understanding of the collective migration of photo-excited non-equilibrium carriers steered by IEFs at the semiconductor/solution or semiconductor/co-catalyst interfaces still remains unexplored.

Bismuth oxyhalide (BIOX, X = Cl, Br, I) photocatalysts have attracted widespread attention due to their unique layered structure consisting of fluoride-like [Bi\textsubscript{2}O\textsubscript{2}Cl\textsubscript{2}] units sandwiched by two [X\textsuperscript{-}] slabs. The strong intralayer covalent bonding along with the 2D layer and the weak interlayer van der Waals interaction perpendicular to the 2D layer gives rise to a lamellar growth habit, which endows them with anisotropic carrier transfer properties. It was reported that the anisotropic facets can drive photo-generated electrons and holes to [001] reductive and [110] oxidative sites, forming a [001]/[110] binary facet junction in the BiOBr platelets. Herein, we take advantage of the well-defined morphology of BiOBr platelets and the cascade binary junctions to track the anisotropic carrier transport dynamics steered by IEFs, using metal and oxide nanoparticles as reduction and oxidation probes. Two contiguous IEFs at the [001] facet/solution and [200] facet/solution junctions could efficiently guide electrons and holes to [001] and [200] surfaces, respectively. The spatial distribution of photo-deposited metal nanoparticles is found to exhibit a characteristic Gaussian curve. An analytical model, modified from the Haynes-Shockley model, satisfactorily explains the Gaussian curve and allows us to identify two important parameters, including the drift distance of electrons influenced by IEFs and the diffusion length of electrons, which is useful for the rational design of BiOBr platelets with promoted photocatalytic efficiency. The overall photocatalytic performance is optimized either by tailoring particle sizes or regulating IEF-relevant drift distances of electrons, when the platelet size is about twice the drift distance. Our study demonstrates the capacity of a full utilization of solar energy by precisely guiding a unidirectional and steady charge flow. Our findings propose a conceptual strategy to measure charge carrier transport modulated by IEFs, which could be extended to a broad spectrum of particulate photocatalytic systems, especially in nanocomposites containing heterogeneous interfaces with IEFs, deepening insights into the intrinsic transport properties of charge carriers in semiconductor photocatalysts.

Results

Synthesis of well-defined BiOBr platelets enclosed by anisotropic facets. BiOBr photocatalysts were synthesized by a hydrothermal method (see Method section for details). X-ray diffraction (XRD) pattern (Fig. 1a) of platelets is ascribed to a tetragonal phase of BiOBr (PDF #09–0393). Energy-dispersive X-ray spectroscopy (EDS) maps reveal the homogeneous distribution of Bi, O, and Br elements within platelets (Fig. 1b). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images show that the BiOBr platelets exhibit well-defined square morphology, with a mean lateral size and thickness of 2.5 \( \mu \text{m} \) and 110 nm, respectively.

Fig. 1 Microscopic characterization of BiOBr platelets. a XRD pattern, b EDS maps, c SEM morphology (inset: statistical histogram of the lateral size distributions of BiOBr platelets), d TEM image of BiOBr platelets. A typical selected-area electron diffraction (SAED) pattern of BiOBr platelets is given in the inset. e Enlarged HRTEM image recorded at the edge of a platelet. f Schematic diagram depicting the crystal habit of BiOBr platelets. Source data are provided as a Source Data file.
HAADF image recorded at Edge 1 of crosses. Right panel: Their positions are plotted in a coordinate system. Edge 1 or edge 2, which can be described by a Gaussian profile. The centers of Ag nanoparticles are marked by purple crosses. Right panel: Their positions are plotted in a coordinate system. Statistical histograms of the distances from the centers of Ag nanoparticles to edge 1 or edge 2, which can be described by a Gaussian profile. The centers of Ag nanoparticles are marked by purple crosses. Right panel: their positions are plotted in a coordinate system.

**Fig. 2 Anisotropic charge separation behavior.** a Low magnification, expanded TEM images showing the aggregation of Ag nanoparticles on the (001) basal facets, with a schematic diagram given in the bottom left panel (inset: EDS map). b Left panel: HAADF image recorded at Edge 1 of c showing the aggregation of Ag nanoparticles in a line pattern. The centers of Ag nanoparticles are marked by purple crosses. Right panel: Their positions are plotted in a coordinate system. e Statistical analysis of the spatial distribution of Ag nanoparticles with respect to the platelet edges after counting more than 50 individual BiOBr platelets from multiple TEM images. Source data are provided as a Source Data file.

Intrinsically facet-dependent carrier separation behavior. To investigate the carrier separation nature, photo-deposition of CoOx (as hole probes) and Ag (as electron probes) co-catalysts were employed to identify the oxidation and reduction reactive facets, respectively. High-resolution electron microscopy (HREM) imaging was performed at the platelet edge (Fig. 1e), demonstrating that the side faces are terminated by (200) and (020) planes. These results combined indicate that BiOBr crystals are enclosed by two large (001) facets as the basal planes and four identical (200) planes being the side faces, as illustrated in Fig. 1f.

 Carrier diffusion pathway modulated by lateral IEFs. The IEF exerts an electric force to the carriers, which influences the migration and modulates their spatial distribution in the same direction. The unique platelet geometry enables us to probe the effect of lateral IEFs on the lateral migration dynamics of Ag nanoparticles.
electrons by tracking the spatial distribution of metal particles on [001] facets. A widely employed approach, i.e., the photo-deposition of metal oxide co-catalysts (CoOx and MnOx) on the [200] side faces, was applied to simulate IEFs with varied strengths, and photo-deposited Ag, Pt, and Au nanoparticles were used as probes to track the dynamic migration of photo-excited electrons steered by lateral IEFs (Fig. 3a). Those samples are named after the photo-deposition sequence, such as CoOx-Ag, CoOx-Pt, and CoOx-Au pairs. Extensive TEM imaging and EDS mapping were performed. Metal nanoparticles (Ag, Pt, and Au) line up on the (001) facets (Fig. 3b-d). Statistical analysis (Fig. 3e and Table 1) indicates that the spatial distribution of all the experimental batches exhibits a characteristic feature in terms of a Gaussian profile. This also holds for the MnOx-Ag, Pt, and Au system (Supplementary Fig. 5 and Supplementary Table 1).

Experiments were designed to elucidate the influence of IEF strength on the spatial distribution of Pt nanoparticles by varying the pH values of the solution, such as Pt(pH = 7)/BiOBr, Pt(pH = 4)/BiOBr, and Pt(pH = 1)/BiOBr pairs. TEM, HAADF images, and statistical analysis (Supplementary Fig. 6a–c) reveal that the photo-deposited Pt nanoparticles still follow the similar Gaussian distribution profile (Supplementary Fig. 6d and Supplementary Table 1). More importantly, the positions of Gaussian centers shift to the right as pH decreases, establishing a direct correlation between the drift distance of the charge carrier and the IEF strength. Hence, it is the IEF at the semiconductor/solution interface that steers the collective migration of charge carriers via a general mechanism.

Table 1 A summary of the lateral drift distance, diffusion length, and average thickness for several metal nanoparticles/BiOBr photocatalysts groups.

| Batches          | Lateral drift distance (L_{IEF}, nm) | Standard deviation (σ, nm) | Diffusion length (L_e, nm) | Mean thickness (nm) |
|------------------|-------------------------------------|-----------------------------|---------------------------|---------------------|
| Ag/BiOBr-2.5     | 55.7                                | 10.7                        | 7.6                       | 110                 |
| Ag/BiOBr-0.5     | 48.7                                | 10.3                        | 7.3                       | 48                  |
| Ag/BiOBr-0.1     | 51.8                                | 10.5                        | 7.4                       | 40                  |
| CoOx-Ag/BiOBr-2.5| 50.7                                | 10.4                        | 7.4                       | 110                 |
| CoOx-Pt/BiOBr-2.5| 43.7                                | 9.6                         | 6.8                       | 110                 |
| CoOx-Au/BiOBr-2.5| 31.2                                | 10.3                        | 7.3                       | 110                 |

Source data are provided as a Source Data file.

In principle, a change in pH value affects the redox potential of the solution, which in turn modulates the IEF strength at the solution/semiconductor interface. Accordingly, a series of parallel experiments were designed to elucidate the influence of IEF strength on the spatial distribution of Pt nanoparticles by varying the pH values of the solution, such as Pt(pH = 7)/BiOBr, Pt(pH = 4)/BiOBr, and Pt(pH = 1)/BiOBr pairs. TEM, HAADF images, and statistical analysis (Supplementary Fig. 6a–c) reveal that the photo-deposited Pt nanoparticles still follow the similar Gaussian distribution profile (Supplementary Fig. 6d and Supplementary Table 1). More importantly, the positions of Gaussian centers shift to the right as pH decreases, establishing a direct correlation between the drift distance of the charge carrier and the IEF strength. Hence, it is the IEF at the semiconductor/solution interface that steers the collective migration of charge carriers via a general mechanism.

Theoretical modeling of the dynamic migration of photo-generated carrier modulated by IEFs. Theoretical analysis was conducted to understand the origin of IEFs and their influence on the dynamic migration of carriers. As confirmed by the density functional theory (DFT) calculations (the computational methods...
are described in the Method section. The conduction band (CB) and valence band (VB) edge follow the order of (200) > (001) (Fig. 4a). In the context of the experimentally observed facet-dependent carrier separation behavior in (200)/(001) binary platelets, leading to well-matched cascade band structures between the two facets and the bulk (Fig. 4b). This produces two IEFs (horizontal versus vertical), a lateral one pointing left (IEFx), and a vertical one pointing upward (IEFz), which provides the driving forces for the experimentally observed facet-dependent carrier separation behavior.

Now we start to model the effect of IEFs imposed either by metal oxide nanoparticles or solution to carrier migration, with a schematic carrier transfer pathway of BiOBr platelets given in three zones, (1) space charge region on the (200) surface with lateral IEFz, (2) in the bulk, and (3) space charge region on the (001) facet with vertical IEFx (Supplementary Fig. 7). Thus, a {200} > {001} binary facet junction. Two extreme cases are considered here. For a simple Gaussian function with a plateau function (Supplementary Fig. 9b), the standard deviation (σ) is 2 times of the diffusion length of electrons (L_d) defined as

\[ \Delta \tau \propto e^{-rac{(x-\mu_\tau \tau_{1})^2}{4D_\tau \tau_{1}}}. \]

This corresponds to a Gaussian curve (Supplementary Fig. 9b). Then, the electrons drift in the bulk without the influence of IEFz at τ2. Finally, they are spontaneously guided to the (001) facets by the vertical IEFx at \( \tau_3 \). For the last two stages, the lateral spatial distribution of electrons is not shifted due to the absence of lateral IEFx. The electron profile is equivalent to a convolution of Eq. (1) with a Gaussian function after given a drifting time (Supplementary Fig. 9c), as shown in Eq. (2).

Here \( \Delta \tau \) is the overall distribution of electrons, \( \mu_\tau \), \( \tau_{1} \), and \( \tau_{3} \) are the mean value and lifetime of electrons at the space charge region on the (200), two extreme cases are considered here. For a simple case, when the width of a lateral space region (W_{IEFz}) is negligible compared to the diffusion length of electrons, the carrier retains a Gaussian profile. The mathematical fitting of the Gaussian curve gives \( L_{IEFz} \) and \( L_x \) (Supplementary Fig. 10b). Under the circumstance that \( W_{IEFz} \) is comparable or even larger than \( L_x \), the carrier distribution starts to exhibit a plateau feature in
the center while the Gaussian damping feature is preserved at the edge of the plateau (Supplementary Fig. 10c). The center of the peak corresponds to \( L_{IEF} \). However, more sophisticated mathematics analysis needs to be treated to deconvolute \( L_{IEF} \) and \( L_e \). For the carriers produced in the second and third zones, electrons are evenly excited and drift to the (001) facets, leading to a homogeneous distribution profile and contributing to a uniform background to the carrier distribution profile. Hence, it is the modulation of two contiguous IEFs (horizontal versus vertical) that results in a collective migration of carriers exhibiting a distinct Gaussian profile.

As presented in Figs. 2 and 3, for our cases, statistical analysis reveals that the spatial distribution of metal particles has a Gaussian curve without evident plateau, implying that the width of a lateral space charge layer (\( W_{IEF} \)) is small. Hitherto, the lateral drift distance imposed by lateral \( L_{IEF} \) and \( L_e \) is determined in Table 1 and Supplementary Table 1 by fitting Gaussian functions to the spatial distribution of metal nanoparticles (Figs. 2, 3 and Supplementary Figs. 5, 6), which offers important insights into the carrier migration dynamics in BiOBr platelets. First, by using an electron energy loss spectroscopy (EELS) technique\(^{39-61}\), we revealed a weak correlation between charge dynamic and thickness for identical BiOBr-2.5 platelets, implying that a change in thickness of BiOBr platelets has little effect on the charge dynamic (Supplementary Figs. 11–13). Secondly, \( L_{IEF} \), varies as the origin of IEFs changes, consistent with the fact that different solutions or co-catalysts impose varied IEFs in strength. Third, \( L_{IEF} \) existing at the semiconductor/solution interfaces or semiconductor/metal oxides (CoO\(_x\) or MnO\(_x\)) is nearly on the same scale, ranging from 30 to 55 nanometers. It indicates that those IEFs have close electric strength. Fourth, the intrinsic diffusion length for electrons (\( L_e \)) along the [100] direction is estimated at ca. 7 nm, which is independent of the origin and the strength of IEFs. Fifth, by comparing the CoO\(_x\)-Ag, Pt, Au, and MnO\(_x\)-Ag, Pt, Au pairs, one might expect that Ag, Pt, and Au nanoparticles, as probes of photo-generated electrons, might have the same distribution, because the lateral IEFs, provided by CoO\(_x\) or MnO\(_x\) particles does not change. Unexpectedly, the Gaussian center of Pt nanoparticles is about 10 nm closer to the platelet edge than that of Ag nanoparticles. It implies that a change in the status of the solution may affect the space charge regions on both (001) and (200) facets and modify the migration dynamics of electrons. Last but not least, decreasing pH in the solution environment could effectively increase the drift distance. For instance, the drift distance of Pt (pH = 1)/BiOBr is ~19 nm farther away compared to Pt (pH = 7)/BiOBr batch, using the platelet ledge as a reference. It demonstrates that IEFs do play a vital role in dictating the spatial distribution of carriers.

The current methodology described here is extensible to similar systems, e.g., BiOCl platelets (Supplementary Fig. 14) to determine the intrinsic carrier transport properties, such as carrier diffusion length and drift distance imposed by IEFs. Those parameters serve as important guidelines to enhance the quantum efficiency by rational structure optimization, e.g., regulating the size\(^{62}\) and morphology of photocatalysts\(^{56,63}\).

**Structure optimization of BiOBr platelets with enhanced photocatalytic performance.** Structure optimization was performed by tailoring the sizes of BiOBr platelets. Four batches of BiOBr platelets, with a mean lateral size of 2500, 500, 100, and 50 nm denoted as BiOBr-2.5 (Fig. 1c), BiOBr-0.5, BiOBr-0.1, and BiOBr-0.05 (Supplementary Fig. 15) were fabricated. The optical absorption property and different synthetical methods of BiOBr platelets have a minor effect on their charge dynamics and photocatalytic performance (Supplementary Figs. 16–18). Thus, we focused on investigating the effect of lateral sizes on their charge dynamic behavior. Ag nanoparticles could also be photo-deposited on the (001) surface of BiOBr-0.1 and BiOBr-0.5 platelets and their drift distance/diffusion length were measured as 51.8/7.4 and 48.7/7.3 nm, respectively (Supplementary Fig. 19 and

![Fig. 5 The photocatalytic performance of BiOBr platelets with different lateral sizes.](image-url)
BiOBr-0.1 platelets is 92.0 shown in Fig. 5c, d, the photocatalytic oxygen evolution rate of oxidation and Cr(VI) reduction reactions were carried out. As 0.05 > BiOBr-2.5 (Fig.5b), and electronic impedance spectroscopy density revealed that the separation capacity of photogenerated increased was worth noting that, when the lateral size was reduced to 50 nm, the abovementioned characterizations suggest that the charge and the diffusion length of electrons is ca. 7 nm in the BiOBr plates. The distances of carriers steered by IEFs range from about 30 to 55 nm, and charge carrier separation for photocatalytic redox reactions23. (200) oxidation facets are employed as a model system to characterize was employed to investigate their charge separation efficiencies. Photoluminescence (PL) intensity drops sharply as the lateral size decreases at first and the highest charge separation efficiency was achieved when the size was about 100 nm (Fig. 5a). It was worth noting that, when the lateral size was reduced to 50 nm, increased fluorescence intensity was observed, which might be caused by the reduced strength of directional IEFs. In addition, the BiOBr-0.1 photocatalyst exhibited the longest fluorescence lifetime due to its suitable lateral size (Supplementary Fig. 21). The photocatalytic activity characterization was monitored by the separation capacity of photogenerated carriers follows the order of BiOBr-0.1 > BiOBr-0.5 > BiOBr-0.05 > BiOBr-2.5 (Fig. 5b), and electronic impedance spectroscopy (EIS) characterization measurements demonstrated the same trend (Supplementary Fig. 22). Furthermore, the photocatalytic water oxidation and Cr(VI) reduction reactions were carried out. As shown in Fig 5c, d, the photocatalytic oxygen evolution rate of BiOBr-0.1 platelets is 92.0 μmol h⁻¹, which is 16.4 times higher than that of BiOBr-2.5 platelets and the degradation rate of Cr(VI) also increases when the lateral size of BiOBr platelets is 100 nm. Interestingly, as we manipulate the drift distances by adjusting the IEF strengths at varied pH values, the water oxidation evolution performance of Pt-BiOBr-0.1 platelets is further improved (Supplementary Fig. 23). This offers great promise to optimize the performance of photocatalysts by matching the drift distance with fixed particle size, simply via optimizing the reaction conditions, such as pH values.

Discussion

As summarized in Table 1 and Supplementary Table 1, the drift distances of carriers steered by IEFs range from about 30 to 55 nm, and the diffusion length of electrons is ca. 7 nm in the BiOBr platelets. The abovementioned characterizations suggest that the charge separation efficiency, as well as photocatalytic performances, can be maximized when the particle size (~100 nm) is close to twice the drift distance of carriers (LIEF). This serves as a guideline for the rational design of BiOBr platelets. Notably, it is different from previous knowledge that the size of photocatalysts should be two times the width of the space charge region to maximize light absorption and charge carrier separation for photocatalytic redox reactions23.

In the end, we also photo-deposited Ag nanoparticles on the surfaces of BiVO4 photocatalysts with [010]/[110] facet junctions, where Ag nanoparticles segregated on the surfaces in line patterns (Supplementary Fig. 24). However, for WO3, ZnO, CeO2, CdS, and Ta3N5 photocatalysts without spatially separated oxidative surfaces, the distribution of Ag nanoparticles was random (Supplementary Fig. 25). Those facts explicitly suggest that the current methodology to quantitatively analyze the collective charge transfer dynamics modulated by built-in electric fields is mainly applicable to photocatalyst containing photo-reduction and photo-oxidation facet junctions8–10,20, and new strategies should be developed to understand carrier dynamics within semiconductors with single facets in the future.

In summary, BiOBr platelets exposing (001) reduction and (200) oxidation facets are employed as a model system to investigate the carrier transfer pathway modulated by built-in electric fields. The semiconductor/solution or semiconductor/metal-oxide nanoparticle interfaces provide variant IEFs in strength, which are all found to drive the directional migration of photo-excited electrons to the (001) facet with the similar modulation behavior that is characteristic of a Gaussian profile. Theoretical analysis validates the experimentally observed distribution profiles, which allow us to derive the drift distance steered by IEFs and the intrinsic diffusion length of electrons. This work lays a solid theoretical foundation and offers fundamental insights for understanding the charge transfer dynamics modulated by built-in IEFs in particular photocatalysts. Based upon these findings, a significant enhancement of the photocatalytic performance of BiOBr platelets is achieved by matching particle sizes with the drift distances of electrons, unveiling the intrinsic structure-function relationships of photocatalysts.

Methods

preparation of BiOBr platelets. All chemicals are commercially available and used as received. The typical procedure to prepare large BiOBr platelets (BiOBr-2.5): 1 mmol Bi(NO3)3·5H2O was added in 30 mL ethylene glycol (EG), and the solution was stirred for 30 min to completely dissolve (denoted as solution A). Subsequently, 3 mmol KBr was dissolved uniformly in 30 mL deionized water (marked as solution B). Then, solution A was transferred to a 50 mL syringe and 5 mL into solution B (2 mL/min) with magnetic stirring, resulting in the formation of precipitation. The resulting precipitate was centrifuged and washed with deionized water several times. Next, the samples were redispersed in 30 mL deionized water (pH = 1). The solution was sealed in a Teflon-lined autoclave (50 mL) and then hydrothermally treated at 140 °C for 24 h. After cooling to room temperature, the mixture was collected by centrifugation, washed with deionized water, ethanol and dried at 60 °C overnight. The synthesized BiOBr platelets have an average lateral size of about 2.5 μm and are denoted as BiOBr-2.5.

The synthesis method of BiOBr-0.5 platelets: 1 mmol Bi(NO3)3·5H2O was dispersed in 0.1 M mannitol solution (25 mL) with continuous stirring for 30 min to achieve homogeneous dispersion. Then, 1 M KBr aqueous solution (5 mL) was slowly poured into the above-dispersed solution, resulting in a white precipitate. After stirring for 30 min, the resulting solution was heated at 160 °C for 3 h in a Teflon-lined autoclave (50 mL). The products were washed and dried by the same steps described above after cooling to room temperature. The obtained BiOBr platelets with a lateral size of 500 nm are denoted as BiOBr-0.5.

Preparation of BiOBr-0.5-B platelets: 1 mmol of Bi(NO3)3·5H2O was dissolved in ethylene glycol (30 mL, EG) for 30 min (denoted as solution A). Subsequently, 3 mmol KBr was uniformly dispersed in 30 mL of deionized water (marked as solution B). Then, solution A was transferred to a 30 mL syringe and injected into solution B (2 mL/min), producing white suspensions. After the drift distance of carriers by the same steps described above, and the lateral size of them is ca. 500 nm (denoted as BiOBr-0.5-B).

The synthesis method of BiOBr-0.1 platelets: 5 mmol Bi(NO3)3·5H2O and 0.4 M mannitol were dispersed in 30 mL deionized water by magnetic stirring for 30 min (solution A). Subsequently, 10 mmol KBr was dissolved in aqueous solution B (50 mL). Then, at a rate of 2 mL/min, solution A was injected into solution B with continuous stirring. After the precipitate was harvested by centrifugation, washed with distilled water several times. Finally, the precipitate was dispersed in 30 mL deionized water (pH = 1), and sealed in a Teflon-lined autoclave (50 mL) for hydrothermal treatment at 140 °C for 24 h. The products were dried and used for the same steps described above, and the lateral size of them is ca. 100 nm (denoted as BiOBr-0.1-B).

The synthesis method of BiOBr-0.1-B platelets: 1 mL of oleic acid and 0.5 mL of oleylamine (as surfactants) were added into 15 mL of ethylene glycol (EG) dissolved with 1 mmol of Bi(NO3)3·5H2O (denoted as solution A). Subsequently, 3 mmol KBr was dissolved in 14 mL, pH = 1, deionized water (marked as solution B). Then, solution A was transferred to a 50 mL syringe and injected into solution B (2 mL/min). After stirring for 2 h, the solution was sealed in a Teflon-lined autoclave (50 mL) and then hydrothermally treated at 140 °C for 1 h. The products were washed and dried by the same steps described above, and the lateral size of them is ca. 100 nm (denoted as BiOBr-0.1-B).

The synthesis method of BiOBr-0.05 platelets with an average lateral size of 50 nm (BiOBr-0.05): 5 mmol Bi(NO3)3·5H2O was added in 40 mL ethylene glycol (EG), and the mixture was immediately immersed in an ice-water bath for 30 min under continuous stirring (solution A). Then, 5 mmol KBr was dispersed in 40 mL distilled water and rapidly chilled in an ice-water bath for 30 min (solution B). After that, solution B was poured into solution A, and the mixed solution was stirred in an ice-water bath for 1 h, resulting in a white suspension. The samples
were collected by the same steps described in the above procedures and named BiOBr-0.05.

Photo-deposition of metal oxides and/or metals on BiOBr platelets. To photo-deposit CoO or MnOx particles, 50 mg BiOBr powders and a certain content of Co(NO3)2·6H2O or Mn(NO3)2·4H2O (such as 1 wt.%) were mixed in distilled water (100 mL), and the mixture was then illuminated by a 300 W xenon lamp (an irradiation power density of 1.43 W/cm2) under full-spectrum irradiation for 30 min. After that, the suspension was harvested by filtration and washed with distilled water several times. The resulting sample was finally dried at 60 °C overnight.

For photo-reduction of Ag or Pt particles as probes to track photo-generated electrons, 50 mg of BiOBr powders were added in deionized water (100 mL) containing AgNO3 or H2PtCl6·6H2O as the precursor with an aqueous methanol solution (10 vol %), respectively. Subsequently, the suspension was illuminated by full-spectrum irradiation of a xenon lamp (300 W) for 1 or 3 min to get the Ag/BiOBr or Pt/BiOBr pairs, respectively. In addition, Pt nanoparticles were photo-deposited on BiOBr platelets at different pH values (adjusted by dilute nitric acid). We also investigated the effect of IEs on the photo-reduction reactions. First, metal oxide co-catalysts (CoOx or MnOx) were loaded onto BiOBr platelets to simulate a diversity of IEs, using the above-mentioned photo-oxidation approach. Later, Ag, Pt, or Au particles were used as probes to track the dynamic migration of photo-excited electrons by using the precursors of AgNO3, H2PtCl6·6H2O, or HAuCl4·4H2O, following the same procedure described before. Those samples are named after the photo-deposition sequence, including CoOx/Ag/BiOBr, CoOx/Pt/BiOBr, CoOx/Au/BiOBr, MnOx-Ag/BiOBr, MnOx-Pt/BiOBr, MnOx-Au/ BiOBr pairs.

For comparison, CoOx and Ag co-catalysts were also loaded onto BiOBr platelets via a wet impregnation method. The Co(NO3)2·6H2O solution was injected into the solution of BiOBr platelets, stirred, and evaporated to dryness. Finally, the obtained powders were heated to 300 °C in a muffle furnace for 1 h. Similarly, the prepared Ag particles were also added into the solution of BiOBr platelets, stirred, and evaporated to dryness.

The performance test of photocatalytic water oxidation reactions. The performance of photocatalytic water oxidation was evaluated in the presence of a glass platelets, stirred, and evaporated to dryness. The performance test of photocatalytic reduction of Cr(VI) to Cr(III) was maintained at room temperature. The evolved gases were collected and analyzed by online gas chromatography (Shimadzu, GC-8A) equipped with a thermal conductivity detector (TCD) and a molecular sieve column (5 Å) with Argon as the carrier gas.

The performance test of photocatalytic reduction of Cr(VI) to Cr(III). In a typical case, 20 mg photocatalyst was mixed with 80 mL Cr(VI) aqueous solution (40 ppm) in a 100 mL quartz reactor. Then, the reaction was evacuated under a vacuum pump to completely remove the air before irradiation with a 300 W xenon lamp (λ > 300 nm) under the potential of 0.2 V (versus Ag/AgCl). The electronic impedance spectra (EIS) and Nyquist plots were measured for accurate electronic structure calculations55–58. The kinetic energy cut-off of the plane wave basis set was set to 500 eV. The k-points were generated using the Monkhorst-Pack mesh59. The threshold for energy convergence for each iteration was set to 10−6 eV. Geometries were assumed to be converged when forces on each atom were less than 0.005 eV Å−1. The Van der Waals (vdW) interactions were included using optB86b-vdW functionalities60. The 9 × 9 × 4 k-point mesh was used for bulk BiOBr optimization. Both atomic positions and lattice constants were fully optimized within bulk calculation. The optimized lattice parameters of tetragonal BiOBr bulk are a = b = 3.94 Å and c = 8.13 Å, which are in very good agreement with the experimental results61. The slab models with a finite number of BiOBr sublayers were used for surface calculations. To avoid spurious interactions between periodic images, a vacuum layer of 15 Å thickness was added along the surface normal direction. The (001) and (200) surfaces of BiOBr were simulated by using seven and ten layers of BiOBr sublayers, and the k-point meshes of 9 × 9 × 1 and 4 × 10 × 1. During surface calculations, the lattice parameters were fixed and only atoms on the top layers were fully relaxed (Supplementary Fig. 26). Surface band structures were calculated along the special band path connecting the k-space high-symmetry points of G–M–X–G for the (001) surface, and G–X–S–Y–G for the (200) surface. Electrostatic potentials and work functions of the surface slab models were displayed in Supplementary Fig. 7.

Data availability
The authors declare that the data supporting the findings of this study are available in the paper and its supplementary information files. Source data are provided with this paper.

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**Author contributions**

X.W. and Z.Y. conceived the concept and supervised the research. W.X. and R.Y. performed the DFT calculations. Z.L., X.Y., S.Z., and S.X. performed the experimental work. Y.H., C.Y., and J.S. provided experimental suggestions. All authors designed the experiments, analyzed the data, and drafted the manuscript.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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