Photocatalytic reduction on Bi-based p-block semiconductors

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Abstract

With the constant increase in demand for fuel energy, research on the exploration of renewable energy source is becoming significantly critical. Herein, photocatalysis for the direct conversion of solar to chemical energy has attracted tremendous attention. In particular, due to the energy band edges mainly formed by $p$ orbitals or $s$-$p$ hybridized states, resulting in narrow band gaps and highly dispersive band structures, photocatalysts constructed from $p$-block elements exhibit remarkable visible-light photocatalytic activity. Taking bismuth oxyhalide-based photocatalysts, a typical family of $p$-block semiconductors, as an example, the following perspective mainly focuses on three significant strategies, including constituent adjustment, vacancy engineering, and the construction of heterostructures, on the design and construction of bismuth-based solar-conversion systems with high efficiencies in terms of $H_2$ evolution, $CO_2$ reduction, and $N_2$ fixation. Finally, our thoughts on future challenges to be overcome for the development of advanced photoreduction systems are presented.

**KEYWORDS:** Photocatalysis, $P$-block semiconductor, Bismuth-based photocatalysts, Photoreduction.
Introduction

Nowadays, the pursuit of renewable and ecofriendly energy source is becoming more and more significantly critical due to the constant increase in demand for global energy consumption and balance for less related environmental deterioration. Among various renewable and sustainable energy sources (including solar, wind, geothermal, hydropower and ocean energy), the utilization of inexhaustible solar energy becomes one of key alternative energy resources, which has been intensively investigated during last decade. For example, solar energy could be practically employed to split H$_2$O to H$_2$,\textsuperscript{1-4} reduce CO$_2$ to carbon-based fuels\textsuperscript{5-7} and/or fix N$_2$ to ammonia via photocatalysts.\textsuperscript{8-10} A typical photocatalytic process (Fig. 1) generally involves five essential steps: (1) Absorption - light stimulation for the generation of charge carriers (polarized excitons); (2) Separation - electron-hole separation of photoexcited charge carriers; (3) Transportation - transport of the electron and hole to the surface of the photocatalyst; (4) Reaction - catalytic reduction or oxidation reactions to chemically convert the solar energy; (5) Disassociation - the removal of the products from active sites.\textsuperscript{4,11-14} A high-performance photocatalytic system could be expected, if these key steps are fulfilled in a specific photocatalytic procedure. Accordingly, the intrinsic characteristics of typical photocatalysts, including the band gaps, the positions of the valence and conduction bands (VB and CB), the band dispersion, and surface active sites, are the key factors that have the dominant influence on these essential steps and consequently determine the efficiency and effectiveness of the photocatalytic reactions.
Figure 1. Illustration of the basic processes of photocatalysis.

In particular, photocatalysts constructed from $p$-block elements have been reported to exhibit high visible-light photocatalytic activity due to the $p$ orbitals or $s$-$p$ hybridized states\textsuperscript{15-18}. These states generally form energy band edges, which dominate the physical and chemical properties of these $p$-block photocatalysts. In general, the $p$ electrons involved in hybridized states can lower the CB and/or move up the VB in semiconductors, resulting in much narrower band gaps than those of $d$-block semiconductors (such as TiO$_2$ and ZnO, etc.). This is of critical importance for the semiconductors used in optoelectrics and photocatalysis, which must work under the identical solar spectrum. Moreover, spatially anisotropic $p$ and $s$-$p$ hybridization states also could result in highly dispersive band structures, which not only promotes the mobility of photoexcited charge carriers \textit{via} reducing their effective mass, but also enhances both charge
separation and transportation in the photocatalytic process.\textsuperscript{14, 19} All these unique characteristics potentially make $p$-block semiconductors appealing for solar-light-driven photocatalysis. In Fig. 2, all the promising $p$-block elements that are potentially suitable to construct $p$-block materials are highlighted with a black frame in the periodic table. (Note that some $d$-block elements, such as Ag, are also selected, as their $d$ orbitals are completely filled and only their $s$ orbitals participate in hybridization). Through scientific selection of specific elements, which have valence electrons residing in $s$ or $p$ orbitals, emerging advanced visible-light driven photocatalysts with desirable band structures can be designed and developed.\textsuperscript{19}

![Figure 2](image)

Figure 2. Candidate elements for materials with high carrier mobility in the periodic table (Red and black elements are possible cations and anions, respectively.\textsuperscript{19} Grey ones are not considered.) Reproduced with permission.
Recently, bismuth-based (Bi-based) semiconductors, as a family of typical $p$-block compounds, have attracted considerable attention, because of their unique electronic and structural properties, which fulfil essential criteria required for effective and efficient photocatalytic performance.\textsuperscript{20-22} Taking BiOX (X = Cl, Br, I), with Bi, O and X belonging to $p$-block elements, as an example, theoretical calculations show that the $p$ orbitals participate in electronic hybridization in both the CB minimum (CBM) and the VB maximum (VBM). In addition, BiOX has a layered crystal structure, in which [Bi$_2$O$_2$] slabs are interleaved by double slabs of halogen atoms. This unique layered structure can induce an internal electric field, which could promote efficient charge separation in addition to the high mobility of charge carriers.\textsuperscript{23-26}

Generally, photoreduction reactions are regarded as playing a more significant role than phtooxidation reactions for solving the energy crisis. Hydrogen from H$_2$O splitting and liquid fuels from CO$_2$ conversion can represent efficient energy sources, and ammonia from N$_2$ fixation under mild conditions may meet the large needs of the fertilizer industry. Practical applications of Bi-based $p$-block semiconductors in photocatalysis remain a challenge, however, due to their low photocatalytic efficiency.\textsuperscript{5, 6} In most cases, the large band gap and unsuitable energetic positions in the band structure can lead to limited visible-light absorption and low solar-conversion efficiency. Furthermore, the low concentration of active sites on the exposed accessible surfaces is a major factor
that limits their photocatalytic efficiency.\textsuperscript{23,27-29} To overcome these scientific and technical limitations, three key strategies have been proposed and developed to improve the photocatalytic efficiencies of Bi-based \textit{p}-block semiconductors, including constituent adjustment,\textsuperscript{30-36} vacancy engineering,\textsuperscript{37-41} and construction of heterostructures.\textsuperscript{1,7,42-44}

This short review will provide a special overview of this emerging \textit{p}-block Bi-based family of semiconductors for photocatalytic H\textsubscript{2} evolution, CO\textsubscript{2} reduction, and N\textsubscript{2} fixation, including the proposed working mechanisms of the three key strategies, constituent adjustment, vacancy engineering and construction of heterostructures. A special emphasis is placed on a mechanistic understanding of the correlations between the electronic structures and desirable photocatalysis. Finally, we will briefly point out the current challenges and propose our perspectives on Bi-based and other \textit{p}-block photocatalysts. Briefly, the understanding of those advanced strategies to improve the efficiency of photocatalysts with overall enhanced performance that is presented in this review may provide new guidance for the design and exploration of new photocatalysts with high activity and excellent durability.

**Strategies to enhance photoreduction activities**

Considering that the electronic potentials for H\textsubscript{2} generation, CO\textsubscript{2} reduction, and N\textsubscript{2} fixation are different, the band structure parameters, such as the VB, CB, and band-gap energy ($E_g$), are crucial for photocatalytic activity.\textsuperscript{30, 45-49} The
photogenerated electrons of photocatalysts need to lie on a more negative potential level than that of the targeted catalytic reductions. Here, we summarize three key strategies, constituent adjustment, vacancy engineering, and construction of heterostructures, which are currently attracting considerable interest and investigations in order to tune the electronic structures and band structure of Bi-based semiconductors to obtain attractive photocatalytic performance.

**Constituent adjustment**

For Bi-based semiconductors, the band structure is mainly composed of Bi, O, and other halogen elements. The VBM is mainly composed of O 2p and X np states (X = Cl, Br, and I), while the CBM in most cases is constructed from Bi 6p states. Based on previous reports, when the coordination of the electrons and potential field was changed, the electronic and band structures will be altered simultaneously. Therefore, the band structures of Bi$_x$O$_y$X$_z$ are expected to be manipulated via altering the halogen species (X) and adjusting the ratios (x:y:z) of Bi:O:X. This provides possible synthetic approaches to prepare visible-light photocatalysts with the desired electronic structure and other physicochemical properties.

**Adjustment of the halogen component**
In general, BiOX compounds are characterized by \([\text{Bi}_2\text{O}_2]\) slabs interleaved by double slabs of halogen atoms. The localized X\( np\) states shift closer toward the VBM, and thus, the band gap of BiOX can decrease monotonically by changing the X\( np\) states from Cl to Br or I.\(^{26,51-53}\) As shown in the Figure 3a, b, the band gap of BiOX can be gradually narrowed from 4.2 eV for BiOF to 3.4 eV for BiOCl, to 2.8 eV for BiOBr, and 1.9 eV for BiOI. The absorption edges of the samples are shifted monotonically to longer wavelengths through the substitution of the halogen atoms. Therefore, suitable adjustment of the halogen component is favourable for enabling Bi-based photocatalysts to achieve a shift in the band gap.
Figure 3. (a) Calculated band gap and the band alignment of the BiOX (X = Cl, Br, I, and F) compounds by density functional theory (DFT); 26 (b) ultraviolet-visible (UV−vis) spectra of BiOX (X = Cl, Br, and I); 51 (c) UV−vis spectra of BiOCl_{1−x}Br_x; 54 (d) comparison of the band structures of Bi_2O_3 and bismuth oxyhalides. 50 Reproduced with permission.

Furthermore, when the ratio of different halides is changed through the hydrothermal method, a new family of BiOM_{x}X_{1−x} (M, X = F, Cl, Br, I) photocatalysts can be obtained via a self-assembly process, such as BiOCl_{1−x}Br_x, BiOCl_{1−x}I_x, BiOB_{1−x}I_x etc.. Reports on these have demonstrated that the photocatalytic activities of these semiconductors with hybrid halides are much higher than for those having individual halogens (BiOCl, BiOBr, and BiOI). For
example, as shown in Figure 3c, with the gradual replacement of Cl atoms by Br or increasing $x$ from 0.3 to 0.8, their absorption edges show a continuous redshift from 400 nm to 420 nm.$^{54}$ This result indicates that the band gaps of BiOCl$_{1-x}$Br$_x$ microspheres are narrowed gradually with an increasing Br-to-Cl molar ratio, which suggests that the band gap of BiOCl$_{1-x}$Br$_x$ microspheres can be well-tuned by making rational changes in the composition molar ratio of Cl-to-Br atoms.

**Ratio adjustment of Bi:O:X**

The bismuth-rich strategy, increasing the bismuth content via adjusting the ratio of Bi:O:X in Bi$_x$O$_y$X$_z$, has been reported as a widely used approach for enhancing the photocatalytic reduction activity of these compounds.$^{31, 33-36, 55-57}$ In the sequence of BiOX (Figure 3d), although both O 2$p$ and X $np$ ($n$ =3, 4, and 5 for X = Cl, Br, and I, respectively) states dominate the VB, Bi 6$p$ states contribute to the most of the CB. When the mole ratios of Bi and O contents are increased in Bi$_x$O$_y$X$_z$, the CB and VB edges can be regulated, and the band structures change simultaneously. This will result in the shift of their band structure and band positions with enhanced optical absorption, and also strengthens the hybridization of the CB to favour electron migration and promote the separation of photogenerated electron-hole pairs.$^{50}$
Figure 4. (a) The crystal structure of Bi$_{24}$O$_{31}$Br$_{10}$ (yellow balls: Bi, green balls: Br, and red balls: O). (b) Schematic illustration of the energy band structure of Bi$_{24}$O$_{31}$Br$_{10}$ with redox potentials. (c) Cycling tests of hydrogen evolution over Bi$_{24}$O$_{31}$Br$_{10}$ under visible-light irradiation.\(^{17}\) (d) Simulated charge density contour plot of Bi$_{4}$O$_{5}$Br$_{2}$ for the (100) surface. (e) Photocatalytic reduction activity of Bi$_{4}$O$_{5}$Br$_{2}$ towards CO$_{2}$ conversion and (f) comparison of fuel generation between BiOBr and Bi$_{4}$O$_{5}$Br$_{2}$.\(^{55}\) Reproduced with permission.

For example, a Bi-based photocatalyst, Bi$_{24}$O$_{31}$Br$_{10}$, with different Bi, O, and Br proportions, was explored with reasonable reduction activity.\(^{17}\) Its crystal structure was constructed from BiO$_{5}$ polyhedra and Br\(^{-}\) ions (Figure 4a). From density functional theory (DFT), changing the proportions of Bi, O, and Br can lead to the variation of orbital hybridization and uplifting of the CBM. So, the
CBM of Bi$_{24}$O$_{31}$Br$_{10}$ is more negative than the electronic potential of H$^+$/H$_2$, demonstrating that it is likely to have considerable photocatalytic H$_2$ evolution activity under visible-light irradiation. The Mott–Schottky test shows that the CBM fits the electronic potential requirements for splitting water to H$_2$. As shown in Figure 4b and 4c, the negative value of the flat-band potential clearly indicates that Bi$_{24}$O$_{31}$Br$_{10}$ can effectively produce H$_2$ from water under visible-light irradiation, presenting much higher photocatalytic reduction activity and enhanced photostability than BiOBr.

Apart from the investigation on photocatalytic H$_2$ evolution under visible light, these Bi-rich bismuth oxyhalides often show promising potential in solar photocatalytic conversion of CO$_2$ into chemical fuels. In particular, Bi$_x$O$_y$X$_z$ compounds with decreased CBM potential also show excellent photocatalytic performance compared with the typical photocatalysts for CO$_2$ conversion.$^{33, 55, 57}$ For example, Bi$_4$O$_5$Br$_2$ with efficient photoreduction CO$_2$ activity has been reported, in which both thickness-ultrathin and bismuth-rich strategies were applied in order to enhance its photocatalytic performance.$^{55}$ As shown in Figure 4d-f, a Bi$_4$O$_5$Br$_2$ microspheres, assembled from ultrathin nanosheets (thickness: ~3.7 nm), exhibit improved charge separation, resulting in a much higher efficiency of photocatalytic CO$_2$ reduction in comparison with BiOBr nanosheets under identical visible light irradiation/stimulation. In addition, Bi$_4$O$_5$X$_2$ (X = Br, I)$^{57, 58}$ and Bi$_5$O$_7$I$^{59}$ were also reported to achieve CO$_2$ photoreduction to CH$_4$ and CO under visible light irradiation, in which the apparent quantum of the final
solar fuels (CO and CH$_4$) generated by Bi$_4$O$_3$I$_2$ reached 0.37% under 420 nm monochromatic light.

**Vacancy engineering**

In crystallography, an atom missing from one of the lattice sites is known as a "vacancy" defect. The vacancy is a type of point defect in the crystal. It can cause local structural distortion and electronic structure modification, leading to the different physical properties, such as in optical absorption, conductivity, and stability.$^{39-41, 60}$ Furthermore, vacancy-based defects can also act as active sites on the surfaces to participate in the reaction through increasing the adsorption capacity of the reactants (water, gas, or organic molecules) and lowering the activation barrier for the reactants.$^{9, 38, 61}$ For example, the most common and effective oxygen vacancies, as reported for TiO$_2$, WO$_3$, ZnO, etc., can generate an intermediate level and play a critical role in separating charge carriers, thereby lead to enhanced visible-light adsorption and photocatalytic activity towards water splitting, CO$_2$ reduction, and N$_2$ fixation.

**Oxygen vacancy**

The oxygen vacancy has clearly been deeply studied, because if can modulate both the coordination structures and the electronic states, thus influencing the photocatalytic efficiency, products, and catalytic mechanism.$^{73-76}$ Normally, in Bi-based semiconductor, oxygen vacancies can be obtained through UV light
irradiation,$^{37,77}$ high temperature treatment,$^{24}$ hydrogenated$^{28,78}$ and concentrated alcohol group solvents,$^{16,60,79}$ etc.

Black ultrathin BiOCl (BU-BiOCl) nanosheets with oxygen vacancy can be synthesized by using a high viscosity alcohol group concentration solvent. It exhibits excellent efficient, visible-light driven photocatalytic activity towards H$_2$ production compared to using bulk BiOCl.$^{77}$ In typical electron spin resonance (ESR) spectra (Figure 5a), a special peak signal (g-factor, $g = 2.001$) appeared in a BU-BiOCl sample, while, in contrast, no obvious signal was detected for bulk BiOCl. It has been confirmed that the above signal peak occurred due to the presence of oxygen vacancies in BiOCl.$^{80}$ Meanwhile, the colour of BU-BiOCl was changed from white to brown-black, and the light-absorption range of BU-BiOCl covers both UV-vis and near-infrared light wavelengths (as shown in Figure 5b). From Figure 5c, BU-BiOCl exhibits an average photoactivity (2.51 mmol/h) during $\lambda \geq 420$ nm light irradiation for 5 h, which is much higher than those of bulk BiOCl (0.12 mmol/h) and TiO$_2$ (0.16 mmol/h) under identical control conditions. Theoretical calculation analysis is shown in Figure 5d, which agrees with the UV-vis light absorption result that the band gaps of BU-BiOCl are much larger than that of bulk BiOCl. On the other hand, the CBM and VBM potentials of BU-BiOCl were higher and lower than those of bulk BiOCl, respectively. This suggests that the photoinduced electrons and holes of BU-BiOCl can respectively display higher reducing power and oxidizing power than bulk BiOCl. The theoretical calculations combined with experimental results
allow us to conclude that oxygen vacancy in BiOCl can lead to enhanced light absorption especially in the visible light region, and better separation efficiency of photoinduced charge carriers through changes in the electronic structure. Meanwhile, the photoinduced charge carrier lifetime increased from 0.5 to 3.12 ns, when oxygen vacancies were introduced.

**Figure 5.** (a) Electron spin resonance spectra of BU-BiOCl and bulk BiOCl; (b) UV-vis diffuse reflectance spectra of BU-BiOCl and bulk BiOCl, with the inset showing a photograph of BU-BiOCl and bulk BiOCl; (c) Long-term stability in H₂ production of TiO₂, TiO₂/Pt, bulk BiOCl, bulk BiOCl/Pt, BU-BiOCl, and BU-BiOCl/Pt under visible light irradiation; (d) Total density of states (DOS) and partial DOS of bulk BiOCl and BU-BiOCl. Reproduced with permission.

More importantly, surface oxygen vacancies (OVs) can directly participate in the photochemical reactions though promoting electron migration from the
materials to adsorbates and decreasing the reaction barrier. This is because OVs in BiOX could help to activate small molecules on the surfaces of photocatalysts via providing many extra active sites for effectively adsorbing reactants (water, gas, or organic molecules). Based on some experimental studies, new absorption peaks gradually appeared in the visible light range with UV light irradiation after the introduction of abundant vacancies on the surfaces of BiOBr, as shown in Figure 6a. The electron paramagnetic resonance (EPR) spectra in Figure 6b indicate that the EPR signal at $g = 2.004$ is increased with the light irradiation, which could be ascribed to the increased oxygen vacancies. In addition, DFT calculations (Figure 6c) reveal that oxygen vacancies can introduce several new defect levels into the band gap, thus narrowing it, and hence giving the possibility of realizing visible light CO$_2$ reduction. Moreover, those vacancies can make the charge distribution more delocalized to stabilize the reduction intermediates of CO$_2$ photoreduction and lower the reaction energy barriers.

According to further in-situ Fourier transform infrared (FTIR) spectroscopy investigations related to the CO$_2$ photoreduction process (Figure 6d), CO$_2$ photoreduction on samples may proceed through three key steps: (1) Initial CO$_2$ adsorption on the catalyst surfaces, while, H$_2$O dissociates into hydroxyl and hydrogen ions on these surfaces; (2) Subsequently, the adsorbed CO$_2^*$ molecules interaction with the surface protons, followed by the gradual generation of the
COOH* intermediate; (3) A further COOH* intermediate protonation process takes place, through which there is a progressive yield of CO* molecules. More production of COOH* groups on the oxygen-deficient BiOBr atomic layers means that the oxygen vacancy is beneficial to the stability of the COOH* intermediate and increases the output of the final CO. Consequently, the oxygen-deficient BiOBr atomic layers realized visible-light-driven CO\textsubscript{2} reduction to CO at a rate of 87.4 mmol g\textsuperscript{-1} h\textsuperscript{-1}, which is 20 times and 24 times higher than those of BiOBr atomic layers and bulk BiOBr without oxygen vacancy.\textsuperscript{37}

Figure 6. (a) UV-vis diffuse reflectance spectra for BiOBr atomic layers after UV irradiation for different periods of time; (b) EPR spectra; (c) Calculated density of states (left), the charge
density distribution (middle), and the charge density contour plots (right) at the conduction band and edge for (A-C) bulk BiOBr, (D-F) BiOBr atomic layers, and (G-I) oxygen-deficient BiOBr atomic layers (d) In-situ FTIR spectra for co-adsorption of a mixture of CO$_2$ and H$_2$O vapour on the oxygen-deficient BiOBr atomic layers.$^{37}$ Reproduced with permission.

Similar effects were also observed in nitrogen fixation applications.$^9$, $^{83-85}$ Judging from the band structure, electrons at the CBM of BiOBr cannot directly reduce N$_2$ or form solvated electrons (Figure 7a). BiOBr-OV, however, could steadily generate NH$_3$ in pure water without any sacrificial agent under visible light, while no reactivity for N$_2$ fixation was obtained from the defect-free BiOBr (Figure 7b). Theoretical calculations have shown that N$_2$ could be adsorbed on the OV through coordinating with the two OV-connected and partially reduced Bi atoms with an end-on bound structure, with the exchange and transfer of electrons mainly taking place between the OV and N$_2$ (Figure 7c). From the in-situ FTIR spectra (Figure 7d), OVs could serve as the trustworthy sites for the activation of stubborn N=N triple bonds to enhance the kinetic feasibility of N$_2$ fixation via energy-accessible intermediary steps, while the involvement of N$_2$ fixation pathways with distinct selective N$_2$ fixation products (for example, N$_2$H$_2$, N$_2$H$_4$, and NH$_3$) showed high dependence on the N$_2$ adsorption structures on OVs.$^{84}$
Figure 7. Photocatalytic N$_2$ fixation over the as-prepared BiOBr nanosheets: (a) Electronic energy-level diagram of BiOBr-001-OV; (b) Quantitative determination of the generated NH$_3$ under visible light ($\lambda > 420$ nm). (c) Theoretical prediction of N$_2$ activation on an OV of BiOBr (001); (d) In-situ FTIR spectra recorded during the photocatalytic N$_2$ fixation over BiOBr-001-OV.$^{84}$ Reproduced with permission.

Another compelling advantage of solar N$_2$ fixation lies in the facile creation of OV$s$ via light irradiation, which could generate sufficient light-switching surface OV$s$ with suitable adsorption edges (Figure 8a.$^{86}$ As a result, Bi$_5$O$_7$Br-nanotube (NT) delivers excellent visible light-driven photocatalytic N$_2$ fixation performance with an NH$_3$ generation rate of 1.38 mmol h$^{-1}$ g$^{-1}$ in water without
any organic scavengers or noble co-catalysts (Figure 8b). Through the FTIR spectra (Figure 8c), the photocatalytic N\textsubscript{2} fixation pathway of Bi\textsubscript{5}O\textsubscript{7}Br-NT can be determined (Figure 8d). N\textsubscript{2} molecules are chemisorbed and activated on the photoinduced OV sites, and the photoexcited electrons are injected into the activated N\textsubscript{2} to be reduced to NH\textsubscript{3}. After the solar N\textsubscript{2} fixation reaction, the photoinduced OVs would be refilled by seizing O atoms from water, leading to a good recovery to the original stable OV-free composition. This interesting result provides innovative insights into rational design and engineering for the creation of highly active Bi-rich bismuth oxybromide photocatalysts.
Figure 8. (a) UV–vis absorption spectra of the as-prepared ultrafine Bi$_5$O$_7$Br nanotubes before and after light irradiation; the corresponding Tauc plots are in the right inset, and photographs of the sample before and after irradiation are in the left inset. (b) NH$_3$ generated by the as-prepared ultrafine Bi$_5$O$_7$Br nanotubes and BiOBr-001-OV nanosheets under visible light (λ > 400 nm) irradiation; (c) In-situ direct reflectance FTIR spectra from as-prepared ultrafine Bi$_5$O$_7$Br nanotubes during the photocatalytic N$_2$ fixation; (c) Schematic illustration of the photocatalytic N$_2$ fixation model on the Bi$_5$O$_7$Br nanotube surface. Reproduced with permission.

2.2.2 Other vacancies
Figure 9. (a) Schematic diagram of the positions of the VBM and CBM of BiOCl and Bi-vacancy-BiOCl;\(^87\) (b) Charge separation and the possible reaction mechanism of BiO\(1-x\)Cl\(1-y\).\(^88\) Reproduced with permission.

In general, if the crystal includes more than one element, as in the case of BiOX, it is expected to be able to produce that many types of vacancies, bismuth, oxygen and halogen vacancies in this case. Unlike oxygen vacancy, however, fewer studies have been reported on bismuth and halogen vacancies in BiOX. Recently, Teng's group\(^87\) reported that BiOCl nanosheets with surface bismuth defects (V-BOC) demonstrated very much higher photocatalytic activity towards the degradation of methyl orange (MO) in aqueous solution than pure BiOCl nanosheets. It was found that the bismuth vacancy had greatly up-shifted the valence band and efficiently enhanced the separation and transfer rates of photogenerated electrons and holes, as shown in the Figure 9a.
Furthermore, if the dual vacancies strategy (O and Cl vacancies) is introduced into BiOX, this will give rise to enormous amelioration of the crystal and electronic structures, as well as the surface states.\textsuperscript{88} As shown in Figure 9b for BiO\textsubscript{1-x}Cl\textsubscript{1-y}, both the CBM and the VBM positions shifted downward, while the CBM showed a much greater downshift. This phenomenon not only leads to a narrowed band gap, but also triggers a visible-light active photocatalytic reaction as well as molecular oxygen species activation. In addition, the lowered VBM also endows BiO\textsubscript{1-x}Cl\textsubscript{1-y} with a stronger photooxidation driving force and highly selective CO\textsubscript{2} to CO reduction activity.

Above all, the reaction rate can be improved through changing the catalyst structure, increasing the adsorption capacity of the reactants (water, gas, or organic molecules) and lowering the reactant activation barrier by introducing element vacancies, including oxygen vacancy, bismuth vacancy, and halogen vacancy. All three vacancies could lead to a narrowed band gap and the generation of an active defect level, thus endowing BiOX with visible-light photocatalytic activity. Due to the insufficient experimental characterization, bismuth and halogen vacancies are rarely reported, so more decent experimental investigations combined with theoretical calculations are much needed to explore the mechanism.

\textbf{Construction of heterostructures.}
Besides constituent adjustment and vacancy engineering, the construction of heterostructures to integrate multiple semiconductors and/or metallic nanomaterials into one photocatalytic system is also widely utilised to improve photocatalytic activity. For the heterostructures constructed from semiconductors and metallic nanomaterials, the introduction of metallic phases on the surfaces of semiconductors can not only increase the conductivity and extend the light absorption of the obtained photocatalytic system, but also enables them to act as active sites to adsorb and activate the reactant molecules. In contrast, for the semiconductor/semiconductor heterostructures, the combination of semiconductors enables band alignments to promote charge separation, and the internal electric field built among the interfaces of heterostructures can further accelerate charge transfer and migration. So, Bi$_x$O$_y$X$_z$-based heterostructures combined with metallic nanomaterials or two-dimensional (2D) semiconductors can be expected to exhibit excellent photoreduction activities.

**Metallic nanomaterial/Bi$_x$O$_y$X$_z$ heterostructures.**

The application of metallic co-catalysts to form metallic nanomaterial/Bi$_x$O$_y$X$_z$ heterostructures is a significant strategy to enhance the photocatalytic reduction activity towards CO$_2$ reduction and H$_2$ evolution. Normally, the photogenerated electrons or holes are inclined to transfer to the corresponding metallic co-catalyst, which acts as a sink for the electrons or holes, resulting in selective spatial separation and lifetime enhancement of photogenerated carriers in
photocatalysts. Moreover, the loaded metallic co-catalysts can further serve as redox active sites to promote the photocatalytic reaction.

In recent research, a strategy of dual-co-catalyst/Bi$_x$O$_y$X$_z$ heterostructures was proposed to prohibit the recombination of photo-excited electron-hole pairs, so photo-excited electrons can be utilised efficiently for CO$_2$ reduction. As recent research has revealed, Au nanoparticles and MnO$_x$ layers were selectively deposited on BiOI nanosheets with photo-excitation, and this Au/BiOI/MnO$_x$ heterostructure displayed excellent photocatalytic capacity towards CO$_2$ reduction under UV-vis light irradiation. The CO photoconversion rate of Au/BiOI/MnO$_x$ was ~7.0 times higher than that of pure BiOI. The final production of CO reached 169 μmol g$^{-1}$ with Au/BiOI/MnO$_x$ after 5 h of photoreduction reaction. The same strategy was also applied on BiOCl to boost photocatalytic H$_2$ evolution. Charge separation between the (001) and (110) crystal facets of BiOCl can be optimized by selective deposition of redox co-catalysts to form metallic nanomaterial/Bi$_x$O$_y$X$_z$ heterostructures, and endow BiOCl with excellent photocatalytic H$_2$O splitting activity.
Figure 10. (a) UV-vis-infrared (IR) driven photo-thermo-catalysis mechanism of Bi$_4$O$_5$I$_2$-1.95 for converting CO$_2$ to chemical energy. (b) Rates of CO production under different ranges of sunlight (UV-vis-IR) induced photo-thermo catalysis to convert CO$_2$ to chemical energy over Bi$_4$O$_5$I$_2$-1.00 and Bi$_4$O$_5$I$_2$-1.95. (c) Band alignment at the interface of 1L-Bi$_{12}$O$_{17}$Cl$_2$/IL-MoS$_2$ vertical heterostructure. (d) Schematic illustration of the crystal structure and the transfer process for charge carriers within the heterostructure: the electron-hole separation within 1L-Bi$_{12}$O$_{17}$Cl$_2$, and the electron transfer at the interface along the Bi-S bonds. (e) Cycling tests of photocatalytic hydrogen evolution over 1L-Bi$_{12}$O$_{17}$Cl$_2$/IL-MoS$_2$ vertical heterostructure and 1L-Bi$_{12}$O$_{17}$Cl$_2$. Reproduced with permission.
Apart from these noble metal co-catalysts, the semimetal bismuth with a photothermal property can be used as the co-catalyst to build metallic nanomaterial/Bi$_x$O$_y$X$_z$ heterostructures, in which bismuth nanoparticles not only inhibit the recombination of charge carriers, but also accelerate the conversion of light to thermal energy.\textsuperscript{58, 102} Taking the semimetal Bi mediated Bi$_x$O$_y$X$_z$ as an example, Bi/Bi$_4$O$_5$I$_2$ heterostructures were formed through a molecular precursor hydrolytic process.\textsuperscript{58} Remarkably increased photoreduction activity of Bi/Bi$_4$O$_5$I$_2$ can be achieved, which is attributed to the co-catalyst and photothermal effects of the loaded Bi nanoparticles, and Bi/Bi$_4$O$_5$I$_2$ at an optimal mole ratio displayed excellent photo-thermo-catalytic CO$_2$ conversion to solar fuels (CO and CH$_4$) \textbf{(Figure 10a,b)}. The enhanced photo-induced carrier separation rate and reaction system temperature of Bi/Bi$_4$O$_5$I$_2$ were further investigated. Under full solar-spectrum irradiation (UV-vis-IR), the photoreduction of CO$_2$ to CO and CH$_4$ in the presence of Bi/Bi$_4$O$_5$I$_2$ was enhanced to 40.02 $\mu$mol h$^{-1}$g$^{-1}$ and 7.19 $\mu$mol h$^{-1}$g$^{-1}$, respectively. The light-conversion efficiency was $\sim$ 6.47 times higher than that of pure Bi$_4$O$_5$I$_2$. In addition, transition-metal chalcogenide can also serve as a co-catalyst in photocatalytic systems. For instance, 1T MoS$_2$ monolayers with abundant H$_2$ evolution active sites were assembled selectively and chemically bound on the (Bi$_{12}$O$_{17}$)-end-faces of Bi$_{12}$O$_{17}$Cl$_2$ monolayers to build 2D janus (Cl$_2$)-(Bi$_{12}$O$_{17}$)-(MoS$_2$) bilayer junctions.\textsuperscript{90} The separation, transportation, and consumption of carriers could thus be manipulated at the atomic level \textbf{(Figure}
Visible-light-driven photogenerated charge carriers in BiI$_2$O$_{17}$Cl$_2$ are spatially separated by the internal electric field (IEF) to the (Bi$_{12}$O$_{17}$) and (Cl$_2$) end-faces. The separated electrons can further migrate to MoS$_2$ via Bi-S bonds formed in the interfaces of the vertical heterostructure (Figure 10d). This atomic-level directional charge separation endows the janus bilayers with an ultra-long carrier lifetime of 3,446 ns and a superior visible-light photocatalytic hydrogen evolution (PHE) rate of 33 mmol h$^{-1}$g$^{-1}$, with a quantum efficiency of 36% at 420 nm. Furthermore, 2D bilayer vertical heterojunctions possessed rather good stability without remarkable activity decay over a 100 h cycling test (Figure 10e).

**2D semiconductor/Bi$_x$O$_y$X$_z$ heterostructure**

Bi$_x$O$_y$X$_z$-based semiconductors and other 2D materials such as g-C$_3$N$_4$ can be combined to fabricate 2D/2D heterostructures. The charge separation, transportation, and consumption of 2D/2D heterostructures can be steered via atomic-level structural and interfacial design. In order to fabricate heterojunction photocatalysts with high stability, the efficiency and energy band alignments that can lead to prolonged carrier lifetime should be taken into account. 2D semiconductor/Bi$_x$O$_y$X$_z$ heterostructures with optimized energy band alignments were employed to promote CO$_2$ photoreduction activity. Z-scheme BiOI/g-C$_3$N$_4$ 2D heterojunctions were formed and used for photocatalytic CO$_2$ reduction to produce CO and/or CH$_4$. Due to the enhanced charge transfer, the as-prepared Z-scheme heterojunctions displayed much higher photocatalytic...
efficacy than the pristine samples (Figure 11a,c). Interestingly, the product of photocatalytic CO₂ reduction can be tuned by changing the reaction conditions such as the light spectrum. The reaction mechanism of the heterojunction was further explored via detection of the photoinduced intermediate. The charge transfer mechanism across the heterojunction and the indirect Z-scheme were further investigated by detecting the I³⁻/I⁻ redox mediator and using quantification tests of superoxide radical (•O²⁻) and hydroxyl radical (•OH) (Fig. 11b).
Figure 11. Schematic illustration of CO₂ photoreduction via photoinduced electron-hole separation processes: (a) the charge transfer mechanism of a type II heterojunction (left) and a Z-scheme heterojunction (right); and (b) yields of products for oxygen evolution and CO₂ photoreduction proceeding on BiOI/g-C₃N₄ heterostructures with different BiOI content.¹⁰⁴ (c) Schematic illustration of visible-light conversion on BiOI/g-C₃N₄ heterostructure; and (d) production rates of visible-light-conversion products including H₂, O₂, CO and CH₄ over g-C₃N₄/BiOI and g-C₃N₄/Bi₄O₅I₂.¹⁰⁷ Reproduced with permission.

In addition to the band alignment for the promotion of charge separation, other efforts were also undertaken towards enhancing the limited optical absorption of Bi-based p-block semiconductors and introducing surface active sites through the heterostructure strategy.¹⁰²,¹⁰⁵ Recently, it was reported that a heterostructure composed of 2D Bi₂O₄ nanoparticle decorated on BiOBr nanosheets was constructed in situ via a simple alkali post-treatment method assisted by light irradiation.¹⁰⁶ The combination of NaOH-induced dehalogenation and oxidation by photogenerated holes triggered the synthesis of Bi₂O₄ nanoparticles on the surfaces of BiOBr nanosheets. Moreover, the content of Bi₂O₄ phase in heterostructures can be easily manipulated by tuning the NaOH concentration in the post-treatment, which can provide further help to preserve the predominantly exposed (001) facets of BiOBr nanosheets and remarkably increase the amount of surface active sites. The light absorption of Bi₂O₄/BiOBr heterostructures has been extended to the near-infrared (NIR) region. Thanks to the efficient separation of photogenerated e⁻/h⁺ pairs and the improved surface absorption of
reactants, the constructed Bi-based heterostructures exhibit superior photocatalytic activity to reduce CO₂ to CO and CH₄ under simulated light in comparison with pristine BiOBr.²²

Moreover, the construction of 2D semiconductor/BiₓOᵧXₓ heterostructures was verified to have universal applicability to improve photoreduction activity, which has been widely employed on g-C₃N₄/Bi₄O₅I₂¹⁰⁷ and g-C₃N₄/BiOBr/Au heterostructures.¹⁰⁸ Among them, the g-C₃N₄/Bi₄O₅I₂ heterostructure at an optimal ratio showed the highest photocatalytic reduction activity with 45.6 mol h⁻¹ g⁻¹ of CO generation for CO₂ conversion (Figure 11d).

Other strategies

Besides those modulation strategies mentioned above, researchers have also taken full advantage of some other strategies such as element doping and photosensitization to boost the photoreduction behaviour of Bi-based p-block photocatalysts. The modification of metals or non-metals has been widely applied to enhance their photoreduction efficiency (Figure 12a). In one approach, the energy band structure can be engineered through element doping. At the same time, active sites also can be introduced onto surfaces to facilitate the reaction. For bismuth oxide halide-based photocatalysts, homogeneous carbon doping into the (001) and (010) facets of BiOCl was developed.¹⁰⁹ Because of the extension of the optical absorption spectrum and enhancement of the IEF induced by carbon doping, the H₂ evolution capability of carbon-doped BiOCl was remarkably
enhanced compared to pristine BiOCl, and the optimal rate of H₂ evolution reached 0.42 mmol h⁻¹ g⁻¹ for carbon-doped (010)-faceted BiOCl with NiOₓ as a co-catalyst (Figure 12b,c).

**Figure 12.** (a) Schematic illustration of homogeneous carbon doping strategy on carbon doped BiOCl. (b) UV-visible absorption spectra and (c) the rate of photocatalytic hydrogen evolution of pure and carbon-doped BiOCl with exposed (001) and (010) facets.¹⁰⁹ (d) Schematic illustration of the process of photocatalytic H₂ evolution over Fe(III)-doped BiOCl. (e) Visible-
light-driven H$_2$ evolution over BiOCl and Fe(III)-doped BiOCl.$^{111}$ Reproduced with permission.

It has been reported that the doping of transition metal ions such as Fe(III) on wide-band-gap semiconductors is an efficient method to achieve high visible-light photocatalytic performance,$^{111}$ which was applied to modify the properties of bismuth oxide halide-based photocatalysts. Taking Fe(III) doping on ultrathin BiOCl as an example, the light absorption of BiOCl was extended from the UV to the visible light region resulting from the downshifted CBM of BiOCl.$^{111}$ Meanwhile, the separation and transfer efficiency of charge carriers were enhanced by the improved self-induced electric field along the [001] zone axis and the shortened diffusion length of charge carriers. With those advantages mentioned above, the Fe(III)-doped BiOCl showed much higher photocatalytic efficiency for H$_2$ evolution under visible-light irradiation than the pure BiOCl (Figure 12d,e).

In addition, the application of photosensitization can be very helpful to improve the photoreduction activity of photocatalysts through electron injection from the excited state of the sensitizer into the conduction band of the semiconductor substrate.$^{112}$ By taking advantage of photosensitization, an efficient visible-light-induced photocatalytic system was developed by loading copper phthalocyanine (CuPc), which has intense visible-light absorption (600-800 nm), on BiOCl.$^{113}$ As
expected, enhanced overall water splitting on BiOCl/CuPc was realized in methanol-H$_2$O-rhodamine B (RhB) solution under visible light.

**Summary**

The development of Bi-based *p*-block photocatalysts is the key fundamental research needed for effective solar-energy conversion. Through stoichiometry engineering, vacancy engineering, and the construction of heterostructures, the band structures can be tuned to satisfy the catalytic reduction conditions, while a high-level/degree of active sites are physically and chemically introduced onto the surfaces of photocatalysts. Moreover, charge separation and transportation could be promoted, resulting in significant improvement in solar-energy conversion efficiency. Important results on the design and fabrication of photocatalysts with high photoreduction efficiency by using these strategic methods are summarized in Table 1 on stoichiometry alteration, Table 2 on vacancy engineering, and Table 3 on heterostructures.
Table 1. Stoichiometry alteration for bismuth-based $p$-block semiconductors.

<table>
<thead>
<tr>
<th>Bismuth-based Photocatalyst</th>
<th>Strategies</th>
<th>Conditions</th>
<th>Final Products</th>
<th>Photocatalytic activity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_{12}$O$<em>7$Br$</em>{10}$</td>
<td>0.14M NaOH aqueous solution</td>
<td>0.05g/20 mL H$_2$O and 10 mL of methanol; 300 W xenon lamp, $\lambda$$\geq$400 nm</td>
<td>H$_2$</td>
<td>3.347µmol g$^{-1}$ h$^{-1}$</td>
<td>17</td>
</tr>
<tr>
<td>Bi$_6$O$_5$Br$_2$</td>
<td>Glycerol</td>
<td>40 mg/50 mL of DI water containing 40 vol% CH$_3$OH as sacrificial reagent, 1 wt% Pt; 300 W Xe lamp, $\lambda$$\geq$420 nm</td>
<td>H$_2$</td>
<td>4.21 µmol/h</td>
<td>114</td>
</tr>
<tr>
<td>Bi$_5$O$_7$I$_2$</td>
<td>Glycerol</td>
<td>40 mg/50 mL of DI water containing 40 vol% CH$_3$OH as sacrificial reagent, 1 wt% Pt; 300 W Xe lamp, $\lambda$$\geq$420 nm</td>
<td>H$_2$</td>
<td>2.79 µmol/h</td>
<td>114</td>
</tr>
<tr>
<td>Bi$_4$O$_5$I$_2$</td>
<td>Change molar ratios</td>
<td>0.05 g dispersed on glass; 300 W Xe lamp</td>
<td>CO</td>
<td>CO: 66.43 µmol h$^{-1}$ g$^{-1}$; CH$_4$: 10.39 µmol h$^{-1}$ g$^{-1}$</td>
<td>58</td>
</tr>
<tr>
<td>Bi$_5$O$_7$Br$_2$</td>
<td>Change molar ratios</td>
<td>0.1 g dispersed on glass; 300 W Xe lamp</td>
<td>CO</td>
<td>CO: 19.82 µmol g$^{-1}$ h$^{-1}$</td>
<td>59</td>
</tr>
<tr>
<td>Bi$_5$O$_7$I</td>
<td>Change molar ratios</td>
<td>0.1 g dispersed on glass; 300 W Xe lamp</td>
<td>CO</td>
<td>CO: 11.73 µmol g$^{-1}$ h$^{-1}$</td>
<td>59</td>
</tr>
<tr>
<td>Bi$_5$O$_7$Br$_2$</td>
<td>Hydrolytic process</td>
<td>0.15 g dispersed on glass; 300 W Xe lamp, $\lambda$$\geq$420 nm</td>
<td>CO</td>
<td>CO: 2.73 µmol g$^{-1}$ h$^{-1}$; CH$_4$: 2.04 µmol g$^{-1}$ h$^{-1}$</td>
<td>59</td>
</tr>
<tr>
<td>Bi$_5$O$_7$Br$_2$</td>
<td>Change molar ratios</td>
<td>50 mg dispersed on glass; 300 W Xe lamp, $\lambda$$\geq$420 nm</td>
<td>CO</td>
<td>CO: 2.71 µmol g$^{-1}$ h$^{-1}$; CH$_4$: 1.65 µmol g$^{-1}$ h$^{-1}$</td>
<td>57</td>
</tr>
<tr>
<td>Bi$_5$O$_7$I$_2$</td>
<td>Change molar ratios</td>
<td>50 mg dispersed on glass; 300 W Xe lamp, $\lambda$$\geq$420 nm</td>
<td>CO</td>
<td>CO: 15.87 µmol g$^{-1}$ h$^{-1}$; CH$_4$: 0.18 µmol g$^{-1}$ h$^{-1}$</td>
<td>57</td>
</tr>
<tr>
<td>Bi$_5$O$_7$BrI</td>
<td>Change molar ratios</td>
<td>50 mg dispersed on glass; 300 W Xe lamp, $\lambda$$\geq$420 nm</td>
<td>CO</td>
<td>CO: 22.85 µmol g$^{-1}$ h$^{-1}$; CH$_4$: 2.13 µmol g$^{-1}$ h$^{-1}$</td>
<td>57</td>
</tr>
<tr>
<td>Bi$_5$O$_7$Br</td>
<td>Self-assembled</td>
<td>0.025 g photocatalyst dispersed in 100 mL deionized water; 300 W Xe lamp, $\lambda$$\geq$420 nm</td>
<td>NH$_3$</td>
<td>1380 µmol g$^{-1}$ h$^{-1}$</td>
<td>88</td>
</tr>
<tr>
<td>Bi$_5$O$_7$I</td>
<td>PH value</td>
<td>0.05 g/100 mL water containing 20% CH$_3$OH; 300 W Xe lamp, $\lambda$$\geq$420 nm</td>
<td>NH$_3$</td>
<td>4.62 µmol g$^{-1}$ h$^{-1}$</td>
<td>115</td>
</tr>
</tbody>
</table>
**Table 2. Vacancy engineering for bismuth-based p-block semiconductors.**

<table>
<thead>
<tr>
<th>Bismuth-based Photocatalyst</th>
<th>Strategies</th>
<th>Conditions</th>
<th>Final Products</th>
<th>Photocatalytic activity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiOCl</td>
<td>Alcohol groups react with the oxygen</td>
<td>0.05g/50mL of water containing 10vol% TEOA, 300 W xenon lamp, λ≥420 nm</td>
<td>H₂</td>
<td>2.51 μmol/h</td>
<td>81</td>
</tr>
<tr>
<td>ultrathin BiOBr</td>
<td>Mannitol and PVP</td>
<td>0.01 g/100 ml aqueous solution; 500-W Xe lamp</td>
<td>H₂</td>
<td>0.375 μmol/h</td>
<td>116</td>
</tr>
<tr>
<td>BiOBr</td>
<td>EG</td>
<td>samples on a fluorine-doped tin oxide (FTO) glass slide; 500W Xenon; AM 1.5 filter; λ≥400 nm</td>
<td>CH₄, CO</td>
<td>CH₄: 0.158 μmol g⁻¹ h⁻¹, CO: 4.94 μmol g⁻¹ h⁻¹</td>
<td>117</td>
</tr>
<tr>
<td>ultrathin BiOBr</td>
<td>UV light irradiation</td>
<td>0.1 g/100 ml water 300W Xe lamp, λ≥400 nm</td>
<td>CO</td>
<td>87.4 μmol g⁻¹ h⁻¹</td>
<td>37</td>
</tr>
<tr>
<td>BiOI</td>
<td>Ethylene glycol</td>
<td>300 W Xe lamp 0.15 g dispersed on glass</td>
<td>CH₄, CO</td>
<td>CH₄: 0.063 μmol g⁻¹ h⁻¹, CO: 0.615 μmol g⁻¹ h⁻¹</td>
<td>116</td>
</tr>
<tr>
<td>BiOCl</td>
<td>High viscosity solvent, thermal</td>
<td>0.05g dispersed on glass</td>
<td>CO</td>
<td>2.18 μmol g⁻¹ h⁻¹</td>
<td>119</td>
</tr>
<tr>
<td>BiOCl</td>
<td>Ethylene glycol solution</td>
<td>0.05 g/100 ml water; 300 W xenon; λ≥420 nm</td>
<td>NH₃</td>
<td>223.3 μmol g⁻¹ h⁻¹</td>
<td>84</td>
</tr>
<tr>
<td>BiOBr</td>
<td>Hydrogen</td>
<td>0.02 g/100 ml water; 300 W xenon; λ≥420 nm</td>
<td>NH₃</td>
<td>360.8 μmol g⁻¹ h⁻¹</td>
<td>120</td>
</tr>
</tbody>
</table>
Table 3. Heterostructure strategy for the enhancement of photocatalytic efficiency on bismuth-based p-block semiconductors.

<table>
<thead>
<tr>
<th>Bismuth-based Photocatalysts</th>
<th>Strategies of synthesis</th>
<th>Conditions</th>
<th>Final Products</th>
<th>Photocatalytic activity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiOBr/g-C_{3}N_{4}/Au</td>
<td>Photodeposition</td>
<td>380 nm monochromatic light</td>
<td>CO, CH_{4}</td>
<td>CO: 6.67 μmol·h(^{-1} \cdot g)^{-1}, CH_{4}: 0.92 μmol·h(^{-1} \cdot g)^{-1}</td>
<td>107</td>
</tr>
<tr>
<td>BiOI/C_{3}N_{4}</td>
<td>Solvothermal method</td>
<td>EDTA as the hole scavenger, with I(^{3-}/I(^{-}) redox mediators, under visible light (λ &gt; 420 nm, 300 W Xenon lamp)</td>
<td>CO, CH_{4}</td>
<td>CO: 3.45 μmol·h(^{-1} \cdot g)^{-1}, CH_{4}: 0.164 μmol·h(^{-1} \cdot g)^{-1}</td>
<td>104</td>
</tr>
<tr>
<td>Bi_{2}O_{3}/g-C_{3}N_{4}</td>
<td>Hydrolytic process</td>
<td>I(^{3-}/I(^{-}) redox mediators, under visible light (λ &gt; 420 nm, 300 W Xenon lamp)</td>
<td>CO, CH_{4}</td>
<td>CO: 9.1 μmol·h(^{-1} \cdot g)^{-1}, CH_{4}: 0.164 μmol·h(^{-1} \cdot g)^{-1}</td>
<td>107</td>
</tr>
<tr>
<td>Bi_{4}O_{5}I_{2}/Bi</td>
<td>Solvothermal method</td>
<td>Under simulated solar light (300 W Xenon lamp)</td>
<td>CO, CH_{4}</td>
<td>CO: 40.02 μmol·h(^{-1} \cdot g)^{-1}, CH_{4}: 7.19 μmol·h(^{-1} \cdot g)^{-1}</td>
<td>104</td>
</tr>
<tr>
<td>BiOBr/Bi_{2}O_{4}</td>
<td>NaOH-induced dehalogenation and light triggered photogenerated hole oxidation</td>
<td>Under simulated solar light (300 W Xenon lamp)</td>
<td>CO, CH_{4}</td>
<td>CO: 2.6 μmol·h(^{-1} \cdot g)^{-1}, CH_{4}: 1.85 μmol·h(^{-1} \cdot g)^{-1}</td>
<td>106</td>
</tr>
<tr>
<td>Au/BiOI/MnO_{x}</td>
<td>Photodeposition</td>
<td>Under simulated solar light (300 W Xenon lamp)</td>
<td>CO, CH_{4}</td>
<td>CO: 42.9 μmol·h(^{-1} \cdot g)^{-1}, CH_{4}: 1.36 μmol·h(^{-1} \cdot g)^{-1}</td>
<td>109</td>
</tr>
<tr>
<td>Bi_{2}O_{5}Cl/MoS_{2}</td>
<td>Self-assembly method</td>
<td>Ascorbic acid as the hole scavenger, under visible light (λ &gt; 420 nm, 300 W Xenon lamp)</td>
<td>H_{2}</td>
<td>33 mmol·h(^{-1} \cdot g)^{-1}</td>
<td>107</td>
</tr>
<tr>
<td>BiOCl/Au/MnOx</td>
<td>Photodeposition</td>
<td>Under simulated solar light (500 W Xenon lamp)</td>
<td>H_{2}</td>
<td>1.07*10(^{-2}) mmol·h(^{-1} \cdot g)^{-1}</td>
<td>109</td>
</tr>
<tr>
<td>Carbon-doped BiOCl/NiO_{x}</td>
<td>Hydrothermal method and photodeposition</td>
<td>Trithanolamine as the hole scavenger, under simulated solar light (300 W Xenon lamp)</td>
<td>H_{2}</td>
<td>0.42 mmol·h(^{-1} \cdot g)^{-1}</td>
<td>108</td>
</tr>
<tr>
<td>BiOCl/CuPc</td>
<td>Solvothermal synthesis</td>
<td>Under simulated solar light (500 W Xe lamp)</td>
<td>H_{2}</td>
<td>0.02 mmol·h(^{-1} \cdot g)^{-1}</td>
<td>113</td>
</tr>
<tr>
<td>BiOBr/α-Fe_{2}O_{3}</td>
<td>Hydrothermal synthesis</td>
<td>Under visible light, (λ &gt; 420 nm, 300 W Xenon lamp)</td>
<td>H_{2}</td>
<td>0.016 mmol·h(^{-1} \cdot g)^{-1}</td>
<td>113</td>
</tr>
</tbody>
</table>
Perspectives

Although significant efforts and great advances have been made in the design of Bi-based photocatalytic materials as efficient and robust \textit{p-block} photocatalysts over recent years, there are still several critical challenges remaining that need to be addressed in order to meet the demands of practical production applications. In particular, the correlation between band structures and the photocatalytic mechanism is still unclear, while finding protocols for newly designed \textit{p-block} catalysts with satisfactory performance is still a struggle and needs further improvement and investigation.

The future directions of research on Bi-based and related \textit{p-block} photocatalyst development in photocatalysis should be focused on the following aspects.

- From the analysis of stoichiometry alteration, the DFT calculations show that the upper VB of BiOX consists primarily of hybrids of O 2\textit{p} orbitals and X \textit{n}\textit{p} (\(n = 3, 4,\) and 5 for X = Cl, Br, and I) orbitals, whereas the lower CB is composed mainly of Bi 6\textit{p} orbitals. Therefore, by changing the halogen species and the ratios of Bi:O:X, and replacing Bi- with other metal atoms, new photocatalysts with the desired electronic structure and other physicochemical properties could be obtained with enhanced performance.

- Vacancy engineering has been a significant strategy for modifying photocatalysts to enhance the photoreduction activity. This is because
vacancies can affect the materials structure, and the introduction of defects can lead to lattice distortions and secondary phase formation. Nevertheless, apart from oxygen vacancy, few other kinds of defects/vacancies have been reported, which need to be verified by theoretical and experimental explorations. Furthermore, if these vacancies are occupied/modified by foreign metal atoms via advanced doping approaches, new photocatalytic systems with unprecedented catalytic activity might be achieved due to localized lattice distortions that arise from the dispersion of isolated single metal atoms.

Although the extension of light absorption and the enhanced separation of charge carriers can be achieved via the construction of heterostructures, the introduction of grain boundaries at the interfaces between semiconductors has become a new unexpected obstacle that limits their efficiency, due to the electron scattering and the prolonged travel distance of charge carriers moving to the surface. Incorporating features of each part of the heterostructure rationally into a single nanoparticle to build vertical or lateral heterostructures can significantly reduce and overcome the grain boundary problem.

For the lateral heterostructures, a $p$-$n$ junction pattern can be built in to integrate multiple $n$-type and $p$-type Bi-based semiconductors within a single nanosheet, so that the charge carriers can be separated automatically in-plane and accelerated by the electric field in the interface of the junction.
What is more, because the photogenerated electrons and holes in the interfaces can be transferred spatially in the vertical direction, the vertical \textit{p-n} heterojunction can also be an ideal model to design an efficient photoconversion system. Then, the photoredox reactions can proceed on the different exposed surfaces.

In addition, developing methods for the preparation of atomically-thin heterostructures will be an alternative efficient strategy to minimize the travel distance of charge carriers. At the atomically thin heterostructures, a short diffusion distance for the charge carriers will hinder electron-hole recombination and result in charge carriers that move easily to the surfaces of the heterostructures and then activate reactant molecules. The photoreduction properties of heterostructures can be tuned at the atomic level.
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The authors declare no competing financial interest.

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Jun Chen completed his PhD in Chemistry from the University of Wollongong (Australia) in 2003. He is currently appointed as a full professor at the Intelligent Polymer Research Institute (IPRI), Australian Institute of Innovative Materials, University of Wollongong. Prof. Chen is a chief investigator at The ARC Centre of Excellence for Electromaterials Science (ACES) with extensive skills in electroactive materials and sustainable chips/devices, and has demonstrated experience in high-tech spin-off companies. Prof. Chen has published over 180 journal papers with an H-index of 49, and his current research interests include: soft chip systems, electro-/bio-interfaces/inks, nano/micro-materials and printable device design and fabrication.

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References


63. Morgan, B. J.; Watson, G. W., A density functional theory+ U study of oxygen vacancy formation at the (110),(100),(101), and (001) surfaces of rutile TiO$_2$. *J. Phys. Chem. C* **2009**, *113*, (17), 7322-7328. DOI: 10.1021/jp811288n


77. Ye, L.; Jin, X.; Leng, Y.; Su, Y.; Xie, H.; Liu, C., Synthesis of black ultrathin BiOCl nanosheets for efficient photocatalytic H$_2$ production under visible light irradiation. J. Power Sources 2015, 293, 409-415. DOI: 10.1016/j.jpowsour.2015.05.101
81. Ye, L.; Jin, X.; Leng, Y.; Su, Y.; Xie, H.; Liu, C., Synthesis of black ultrathin BiOCl nanosheets for efficient photocatalytic H$_2$ production under visible light irradiation. J. Power Sources 2015, 293, 409-415. DOI: 10.1016/j.jpowsour.2015.05.101
87. Xu, J.; Teng, Y.; Teng, F., Effect of surface defect states on valence band and charge separation and transfer efficiency. Sci. Rep 2016, 6, 32457. DOI: 10.1038/srep32457


95. Li, H.; Qin, F.; Yang, Z.; Cui, X.; Wang, J.; Zhang, L., New reaction pathway induced by plasmon for selective benzyl alcohol oxidation on BiOCl possessing oxygen vacancies. J. Am. Chem. Soc. 2017, 139, (9), 3513-3521. DOI: 10.1021/jacs.6b12850


100. Dong, X. a.; Zhang, W.; Sun, Y.; Li, J.; Cen, W.; Cui, Z.; Huang, H.; Dong, F., Visible-light-induced charge transfer pathway and photocatalysis mechanism on Bi semimetal@ defective BiOBr hierarchical microstructures. J. Catal. 2018, 357, 41-50. DOI: 10.1016/j.jcat.2017.10.004


The perspective mainly focuses on the design and construction of bismuth-based solar-conversion systems with high efficiencies in photocatalytic reduction.