Photocatalytic reduction on Bi-based *p*-block semiconductors

Dandan Cui^{†‡}, Liang Wang[§], Yi Du^{†§}, Weichang Hao^{*†}, Jun Chen^{*‡}

[†]School of Physics, BUAA-UOW Joint Research Centre, Beihang University, Xueyuan Road No.37 Beijing 100191, China

[‡] ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, Australian Institute for Innovative Materials, Innovation Campus, University of Wollongong, Wollongong, NSW 2500, Australia

[§] Institute for Superconducting and Electronic Materials (ISEM), Australian Institute for Innovative Materials (AIIM), University of Wollongong, Wollongong, NSW 2500, Australia

Corresponding Authors

*W. Hao. E-mail: whao@buaa.edu.cn

*J. Chen. E-mail: junc@uow.edu.au

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_2O to H_2 ,¹⁻⁴ reduce CO_2 to carbon-based fuels⁵⁻⁷ and/or fix N_2 to ammonia via photocatalysts.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.^{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.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 TiO₂ 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 *via* reducing their effective mass, but also enhances both charge

separation and transportation in the photocatalytic process.^{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.¹⁹

I	II											III	IV	V	VI	VII	VIII	
H																		He
Li p^6s^1	Be											B s^2p	C s^2p^2	N s^2p^3	O s^2p^4	F s^2p^5	Ne	
Na p^6s^1	Mg											Al s^2p	Si s^2p^2	P s^2p^3	S s^2p^4	Cl s^2p^5	Ar	
K p^6s^1	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu $d^{10}s^1$	Zn $d^{10}s^2$	Ga s^2p	Ge s^2p^2	As s^2p^3	Se s^2p^4	Br s^2p^5	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag $d^{10}s^1$	Cd $d^{10}s^2$	In s^2p	Sn s^2p^2	Sb s^2p^3	Te s^2p^4	I s^2p^5	Xe	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl s^2p	Pb s^2p^2	Bi s^2p^3	Po s^2p^4	At s^2p^5	Rn	
Fr	Ra	Ac	Rf	Ha	Sg	Bh	Hs	Mt										

Candidates for materials with high carrier mobility

s-block

p-block

d-block

inertness

Figure 2. Candidate elements for materials with high carrier mobility in the periodic table (Red and black elements are possible cations and anions, respectively.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.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 [Bi₂O₂] 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.²³⁻²⁶

Generally, photoreduction reactions are regarded as playing a more significant role than photooxidation reactions for solving the energy crisis. Hydrogen from H₂O splitting and liquid fuels from CO₂ conversion can represent efficient energy sources, and ammonia from N₂ 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.^{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.^{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 *p*-block semiconductors, including constituent adjustment,³⁰⁻³⁶ vacancy engineering,³⁷⁻⁴¹ and construction of heterostructures.^{1, 7, 42-44}

This short review will provide a special overview of this emerging *p*-block Bi-based family of semiconductors for photocatalytic H₂ evolution, CO₂ reduction, and N₂ 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 *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 H₂ generation, CO₂ reduction, and N₂ fixation are different, the band structure parameters, such as the VB, CB, and band-gap energy (E_g), are crucial for photocatalytic activity.^{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 2*p* and X *np* states (X = Cl, Br, and I), while the CBM in most cases is constructed from Bi 6*p* states.^{45, 46} Based on previous reports, when the coordination of the electrons and potential field was changed, the electronic and band structures will be altered simultaneously.^{45, 47, 50} 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 Bi₂O₃ 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_xX_{1-x} (M, X = F, Cl, Br, I) photocatalysts can be obtained via a self-assembly process, such as BiOCl_xBr_{1-x}.^{32, 36, 54} BiOCl_xI_{1-x},⁵⁰ BiOBr_xI_{1-x},³⁴ 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 $\text{BiOCl}_{1-x}\text{Br}_x$ microspheres are narrowed gradually with an increasing Br-to-Cl molar ratio, which suggests that the band gap of $\text{BiOCl}_{1-x}\text{Br}_x$ 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 $\text{Bi}_x\text{O}_y\text{X}_z$, 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 $2p$ and X np ($n=3, 4$, and 5 for $X = \text{Cl}, \text{Br}$, and I , respectively) states dominate the VB, Bi $6p$ states contribute to the most of the CB. When the mole ratios of Bi and O contents are increased in $\text{Bi}_x\text{O}_y\text{X}_z$, 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 $\text{Bi}_{24}\text{O}_{31}\text{Br}_{10}$ (yellow balls: Bi, green balls: Br, and red balls: O). (b) Schematic illustration of the energy band structure of $\text{Bi}_{24}\text{O}_{31}\text{Br}_{10}$ with redox potentials. (c) Cycling tests of hydrogen evolution over $\text{Bi}_{24}\text{O}_{31}\text{Br}_{10}$ under visible-light irradiation.¹⁷ (d) Simulated charge density contour plot of $\text{Bi}_4\text{O}_5\text{Br}_2$ for the (100) surface. (e) Photocatalytic reduction activity of $\text{Bi}_4\text{O}_5\text{Br}_2$ towards CO_2 conversion and (f) comparison of fuel generation between BiOBr and $\text{Bi}_4\text{O}_5\text{Br}_2$.⁵⁵ Reproduced with permission.

For example, a Bi-based photocatalyst, $\text{Bi}_{24}\text{O}_{31}\text{Br}_{10}$, 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 $\text{Bi}_{24}\text{O}_{31}\text{Br}_{10}$ 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 $\text{Bi}_{24}\text{O}_{31}\text{Br}_{10}$ 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, $\text{Bi}_x\text{O}_y\text{X}_z$ compounds with decreased CBM potential also show excellent photocatalytic performance compared with the typical photocatalysts for CO_2 conversion.^{33, 55,}

⁵⁷ For example, $\text{Bi}_4\text{O}_5\text{Br}_2$ 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 $\text{Bi}_4\text{O}_5\text{Br}_2$ 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, $\text{Bi}_4\text{O}_5\text{X}_2$ ($\text{X} = \text{Br}$, I)^{57, 58} and $\text{Bi}_5\text{O}_7\text{I}$ 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 CH₄) generated by Bi₄O₅I₂ 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 TiO₂,⁶²⁻⁶⁶ WO₃,⁶⁷⁻⁷⁰ ZnO,^{71, 72} 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, CO₂ reduction, and N₂ fixation.

Oxygen vacancy

The oxygen vacancy has clearly been deeply studied, because it 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 H₂ 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 TiO₂ (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.⁸¹ 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).^{13, 38, 82} 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.⁶² 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 CO₂ reduction. Moreover, those vacancies can make the charge distribution more delocalized to stabilize the reduction intermediates of CO₂ photoreduction and lower the reaction energy barriers.

According to further *in-situ* Fourier transform infrared (FTIR) spectroscopy investigations related to the CO₂ photoreduction process (**Figure 6d**), CO₂ photoreduction on samples may proceed through three key steps: (1) Initial CO₂ adsorption on the catalyst surfaces, while, H₂O dissociates into hydroxyl and hydrogen ions on these surfaces; (2) Subsequently, the adsorbed CO₂* 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 CO₂ reduction to CO at a rate of 87.4 mmol g⁻¹ h⁻¹, which is 20 times and 24 times higher than those of BiOBr atomic layers and bulk BiOBr without oxygen vacancy.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 CO₂ and H₂O 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 N₂ or form solvated electrons (**Figure 7a**). BiOBr-OV, however, could steadily generate NH₃ in pure water without any sacrificial agent under visible light, while no reactivity for N₂ fixation was obtained from the defect-free BiOBr (**Figure 7b**). Theoretical calculations have shown that N₂ 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 N₂ (**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 N₂ fixation via energy-accessible intermediary steps, while the involvement of N₂ fixation pathways with distinct selective N₂ fixation products (for example, N₂H₂, N₂H₄, and NH₃) showed high dependence on the N₂ adsorption structures on OVs.⁸⁴

Figure 7. Photocatalytic N₂ fixation over the as-prepared BiOBr nanosheets: (a) Electronic energy-level diagram of BiOBr-001-OV; (b) Quantitative determination of the generated NH₃ under visible light ($\lambda > 420 \text{ nm}$). (c) Theoretical prediction of N₂ activation on an OV of BiOBr (001); (d) *In-situ* FTIR spectra recorded during the photocatalytic N₂ fixation over BiOBr-001-OV.⁸⁴ Reproduced with permission.

Another compelling advantage of solar N₂ fixation lies in the facile creation of OVs *via* light irradiation, which could generate sufficient light-switching surface OVs with suitable adsorption edges (**Figure 8a**).⁸⁶ As a result, Bi₅O₇Br-nanotube (NT) delivers excellent visible light-driven photocatalytic N₂ fixation performance with an NH₃ 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 N₂ fixation pathway of Bi₅O₇Br-NT can be determined (**Figure 8d**). N₂ molecules are chemisorbed and activated on the photoinduced OV sites, and the photoexcited electrons are injected into the activated N₂ to be reduced to NH₃. After the solar N₂ 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 Bi₅O₇Br 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) NH₃ generated by the as-prepared ultrafine Bi₅O₇Br nanotubes and BiOBr-001-OV nanosheets under visible light ($\lambda > 400$ nm) irradiation; (c) *In-situ* direct reflectance FTIR spectra from as-prepared ultrafine Bi₅O₇Br nanotubes during the photocatalytic N₂ fixation; (d) Schematic illustration of the photocatalytic N₂ fixation model on the Bi₅O₇Br nanotube surface.⁸⁶ 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 group⁸⁷ 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.⁸⁸ As shown in **Figure 9b** for $\text{BiO}_{1-x}\text{Cl}_{1-y}$, 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 $\text{BiO}_{1-x}\text{Cl}_{1-y}$ with a stronger photooxidation driving force and highly selective CO_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.

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.⁸⁹⁻⁹⁴ 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.⁹⁵ 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.^{96, 97} So, $\text{Bi}_x\text{O}_y\text{X}_z$ -based heterostructures combined with metallic nanomaterials or two-dimensional (2D) semiconductors can be expected to exhibit excellent photoreduction activities.

Metallic nanomaterial/ $\text{Bi}_x\text{O}_y\text{X}_z$ heterostructures.

The application of metallic co-catalysts to form metallic nanomaterial/ $\text{Bi}_x\text{O}_y\text{X}_z$ heterostructures is a significant strategy to enhance the photocatalytic reduction activity towards CO_2 reduction and H_2 evolution.⁹⁸ Normally, the photo-generated 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.⁹⁹ Moreover, the loaded metallic co-catalysts can further serve as redox active sites to promote the photocatalytic reaction.¹⁰⁰

In recent research, a strategy of dual-co-catalyst/ $\text{Bi}_x\text{O}_y\text{X}_z$ 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.¹⁰¹ 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 $169 \mu\text{mol g}^{-1}$ 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/ $\text{Bi}_x\text{O}_y\text{X}_z$ heterostructures, and endow BiOCl with excellent photocatalytic H_2O splitting activity.

Figure 10. (a) UV-vis-infrared (IR) driven photo-thermo-catalysis mechanism of Bi₄O₅I_{2-1.95} for converting CO₂ to chemical energy. (b) Rates of CO production under different ranges of sunlight (UV-vis-IR) induced photo-thermo catalysis to convert CO₂ to chemical energy over Bi₄O₅I_{2-1.00} and Bi₄O₅I_{2-1.95}.⁵⁸ (c) Band alignment at the interface of 1L-Bi₁₂O₁₇Cl₂/1L-MoS₂ 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-Bi₁₂O₁₇Cl₂, and the electron transfer at the interface along the Bi-S bonds. (e) Cycling tests of photocatalytic hydrogen evolution over 1L-Bi₁₂O₁₇Cl₂/1L-MoS₂ vertical heterostructure and 1L-Bi₁₂O₁₇Cl₂.⁹⁰ 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/ $\text{Bi}_x\text{O}_y\text{X}_z$ heterostructures, in which bismuth nanoparticles not only inhibit the recombination of charge carriers, but also accelerate the conversion of light to thermal energy.^{58, 102} Taking the semimetal Bi mediated $\text{Bi}_x\text{O}_y\text{X}_z$ as an example, $\text{Bi}/\text{Bi}_4\text{O}_5\text{I}_2$ heterostructures were formed through a molecular precursor hydrolytic process.⁵⁸ Remarkably increased photoreduction activity of $\text{Bi}/\text{Bi}_4\text{O}_5\text{I}_2$ can be achieved, which is attributed to the co-catalyst and photothermal effects of the loaded Bi nanoparticles, and $\text{Bi}/\text{Bi}_4\text{O}_5\text{I}_2$ at an optimal mole ratio displayed excellent photo-thermo-catalytic CO_2 conversion to solar fuels (CO and CH_4) (**Figure 10a,b**). The enhanced photo-induced carrier separation rate and reaction system temperature of $\text{Bi}/\text{Bi}_4\text{O}_5\text{I}_2$ 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 $\text{Bi}/\text{Bi}_4\text{O}_5\text{I}_2$ was enhanced to $40.02 \mu\text{mol h}^{-1}\text{g}^{-1}$ and $7.19 \mu\text{mol h}^{-1}\text{g}^{-1}$, respectively. The light-conversion efficiency was ~ 6.47 times higher than that of pure $\text{Bi}_4\text{O}_5\text{I}_2$. 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 $(\text{Bi}_{12}\text{O}_{17})$ -end-faces of $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ monolayers to build 2D janus (Cl_2) - $(\text{Bi}_{12}\text{O}_{17})$ -(MoS_2) bilayer junctions.⁹⁰ The separation, transportation, and consumption of carriers could thus be manipulated at the atomic level (**Figure**

10c). Visible-light-driven photogenerated charge carriers in $\text{BiI}_2\text{O}_{17}\text{Cl}_2$ are spatially separated by the internal electric field (IEF) to the $(\text{Bi}_{12}\text{O}_{17})$ 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 $33 \text{ mmol h}^{-1}\text{g}^{-1}$, 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/ $\text{Bi}_x\text{O}_y\text{X}_z$ heterostructure

$\text{Bi}_x\text{O}_y\text{X}_z$ -based semiconductors and other 2D materials such as g- C_3N_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.¹⁰³ 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/ $\text{Bi}_x\text{O}_y\text{X}_z$ heterostructures with optimized energy band alignments were employed to promote CO_2 photoreduction activity. Z-scheme $\text{BiOI/g-C}_3\text{N}_4$ 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

efficiency than the pristine samples (**Figure 11a,c**).¹⁰⁴ 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 ($\cdot\text{O}^{2-}$) and hydroxyl radical ($\cdot\text{OH}$) (**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/Bi_xO_yX_z 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⁻¹g⁻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 NiO_x 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-H₂O-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.

Bismuth-based Photocatalyst	Strategies	Conditions	Final Products	Photocatalytic activity	Reference
$\text{Bi}_{24}\text{O}_{31}\text{Br}_{10}$	0.14M NaOH aqueous solution	0.05g/20 mL H ₂ O and 10 mL of methanol; 300 W xenon lamp, $\lambda \geq 400$ nm	H ₂	$3.347 \mu\text{mol g}^{-1} \text{h}^{-1}$	17
$\text{Bi}_4\text{O}_5\text{Br}_2$	Glycerol	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	H ₂	4.21 $\mu\text{mol/h}$	114
$\text{Bi}_4\text{O}_5\text{I}_2$	Glycerol	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	H ₂	2.79 $\mu\text{mol/h}$	114
$\text{Bi}_4\text{O}_5\text{I}_2$	Change molar ratios	0.05g dispersed on glass; 300W Xe lamp	CO	CO: $66.43 \mu\text{mol h}^{-1} \text{g}^{-1}$; CH ₄ : $10.39 \mu\text{mol h}^{-1} \text{g}^{-1}$	58
$\text{Bi}_4\text{O}_5\text{I}_2$	Change molar ratios	0.1 g dispersed on tglass; 300 W Xe lamp	CO	CO: $19.82 \mu\text{mol g}^{-1} \text{h}^{-1}$	59
$\text{Bi}_5\text{O}_7\text{I}$	Change molar ratios	0.1 g dispersed on glass; 300 W Xe lamp, $\lambda \geq 420$ nm	CO	CO: $11.73 \mu\text{mol g}^{-1} \text{h}^{-1}$	59
$\text{Bi}_5\text{O}_7\text{Br}_2$	Hydrolytic process	0.15 g dispersed on glass; 300 W Xe lamp, $\lambda \geq 400$ nm	CO CH ₄	CO : $2.73 \mu\text{mol g}^{-1} \text{h}^{-1}$ CH ₄ : $2.04 \mu\text{mol g}^{-1} \text{h}^{-1}$	55
$\text{Bi}_4\text{O}_5\text{Br}_2$	Change molar ratios	50 mg dispersed on glass; 300 W Xe lamp, $\lambda \geq 400$ nm	CO CH ₄	CO : $2.71 \mu\text{mol g}^{-1} \text{h}^{-1}$ CH ₄ : $1.65 \mu\text{mol g}^{-1} \text{h}^{-1}$	57
$\text{Bi}_4\text{O}_5\text{I}_2$	Change molar ratios	50 mg dispersed on glass; 300 W Xe lamp, $\lambda \geq 400$ nm	CO CH ₄	CO : $15.87 \mu\text{mol g}^{-1} \text{h}^{-1}$ CH ₄ : $0.18 \mu\text{mol g}^{-1} \text{h}^{-1}$	57
$\text{Bi}_4\text{O}_5\text{BrI}$	Change molar ratios	50 mg dispersed on glass; 300 W Xe lamp, $\lambda \geq 400$ nm	CO CH ₄	CO : $22.85 \mu\text{mol g}^{-1} \text{h}^{-1}$ CH ₄ : $2.13 \mu\text{mol g}^{-1} \text{h}^{-1}$	57
$\text{Bi}_5\text{O}_7\text{Br}$	Self-assembled	0.025 g photocatalyst dispersed in 100 mL deionized water; 300 W Xe lamp, $\lambda \geq 400$ nm	NH ₃	1380 $\mu\text{mol g}^{-1} \text{h}^{-1}$	86
$\text{Bi}_5\text{O}_7\text{I}$	PH value	0.05 g /100 mL water containing 20% CH ₃ OH; 300 W Xe lamp, $\lambda \geq 400$ nm	NH ₃	4.62 $\mu\text{mol g}^{-1} \text{h}^{-1}$	115

Table 2. Vacancy engineering for bismuth-based *p*-block semiconductors.

Bismuth-based Photocatalyst	Strategies	Conditions	Final Products	Photocatalytic activity	Reference
BiOCl	Alcohol groups react with the oxygen	0.05g/50mL of water containing 10vol% TEOA 300 W xenon lamp, $\lambda \geq 420$ nm	H ₂	2.51 $\mu\text{mol/h}$	81
ultrathin BiOBr	Mannitol and PVP	0.01 g /100 ml aqueous solution; 500-W Xe lamp	H ₂	0.375 $\mu\text{mol/h}$	116
BiOBr	EG	samples on a fluorine-doped tin oxide (FTO) glass slide; 500W Xenon; AM 1.5 filter; $\lambda \geq 400$ nm	CH ₄ , CO	CH ₄ : 0.158 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CO: 4.94 $\mu\text{mol g}^{-1} \text{h}^{-1}$	117
ultrathin BiOBr	UV light irradiation	0.1g /100ml water 300W Xe lamp $\lambda \geq 400$ nm	CO	87.4 $\mu\text{mol g}^{-1} \text{h}^{-1}$	37
BiOI	Ethylene glycol	300 W Xe lamp 0.15 g dispersed on glass	CH ₄ , CO	CH ₄ : 0.063 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CO: 0.615 $\mu\text{mol g}^{-1} \text{h}^{-1}$	116
BiOCl	High viscosity solvent, thermal	0.05g dispersed on glass	CO	2.18 $\mu\text{mol g}^{-1} \text{h}^{-1}$	119
BiOCl	Ethylene glycol solution	0.05 g/100ml water; 300 W xenon; $\lambda \geq 420$ nm	NH ₃	223.3 $\mu\text{mol g}^{-1} \text{h}^{-1}$	84
BiOBr	Hydrogen	0.02 g/100ml water; 300 W xenon; $\lambda \geq 420$ nm	NH ₃	360.8 $\mu\text{mol g}^{-1} \text{h}^{-1}$	120

Table 3. Heterostructure strategy for the enhancement of photocatalytic efficiency on bismuth-based *p*-block semiconductors.

Bismuth-based Photocatalysts	Strategies of synthesis	Conditions	Final Products	Photocatalytic activity	Reference
BiOBr/g-C ₃ N ₄ /Au	Photodeposition	380 nm monochromatic light	CO, CH ₄	CO: 6.67 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, CH ₄ : 0.92 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	107
BiOI/C ₃ N ₄	Solvothermal method	EDTA as the hole scavenger, with I ³⁻ /I ⁻ redox mediators, under visible light ($\lambda > 420$ nm, 300 W Xenon lamp)	CO, CH ₄	CO: 3.45 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, CH ₄ : 0.164 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	104
Bi ₄ O ₅ I ₂ /g-C ₃ N ₄	Hydrolytic process	I ³⁻ /I ⁻ redox mediators, under visible light ($\lambda > 420$ nm, 300 W Xenon lamp)	CO, CH ₄	CO: 9.1 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, CH ₄ : 0.164 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	107
Bi ₄ O ₅ I ₂ /Bi	Solvothermal method	Under simulated solar light (300 W Xenon lamp)	CO, CH ₄	CO: 40.02 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, CH ₄ : 7.19 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	58
BiOBr/Bi ₂ O ₄	NaOH-induced dehalogenation and light triggered photogenerated hole oxidation	Under simulated solar light (300 W Xenon lamp)	CO, CH ₄	CO: 2.6 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, CH ₄ : 1.85 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	106
Au/BiOI/MnO _x	Photodeposition	Under simulated solar light (300 W Xenon lamp)	CO, CH ₄	CO: 42.9 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, CH ₄ : 1.36 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	99
Bi ₁₂ O ₁₇ Cl ₂ /MoS ₂	Self-assembly method	Ascorbic acid as the hole scavenger, under visible light ($\lambda > 420$ nm, 300 W Xenon lamp)	H ₂	33 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	90
BiOCl/Au/MnOx	Photodeposition	Under simulated solar light (500 W Xenon lamp)	H ₂	1.07*10 ⁻² $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	
Carbon-doped BiOCl/NiO _x	Hydrothermal method and photodeposition	Triethanolamine as the hole scavenger, under simulated solar light (300 W Xenon lamp)	H ₂	0.42 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	109
BiOCl/CuPc	Solvothermal synthesis	Under simulated solar light (500 W Xe lamp)	H ₂	0.02 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	113
BiOBr/ α -Fe ₂ O ₃	Hydrothermal synthesis	Under visible light, ($\lambda > 420$ nm, 300 W Xenon lamp)	H ₂	0.016 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	121

Perspectives

Although significant efforts and great advances have been made in the design of Bi-based photocatalytic materials as efficient and robust *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 *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 *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*p* orbitals and X *np* (*n* = 3, 4, and 5 for X = Cl, Br, and I) orbitals, whereas the lower CB is composed mainly of Bi 6*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 *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.

Author information

ORCID

Jun Chen:

Weichang Hao: 0000-0002-1597-7151

Yi Du: 0000-0003-1932-6732

Notes

These authors contributed equally to this work (D.C and L.W.).

The authors declare no competing financial interest.

Biographies

Miss Dandan Cui is currently a PhD candidate in Beihang University, and joined in University of Wollongong as a visiting student in 2017. Her research topic is about Innovative 2D Nanocrystals-defective BiOX (X=Cl,Br,I).

Liang Wang is currently a Ph.D. candidate in the Institute for Superconducting and Electronic Materials (ISEM) at the University of Wollongong, Australia. He obtained his B.S. degree in Materials Science from Nanjing University of Science and Technology in 2011 and an M.S. degree in Physics from Beihang University in 2015. His research focuses on the design and synthesis of two-dimensional vertical heterostructures for energy-conversion catalysis.

Yi Du received his Ph.D. from the Institute for Superconducting and Electronic Materials at the University of Wollongong, Australia (2011). His research interests include surface physics and chemistry, 2D materials, and catalysis studied by using scanning tunneling microscopy (STM) and angle-resolved photoemission spectroscopy (ARPES).

Weichang Hao received his B.S. degree (1997) in Materials Engineering from Northeastern University and Ph.D degree (2003) in Materials Physics from Lanzhou University. Then, he worked as postdoctoral fellow in Department of Physics of Beihang University (2003-2005). From 2005 and then, he was a faculty member in Department of Physics, Beihang University. He has been a full Professor of Condensed Matter Physics since 2013. He also conducted research as a Visiting Scholar in Tokyo Institute of Technology (Tokyo Tech) (2008, 2014) and University of Wollongong (UOW) (2011-2012). His scientific interest is focused on the electronic structure of oxide materials, oxide materials for environmental purification and energy conversion and 2D nanostructured materials and related devices. He has published 100 peer reviewed journal articles, and the work was cited more than 1500 times.

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.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (51672018, 51472016 and 51272015), Fundamental Research Fund for Centre University and Australian Research Council (ARC) Centre of Excellence Scheme (CE140100012&DP170102267 &DP170101467). The authors would like to thank the Australian National Fabrication Facility—Materials node. D.C. would like to acknowledge the scholarship support from China Scholarship Council (CSC).

References

1. Zhang, X.; Zhang, Z.; Wu, D.; Zhang, X.; Zhao, X.; Zhou, Z., Computational Screening of 2D Materials and Rational Design of Heterojunctions for Water Splitting Photocatalysts. *Small Methods* **2018**, 2, (5), 1700359. DOI: 10.1002/smt.201700359
2. Zhang, L.; Wang, W.; Sun, S.; Jiang, D.; Gao, E., Selective transport of electron and hole among {0 0 1} and {1 1 0} facets of BiOCl for pure water splitting. *Appl. Catal., B* **2015**, 162, 470-474. DOI: 10.1016/j.apcatb.2014.07.024
3. Takanabe, K., Photocatalytic Water Splitting: Quantitative Approaches toward Photocatalyst by Design. *ACS Catal.* **2017**, 7, (11), 8006-8022. DOI: 10.1021/acscatal.7b02662
4. Ahmad, H.; Kamarudin, S. K.; Minggu, L. J.; Kassim, M., Hydrogen from photo-catalytic water splitting process: A review. *Renewable Sustainable Energy Rev.* **2015**, 43, 599-610. DOI: 10.1016/j.rser.2014.10.101
5. Yu, J.; Low, J.; Xiao, W.; Zhou, P.; Jaroniec, M., Enhanced photocatalytic CO₂-reduction activity of anatase TiO₂ by coexposed {001} and {101} facets. *J. Am. Chem. Soc.* **2014**, 136, (25), 8839-42. DOI: 10.1021/ja5044787
6. Kuriki, R.; Ichibha, T.; Hongo, K.; Lu, D.; Maezono, R.; Kageyama, H.; Ishitani, O.; Oka, K.; Maeda, K., A Stable, Narrow-Gap Oxyfluoride Photocatalyst for Visible-Light Hydrogen Evolution and Carbon Dioxide Reduction. *J. Am. Chem. Soc.* **2018**, 140, (21), 6648-6655. DOI: 10.1021/jacs.8b02822
7. Highfield, J., Advances and recent trends in heterogeneous photo(electro)-catalysis for solar fuels and chemicals. *Molecules* **2015**, 20, (4), 6739-93. DOI: 10.3390/molecules20046739
8. Yuan, S. J.; Chen, J. J.; Lin, Z. Q.; Li, W. W.; Sheng, G. P.; Yu, H. Q., Nitrate formation from atmospheric nitrogen and oxygen photocatalysed by nano-sized titanium dioxide. *Nat Commun.* **2013**, 4, 2249. DOI: 10.1038/ncomms3249
9. Foster, S. L.; Bakovic, S. I. P.; Duda, R. D.; Maheshwari, S.; Milton, R. D.; Minteer, S. D.; Janik, M. J.; Renner, J. N.; Greenlee, L. F., Catalysts for nitrogen reduction to ammonia. *Nat Catal.* **2018**, 1, (7), 490-500. DOI:10.1038/s41929-018-0092-7
10. Chen, J. G.; Crooks, R. M.; Seefeldt, L. C.; Bren, K. L.; Bullock, R. M.; Darensbourg, M. Y.; Holland, P. L.; Hoffman, B.; Janik, M. J.; Jones, A. K.; Kanatzidis, M. G.; King, P.; Lancaster, K. M.; Lyman, S. V.; Pfromm, P.; Schneider, W. F.; Schrock, R. R., Beyond fossil fuel-driven nitrogen transformations. *Science* **2018**, 360, (6391). DOI: 10.1126/science.aar6611
11. Wang, Z.; Liu, Y.; Huang, B.; Dai, Y.; Lou, Z.; Wang, G.; Zhang, X.; Qin, X., Progress on extending the light absorption spectra of photocatalysts. *Phys. Chem. Chem. Phys.* **2014**, 16, (7), 2758-74 DOI: 10.1039/C3CP53817F
12. Wan, J.; Lacey, S. D.; Dai, J.; Bao, W.; Fuhrer, M. S.; Hu, L., Tuning two-dimensional nanomaterials by intercalation: materials, properties and applications. *Chem. Soc. Rev.* **2016**, 45, (24), 6742-6765. DOI: 10.1039/C5CS00758E
13. Feng, H.; Xu, Z.; Ren, L.; Liu, C.; Zhuang, J.; Hu, Z.; Xu, X.; Chen, J.; Wang, J.; Hao, W.; Du, Y.; Dou, S. X., Activating Titania for Efficient Electrocatalysis by Vacancy Engineering. *ACS Catal.* **2018**, 8, (5), 4288-4293. DOI: 10.1021/acscatal.8b00719
14. Feng, H.; Du, Y.; Wang, C.; Hao, W., Efficient visible-light photocatalysts by constructing dispersive energy band with anisotropic *p* and *s-p* hybridization states. *Curr. Opin. Green Sustainable Chem.* **2017**, 6, 93-100. DOI: 10.1016/j.cogsc.2017.05.008
15. Feng, H.; Xu, Z.; Wang, L.; Yu, Y.; Mitchell, D.; Cui, D.; Xu, X.; Shi, J.; Sannomiya, T.; Du, Y.; Hao, W.; Dou, S. X., Modulation of Photocatalytic Properties by Strain in 2D BiOBr Nanosheets. *ACS Appl. Mater. Interfaces.* **2015**, 7, (50), 27592-6. DOI: 10.1021/acsami.5b08904
16. Cui, D.; Wang, L.; Xu, K.; Ren, L.; Wang, L.; Yu, Y.; Du, Y.; Hao, W., Band-gap engineering of BiOCl with oxygen vacancies for efficient photooxidation properties under visible-light irradiation. *J. Mater. Chem. A* **2018**, 6, (5), 2193-2199. DOI: 10.1039/C7TA09897A
17. Shang, J.; Hao, W.; Lv, X.; Wang, T.; Wang, X.; Du, Y.; Dou, S.; Xie, T.; Wang, D.; Wang, J., Bismuth Oxybromide with Reasonable Photocatalytic Reduction Activity under Visible Light. *ACS Catal.* **2014**, 4, (3), 954-961. DOI: 10.1021/cs401025u

18. Li, L.; Chen, T.; Liu, Z.; Feng, P., Novel BiO_{2-x} photocatalyst: Typical hierarchical architecture and commendable activity. *Mater. Lett.* **2018**, 212, 267-270. DOI: 10.1016/j.matlet.2017.10.078
19. Xu, Z.; Xu, K.; Feng, H.; Du, Y.; Hao, W., s-p orbital hybridization: a strategy for developing efficient photocatalysts with high carrier mobility. *Sci. Bull* **2018**, 63, (8), 465-468. DOI: 10.1016/j.scib.2018.02.020
20. Ye, L.; Su, Y.; Jin, X.; Xie, H.; Zhang, C., Recent advances in BiOX (X= Cl, Br and I) photocatalysts: synthesis, modification, facet effects and mechanisms. *Environ Sci-Nano* **2014**, 1, (2), 90-112. DOI: 10.1039/C3EN00098B
21. Li, M.; Huang, H.; Yu, S.; Tian, N.; Zhang, Y., Facet, Junction and Electric Field Engineering of Bismuth-Based Materials for Photocatalysis. *ChemCatChem* **2018**, 10, 1-21 DOI: 10.1002/cctc.201800859
22. Jin, X.; Ye, L.; Xie, H.; Chen, G., Bismuth-rich bismuth oxyhalides for environmental and energy photocatalysis. *Coordin Chem Rev* **2017**, 349, 84-101. DOI: 10.1016/j.ccr.2017.08.010
23. Zhao, K.; Zhang, L.; Wang, J.; Li, Q.; He, W.; Yin, J. J., Surface structure-dependent molecular oxygen activation of BiOCl single-crystalline nanosheets. *J. Am. Chem. Soc.* **2013**, 135, (42), 15750-3. DOI: 10.1021/ja4092903
24. Wu, X.; Zhang, K.; Zhang, G.; Yin, S., Facile preparation of BiOX (X = Cl, Br, I) nanoparticles and up-conversion phosphors/BiOBr composites for efficient degradation of NO gas: Oxygen vacancy effect and near infrared light responsive mechanism. *Chem Eng J* **2017**, 325, 59-70. DOI: 10.1016/j.cej.2017.05.044
25. Wang, G.; Luo, X.; Huang, Y.; Kuang, A.; Yuan, H.; Chen, H., BiOX/BiOY (X, Y = F, Cl, Br, I) superlattices for visible light photocatalysis applications. *RSC Advances* **2016**, 6, (94), 91508-91516. DOI: 10.1039/C6RA14915D
26. Ganose, A. M.; Cuff, M.; Butler, K. T.; Walsh, A.; Scanlon, D. O., Interplay of Orbital and Relativistic Effects in Bismuth Oxyhalides: BiOF, BiOCl, BiOBr, and BiOI. *Chem. Mater.* **2016**, 28, (7), 1980-1984. DOI: 10.1021/acs.chemmater.6b00349
27. Nosaka, Y.; Nishikawa, M.; Nosaka, A. Y., Spectroscopic investigation of the mechanism of photocatalysis. *Molecules* **2014**, 19, (11), 18248-67. DOI: 10.3390/molecules191118248
28. Liu, Y.; Feng, H.; Yan, X.; Wang, J.; Yang, H.; Du, Y.; Hao, W., The origin of enhanced photocatalytic activities of hydrogenated TiO₂ nanoparticles. *Dalton Trans.* **2017**, 46, (32), 10694-10699. DOI: 10.1039/C7DT00827A
29. Li, G.; Blake, G. R.; Palstra, T. T., Vacancies in functional materials for clean energy storage and harvesting: the perfect imperfection. *Chem. Soc. Rev.* **2017**, 46, (6), 1693-1706. DOI: 10.1039/C6CS00571C
30. Bhachu, D. S.; Moniz, S. J. A.; Sathasivam, S.; Scanlon, D. O.; Walsh, A.; Bawaked, S. M.; Mokhtar, M.; Obaid, A. Y.; Parkin, I. P.; Tang, J.; Carmalt, C. J., Bismuth oxyhalides: synthesis, structure and photoelectrochemical activity. *Chem. Sci.* **2016**, 7, (8), 4832-4841. DOI: 10.1039/C6SC00389C
31. Xie, J.; Cao, Y.; Jia, D.; Li, Y., Dahlia-shaped BiOCl_xI_{1-x} structures prepared by a facile solid-state method: Evidence and mechanism of improved photocatalytic degradation of rhodamine B dye. *J. Colloid Interface Sci* **2017**, 503, 115-123. DOI: 10.1016/j.jcis.2017.05.016
32. Wu, T.; Li, X.; Zhang, D.; Dong, F.; Chen, S., Efficient visible light photocatalytic oxidation of NO with hierarchical nanostructured 3D flower-like BiOCl_xBr_{1-x} solid solutions. *J. Alloy. Compd.* **2016**, 671, 318-327. DOI: 10.1016/j.jallcom.2016.01.267
33. Liu, D.; Yao, W.; Wang, J.; Liu, Y.; Zhang, M.; Zhu, Y., Enhanced visible light photocatalytic performance of a novel heterostructured Bi₄O₅Br₂/Bi₂₄O₃₁Br₁₀/Bi₂SiO₅ photocatalyst. *Appl. Catal. B* **2015**, 172-173, 100-107. DOI: 10.1016/j.apcatb.2015.01.037
34. Li, X.; Chen, T.; Lin, H.; Cao, J.; Huang, H.; Chen, S., Intensive photocatalytic activity enhancement of Bi₅O₇I via coupling with band structure and content adjustable BiOBr_xI_{1-x}. *Sci. Bull* **2018**, 63, (4), 219-227. DOI: 10.1016/j.scib.2017.12.016
35. Jin, X.; Lv, C.; Zhou, X.; Zhang, C.; Meng, Q.; Liu, Y.; Chen, G., Molecular adsorption promotes carrier migration: Key step for molecular oxygen activation of defective Bi₄O₅I₂. *Appl. Catal. B* **2018**, 226, 53-60. DOI: 10.1016/j.apcatb.2017.12.008

36. Bai, Y.; Yang, P.; Wang, P.; Fan, Z.; Xie, H.; Wong, P. K.; Ye, L., Solid phase fabrication of Bismuth-rich $\text{Bi}_3\text{O}_4\text{Cl}_x\text{Br}_{1-x}$ solid solution for enhanced photocatalytic NO removal under visible light. *J Taiwan Inst Chem Eng* **2018**, *82*, 273-280. DOI: 10.1016/j.jtice.2017.10.021
37. Wu, J.; Li, X.; Shi, W.; Ling, P.; Sun, Y.; Jiao, X.; Gao, S.; Liang, L.; Xu, J.; Yan, W., Efficient Visible-Light-Driven CO_2 Reduction Mediated by Defect-Engineered BiOBr Atomic Layers. *Angew. Chem.* **2018**, *130*, (28), 8855-8859. DOI: 10.1002/ange.201803514
38. Wang, H.; Yong, D.; Chen, S.; Jiang, S.; Zhang, X.; Shao, W.; Zhang, Q.; Yan, W.; Pan, B.; Xie, Y., Oxygen-Vacancy-Mediated Exciton Dissociation in BiOBr for Boosting Charge-Carrier-Involved Molecular Oxygen Activation. *J. Am. Chem. Soc.* **2018**, *140*, (5), 1760-1766. DOI: 10.1021/jacs.7b1099
39. Queisser, H. J.; Haller, E. E., Defects in semiconductors: some fatal, some vital. *Science* **1998**, *281*, (5379), 945-950. DOI: 10.1126/science.281.5379.945
40. Janusz, N., Titanium dioxide-based semiconductors for solar-driven environmentally friendly applications: impact of point defects on performance. *Energy Environ. Sci.*, **2008**, *1*, 565-572 DOI: 10.1039/B809111K
41. Alkauskas, A.; McCluskey, M. D.; Van de Walle, C. G., Tutorial: Defects in semiconductors—Combining experiment and theory. *J. Appl. Phys.* **2016**, *119*, (18), 181101. DOI: 10.1063/1.4948245
42. Wetchakun, N.; Chaiwichain, S.; Inceesungvorn, B.; Pingmuang, K.; Phanichphant, S.; Minett, A. I.; Chen, J., $\text{BiVO}_4/\text{CeO}_2$ nanocomposites with high visible-light-induced photocatalytic activity. *ACS Appl. Mater. Interfaces*. **2012**, *4*, (7), 3718-3723. DOI: 10.1021/am300812n
43. Huang, H.; Han, X.; Li, X.; Wang, S.; Chu, P. K.; Zhang, Y., Fabrication of multiple heterojunctions with tunable visible-light-active photocatalytic reactivity in BiOBr-BiOI full-range composites based on microstructure modulation and band structures. *ACS Appl. Mater. Interfaces* **2015**, *7*, (1), 482-92. DOI: 10.1021/am5065409
44. Kudo, A.; Miseki, Y., Heterogeneous photocatalyst materials for water splitting. *Chem. Soc. Rev.* **2009**, *38*, (1), 253-78. DOI: 10.1039/B800489G
45. Yang, W.; Wen, Y.; Chen, R.; Zeng, D.; Shan, B., Study of structural, electronic and optical properties of tungsten doped bismuth oxychloride by DFT calculations. *Phys. Chem. Chem. Phys.* **2014**, *16*, (39), 21349-55. DOI: 10.1039/C4CP02801E
46. Dutta, S.; Das, T.; Datta, S., Impact of bi-axial strain on the structural, electronic and optical properties of photo-catalytic bulk bismuth oxyhalides. *Phys. Chem. Chem. Phys.* **2017**, *20*, (1), 103-111. DOI: 10.1039/C7CP07366F
47. Kato, D.; Hongo, K.; Maezono, R.; Higashi, M.; Kunioku, H.; Yabuuchi, M.; Suzuki, H.; Okajima, H.; Zhong, C.; Nakano, K.; Abe, R.; Kageyama, H., Valence Band Engineering of Layered Bismuth Oxyhalides toward Stable Visible-Light Water Splitting: Madelung Site Potential Analysis. *J. Am. Chem. Soc.* **2017**, *139*, (51), 18725-18731. DOI: 10.1021/jacs.7b11497
48. Nahar, S.; Zain, M. F. M.; Kadhum, A. A. H.; Hasan, H. A.; Hasan, M. R., Advances in Photocatalytic CO_2 Reduction with Water: A Review. *Materials* **2017**, *10*, (6). DOI: 10.3390/ma10060629
49. Li, K.; An, X.; Park, K. H.; Khraisheh, M.; Tang, J., A critical review of CO_2 photoconversion: Catalysts and reactors. *Catal. Today* **2014**, *224*, 3-12. DOI: 10.1016/j.cattod.2013.12.006
50. Xiao, X.; Liu, C.; Hu, R.; Zuo, X.; Nan, J.; Li, L.; Wang, L., Oxygen-rich bismuth oxyhalides: generalized one-pot synthesis, band structures and visible-light photocatalytic properties. *J. Mater. Chem* **2012**, *22*, (43), 22840. DOI: 10.1039/C2JM33556E
51. Lv, J.; Hu, Q.; Cao, C.; Zhao, Y., Modulation of valence band maximum edge and photocatalytic activity of BiOX by incorporation of halides. *Chemosphere* **2018**, *191*, 427-437. DOI: 10.1016/j.chemosphere.2017.09.149
52. Tang, Z. K.; Yin, W. J.; Le, Z.; Wen, B.; Zhang, D. Y.; Liu, L. M.; Lau, W. M., Spatial separation of photo-generated electron-hole pairs in BiOBr/BiOI bilayer to facilitate water splitting. *Sci. Rep* **2016**, *6*, 32764. DOI: 10.1038/srep32764
53. Huizhong, A.; Yi, D.; Tianmin, W.; Cong, W.; Weichang, H.; Zhang, J., Photocatalytic properties of biox (X= Cl, Br, and I). *Rare Metals* **2008**, *27*, (3), 243-250. DOI: 10.1016/S1001-0521(08)60123-0

54. Qin, Q.; Guo, Y.; Zhou, D.; Yang, Y.; Guo, Y., Facile growth and composition-dependent photocatalytic activity of flowerlike $\text{BiOCl}_{1-x}\text{Br}_x$ hierarchical microspheres. *Appl. Surf. Sci.* **2016**, *390*, 765-777. DOI: 10.1016/j.apsusc.2016.08.134
55. Ye, L.; Jin, X.; Liu, C.; Ding, C.; Xie, H.; Chu, K. H.; Wong, P. K., Thickness-ultrathin and bismuth-rich strategies for BiOBr to enhance photoreduction of CO_2 into solar fuels. *Appl. Catal. B* **2016**, *187*, 281-290. DOI: 10.1016/j.apcatb.2016.01.044
56. Wang, L.; Shang, J.; Hao, W.; Jiang, S.; Huang, S.; Wang, T.; Sun, Z.; Du, Y.; Dou, S.; Xie, T.; Wang, D.; Wang, J., A dye-sensitized visible light photocatalyst- $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$. *Sci. Rep* **2014**, *4*, 7384. DOI: 10.1038/srep07384
57. Bai, Y.; Ye, L.; Chen, T.; Wang, P.; Wang, L.; Shi, X.; Wong, P. K., Synthesis of hierarchical bismuth-rich $\text{Bi}_4\text{O}_5\text{Br}_x\text{I}_{2-x}$ solid solutions for enhanced photocatalytic activities of CO_2 conversion and Cr (VI) reduction under visible light. *Appl. Catal., B* **2017**, *203*, 633-640. DOI: 10.1016/j.apcatb.2016.10.066
58. Bai, Y.; Yang, P.; Wang, P.; Xie, H.; Dang, H.; Ye, L., Semimetal bismuth mediated UV-vis-IR driven photo-thermocatalysis of $\text{Bi}_4\text{O}_5\text{I}_2$ for carbon dioxide to chemical energy. *Journal of CO₂ Utilization* **2018**, *23*, 51-60. DOI: 10.1016/j.jcou.2017.11.007
59. Ding, C.; Ye, L.; Zhao, Q.; Zhong, Z.; Liu, K.; Xie, H.; Bao, K.; Zhang, X.; Huang, Z., Synthesis of $\text{Bi}_x\text{O}_y\text{I}_z$ from molecular precursor and selective photoreduction of CO_2 into CO. *J. CO₂ Util* **2016**, *14*, 135-142. DOI: 10.1016/j.jcou.2016.04.012
60. Zhang, X.; Zhao, L.; Fan, C.; Liang, Z.; Han, P., Effects of oxygen vacancy on the electronic structure and absorption spectra of bismuth oxychloride. *Comput. Mater. Sci.* **2012**, *61*, 180-184. DOI: 10.1016/j.commatsci.2012.04.023
61. Zhang, L.; Jia, Y.; Gao, G.; Yan, X.; Chen, N.; Chen, J.; Soo, M. T.; Wood, B.; Yang, D.; Du, A., Graphene Defects Trap Atomic Ni Species for Hydrogen and Oxygen Evolution Reactions. *Chem* **2018**, *4*, (2), 285-297. DOI: 10.1016/j.chempr.2017.12.005
62. Nakamura, I.; Negishi, N.; Kutsuna, S.; Ihara, T.; Sugihara, S.; Takeuchi, K., Role of oxygen vacancy in the plasma-treated TiO_2 photocatalyst with visible light activity for NO removal. *J. Mol. Catal. A: Chem* **2000**, *161*, (1-2), 205-212. DOI: 10.1016/S1381-1169(00)00362-9
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
64. Linsebigler, A.; Lu, G.; Yates Jr, J. T., CO chemisorption on TiO_2 (110): Oxygen vacancy site influence on CO adsorption. *J. Chem. Phys* **1995**, *103*, (21), 9438-9443. DOI: 10.1063/1.470005
65. Hirakawa, H.; Hashimoto, M.; Shiraiishi, Y.; Hirai, T., Photocatalytic Conversion of Nitrogen to Ammonia with Water on Surface Oxygen Vacancies of Titanium Dioxide. *J. Am. Chem. Soc.* **2017**, *139*, 10929-10936. DOI: 10.1021/jacs.7b06634
66. Wendt, S.; Schaub, R.; Matthiesen, J.; Vestergaard, E. K.; Wahlström, E.; Rasmussen, M. D.; Thostrup, P.; Molina, L.; Lægsgaard, E.; Stensgaard, I., Oxygen vacancies on TiO_2 (1 1 0) and their interaction with H_2O and O_2 : A combined high-resolution STM and DFT study. *Surf. Sci.* **2005**, *598*, (1-3), 226-245. DOI: 10.1016/j.susc.2005.08.041
67. Wang, F.; Di Valentin, C.; Pacchioni, G., Doping of WO_3 for photocatalytic water splitting: hints from density functional theory. *J. Phys. Chem. C* **2012**, *116*, (16), 8901-8909. DOI: 10.1021/jp300867j
68. Li, W.; Da, P.; Zhang, Y.; Wang, Y.; Lin, X.; Gong, X.; Zheng, G., WO_3 nanoflakes for enhanced photoelectrochemical conversion. *ACS nano* **2014**, *8*, (11), 11770-11777. DOI: 10.1021/nn5053684
69. Karazhanov, S. Z.; Zhang, Y.; Mascarenhas, A.; Deb, S.; Wang, L.-W., Oxygen vacancy in cubic WO_3 studied by first-principles pseudopotential calculation. *Solid State Ionics* **2003**, *165*, (1-4), 43-49. DOI: 10.1016/j.ssi.2003.08.012
70. Epifani, M.; Comini, E.; Díaz, R. I.; Andreu, T.; Genç, A.; Arbiol, J.; Siciliano, P.; Faglia, G.; Morante, J. R., Solvothermal, chloroalkoxide-based synthesis of monoclinic WO_3 quantum dots and gas-sensing enhancement by surface oxygen vacancies. *ACS Appl. Mater. Interfaces* **2014**, *6*, (19), 16808-16816. DOI: 10.1021/am504158r

71. Leiter, F.; Alves, H.; Hofstaetter, A.; Hofmann, D.; Meyer, B., The oxygen vacancy as the origin of a green emission in undoped ZnO. *Phys. Stat. sol. (b)* **2001**, 226, (1), R4-R5. DOI: 10.1002/1521-3951(200107)226
72. Wang, J.; Wang, Z.; Huang, B.; Ma, Y.; Liu, Y.; Qin, X.; Zhang, X.; Dai, Y., Oxygen vacancy induced band-gap narrowing and enhanced visible light photocatalytic activity of ZnO. *ACS Appl. Mater. Interfaces* **2012**, 4, (8), 4024-4030. DOI: 10.1021/am300835p
73. Zhao, Z.; Zhou, Y.; Wang, F.; Zhang, K.; Yu, S.; Cao, K., Polyaniline-decorated {001} facets of Bi₂O₂CO₃ nanosheets: in situ oxygen vacancy formation and enhanced visible light photocatalytic activity. *ACS Appl. Mater. Interfaces* **2014**, 7, (1), 730-737. DOI: 10.1021/am507089x
74. Lv, Y.; Yao, W.; Ma, X.; Pan, C.; Zong, R.; Zhu, Y., The surface oxygen vacancy induced visible activity and enhanced UV activity of a ZnO_{1-x} photocatalyst. *Catal. Sci. Technol* **2013**, 3, (12), 3136-3146. DOI: 10.1039/C3CY00369H
75. Pan, X.; Yang, M.-Q.; Fu, X.; Zhang, N.; Xu, Y.-J., Defective TiO₂ with oxygen vacancies: synthesis, properties and photocatalytic applications. *Nanoscale* **2013**, 5, (9), 3601-3614. DOI: 10.1039/C3NR00476G
76. Tan, H.; Zhao, Z.; Zhu, W.-b.; Coker, E. N.; Li, B.; Zheng, M.; Yu, W.; Fan, H.; Sun, Z., Oxygen vacancy enhanced photocatalytic activity of perovskite SrTiO₃. *ACS Appl. Mater. Interfaces* **2014**, 6, (21), 19184-19190. DOI: 10.1021/am5051907
77. Ye, L.; Jin, X.; Leng, Y.; Su, Y.; Xie, H.; Liu, C., Synthesis of black ultrathin BiOCl nanosheets for efficient photocatalytic H₂ production under visible light irradiation. *J. Power Sources* **2015**, 293, 409-415. DOI: 10.1016/j.jpowsour.2015.05.101
78. Wang, G.; Wang, H.; Ling, Y.; Tang, Y.; Yang, X.; Fitzmorris, R. C.; Wang, C.; Zhang, J. Z.; Li, Y., Hydrogen-treated TiO₂ nanowire arrays for photoelectrochemical water splitting. *Nano lett.* **2011**, 11, (7), 3026-3033. DOI: 10.1021/nl201766h
79. Zhang, K.; Liang, J.; Wang, S.; Liu, J.; Ren, K.; Zheng, X.; Luo, H.; Peng, Y.; Zou, X.; Bo, X.; Li, J.; Yu, X., BiOCl Sub-Microcrystals Induced by Citric Acid and Their High Photocatalytic Activities. *Cryst Growth Des.* **2012**, 12, (2), 793-803. DOI: 10.1021/cg201112j
80. Lei, F.; Sun, Y.; Liu, K.; Gao, S.; Liang, L.; Pan, B.; Xie, Y., Oxygen vacancies confined in ultrathin indium oxide porous sheets for promoted visible-light water splitting. *J. Am. Chem. Soc.* **2014**, 136, (19), 6826-6829. DOI: 10.1021/ja501866r
81. Ye, L.; Jin, X.; Leng, Y.; Su, Y.; Xie, H.; Liu, C., Synthesis of black ultrathin BiOCl nanosheets for efficient photocatalytic H₂ production under visible light irradiation. *J. Power Sources* **2015**, 293, 409-415. DOI: 10.1016/j.jpowsour.2015.05.101
82. Li, H.; Shang, J.; Yang, Z.; Shen, W.; Ai, Z.; Zhang, L., Oxygen vacancy associated surface Fenton chemistry: surface structure dependent hydroxyl radicals generation and substrate dependent reactivity. *Environ Sci Technol* **2017**, 51, (10), 5685-5694. DOI: 10.1021/acs.est.7b00040
83. Li, J.; Li, H.; Zhan, G.; Zhang, L., Solar Water Splitting and Nitrogen Fixation with Layered Bismuth Oxyhalides. *Acc. Chem. Res* **2017**, 50, (1), 112-121. DOI: 10.1021/acs.est.7b00040
84. Li, H.; Shang, J.; Ai, Z.; Zhang, L., Efficient Visible Light Nitrogen Fixation with BiOBr Nanosheets of Oxygen Vacancies on the Exposed {001} Facets. *J. Am. Chem. Soc.* **2015**, 137, (19), 6393-9. DOI: 10.1021/jacs.5b03105
85. Xu, C.; Qiu, P.; Li, L.; Chen, H.; Jiang, F.; Wang, X., Bismuth Subcarbonate with Designer Defects for Broad-Spectrum Photocatalytic Nitrogen Fixation. *ACS Appl. Mater. Interfaces.* **2018**, 10, 25321-25328. DOI: 10.1021/acsami.8b05925
86. Wang, S.; Hai, X.; Ding, X.; Chang, K.; Xiang, Y.; Meng, X.; Yang, Z.; Chen, H.; Ye, J., Light-Switchable Oxygen Vacancies in Ultrafine Bi₅O₇Br Nanotubes for Boosting Solar-Driven Nitrogen Fixation in Pure Water. *Adv. Mater.* **2017**, 29, (31), 1701774. DOI: 10.1002/adma.201701774
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
88. Li, M.; Zhang, Y.; Li, X.; Wang, Y.; Dong, F.; Ye, L.; Yu, S.; Huang, H., Nature-derived approach to oxygen and chlorine dual-vacancies for efficient photocatalysis and photoelectrochemistry. *ACS Sustain. Chem. Eng.* **2018**, 6, (2), 2395-2406. DOI: 10.1021/acssuschemeng.7b03847
89. Zhou, Y.; Zhang, Y.; Lin, M.; Long, J.; Zhang, Z.; Lin, H.; Wu, J. C.-S.; Wang, X., Monolayered Bi₂WO₆ nanosheets mimicking heterojunction interface with open surfaces for photocatalysis. *Nat. Commun* **2015**, 6, 8340. DOI: 10.1038/ncomms9340

90. Li, J.; Zhan, G.; Yu, Y.; Zhang, L., Superior visible light hydrogen evolution of Janus bilayer junctions via atomic-level charge flow steering. *Nat. Commun* **2016**, *7*, 11480. DOI: 10.1038/ncomms11480
91. Ran, J.; Gao, G.; Li, F.-T.; Ma, T.-Y.; Du, A.; Qiao, S.-Z., Ti₃C₂ MXene co-catalyst on metal sulfide photo-absorbers for enhanced visible-light photocatalytic hydrogen production. *Nat. Commun* **2017**, *8*, 13907. DOI: 10.1038/ncomms13907
92. Mahadeo, A.; Hee-Suk, Ch.; Su-Yong, L.; Min Cho, Jum.; S, J., In-Situ Noble Fabrication of Bi₂S₃/BiVO₄ Hybrid Nanostructure through a Photoelectrochemical Transformation Process for Solar Hydrogen Production. *ACS Sustainable Chem. Eng.* **2018**, *6*, 12489-12501. DOI: 10.1021/acssuschemeng.8b03140
93. Zhou, B.; Song, J.; Xie, C.; Chen, Ch.; Qian, Q.; Han, B., Mo – Bi – Cd Ternary Metal Chalcogenides: Highly Efficient Photocatalyst for CO₂ Reduction to Formic Acid Under Visible. *ACS Sustainable Chem. Eng.* **2018**, *6*, 5754-575994. DOI: 10.1021/acssuschemeng.8b00956
94. Zhang, K.; Kim, J. K.; Park, B.; Qian, S.; Jin, B.; Sheng, X.; Zeng, H.; Shin, H.; Oh, S. H.; Lee, C.-L., Defect-induced epitaxial growth for efficient solar hydrogen production. *Nano lett.* **2017**, *17*, (11), 6676-6683. DOI: 10.1021/acs.nanolett.7b02622
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
96. Gong, Y.; Lin, J.; Wang, X.; Shi, G.; Lei, S.; Lin, Z.; Zou, X.; Ye, G.; Vajtai, R.; Yakobson, B. I., Vertical and in-plane heterostructures from WS₂/MoS₂ monolayers. *Nat. Mater* **2014**, *13*, (12), 1135. DOI : 10.1038/nmat4091
97. He, R.; Xu, D.; Cheng, B.; Yu, J.; Ho, W., Review on nanoscale Bi-based photocatalysts. *Nanoscale Horizons* **2018**, *3*, 464-504 DOI: 10.1039/C8NH00062J
98. Yu, Y.; Cao, C.; Liu, H.; Li, P.; Wei, F.; Jiang, Y.; Song, W., A Bi/BiOCl heterojunction photocatalyst with enhanced electron-hole separation and excellent visible light photodegrading activity. *J. Mater. Chem. A* **2014**, *2*, (6), 1677-1681. DOI: 10.1039/C3TA14494A
99. Wu, Y.; Xiang, J.; Yang, C.; Lu, W.; Lieber, C. M., Single-crystal metallic nanowires and metal/semiconductor nanowire heterostructures. *Nature* **2004**, *430*, (6995), 61. DOI: 10.1038/nature02674
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 microspheres. *J. Catal.* **2018**, *357*, 41-50. DOI: 10.1016/j.jcat.2017.10.004
101. Bai, Y.; Ye, L.; Wang, L.; Shi, X.; Wang, P.; Bai, W., A dual-cocatalyst-loaded Au/BiOI/MnO_x system for enhanced photocatalytic greenhouse gas conversion into solar fuels. *Environ Sci Nano* **2016**, *3*, (4), 902-909. DOI: 10.1039/C6EN00139D
102. Chen, D.; Fang, J.; Lu, S.; Zhou, G.; Feng, W.; Yang, F.; Chen, Y.; Fang, Z., Fabrication of Bi modified Bi₂S₃ pillared g-C₃N₄ photocatalyst and its efficient photocatalytic reduction and oxidation performances. *Appl. Surf. Sci.* **2017**, *426*, 427-436. DOI: 10.1016/j.apsusc.2017.07.139
103. Ran, J.; Guo, W.; Wang, H.; Zhu, B.; Yu, J.; Qiao, S. Z., Metal-Free 2D/2D Phosphorene/g-C₃N₄ Van der Waals Heterojunction for Highly Enhanced Visible-Light Photocatalytic H₂ Production. *Adv. Mater* **2018**, *30*, (25), 1800128. DOI: 10.1002/adma.201800128
104. Wang, J.-C.; Yao, H.-C.; Fan, Z.-Y.; Zhang, L.; Wang, J.-S.; Zang, S.-Q.; Li, Z.-J., Indirect Z-scheme BiOI/g-C₃N₄ photocatalysts with enhanced photoreduction CO₂ activity under visible light irradiation. *ACS Appl. Mater. Interfaces* **2016**, *8*, (6), 3765-3775. DOI: 10.1021/acsaami.5b09901
105. Wang, H.; Zhang, W.; Li, X.; Li, J.; Cen, W.; Li, Q.; Dong, F., Highly enhanced visible light photocatalysis and in situ FT-IR studies on Bi metal@ defective BiOCl hierarchical microspheres. *Appl. Catal.B* **2018**, *225*, 218-227. DOI: 10.1016/j.apcatb.2017.11.079
106. Wu, D.; Ye, L.; Yue, S.; Wang, B.; Wang, W.; Yip, H. Y.; Wong, P. K., Alkali-Induced in Situ Fabrication of Bi₂O₄-Decorated BiOBr Nanosheets with Excellent Photocatalytic Performance. *J. Phys. Chem. C* **2016**, *120*, (14), 7715-7727. DOI: 10.1021/acs.jpcc.6b02365
107. Bai, Y.; Ye, L.; Wang, L.; Shi, X.; Wang, P.; Bai, W.; Wong, P. K., g-C₃N₄/Bi₄O₅I₂ heterojunction with I³⁻/I⁻ redox mediator for enhanced photocatalytic CO₂ conversion. *Appl. Catal.B* **2016**, *194*, 98-104. DOI: 10.1016/j.apcatb.2016.04.052

108. Bai, Y.; Chen, T.; Wang, P.; Wang, L.; Ye, L.; Shi, X.; Bai, W., Size-dependent role of gold in g-C₃N₄/BiOBr/Au system for photocatalytic CO₂ reduction and dye degradation. *Sol. Energy Mater Sol. Cells* **2016**, *157*, 406-414. DOI: 10.1016/j.solmat.2016.07.001
109. Li, J.; Zhao, K.; Yu, Y.; Zhang, L., Facet-Level Mechanistic Insights into General Homogeneous Carbon Doping for Enhanced Solar-to-Hydrogen Conversion. *Adv.Funct.Mater.* **2015**, *25*, (14), 2189-2201. DOI: 10.1002/adfm.201404178
110. Arana, J.; Díaz, O. G.; Saracho, M. M.; Rodriguez, J. D.; Melián, J. H.; Peña, J. P., Photocatalytic degradation of formic acid using Fe/TiO₂ catalysts: the role of Fe³⁺/Fe²⁺ ions in the degradation mechanism. *Appl. Catal. B* **2001**, *32*, (1-2), 49-61. DOI: 10.1016/S0926-3373(00)00289-7
111. Mi, Y.; Wen, L.; Wang, Z.; Cao, D.; Xu, R.; Fang, Y.; Zhou, Y.; Lei, Y., Fe (III) modified BiOCl ultrathin nanosheet towards high-efficient visible-light photocatalyst. *Nano Energy* **2016**, *30*, 109-117. DOI: 10.1016/j.nanoen.2016.10.001
112. Wang, L.; Shang, J.; Hao, W.; Jiang, S.; Huang, S.; Wang, T.; Sun, Z.; Du, Y.; Dou, S.; Xie, T., A dye-sensitized visible light photocatalyst-Bi₂₄O₃₁Cl₁₀. *Sci. Rep* **2014**, *4*, 7384. DOI: 10.1038/srep07384
113. Zhang, L.; Wang, W.; Sun, S.; Sun, Y.; Gao, E.; Xu, J., Water splitting from dye wastewater: a case study of BiOCl/copper (II) phthalocyanine composite photocatalyst. *Appl. Catal.B* **2013**, *132*, 315-320. DOI: 10.1016/j.apcatb.2012.12.003
114. Bai, Y.; Chen, T.; Wang, P.; Wang, L.; Ye, L., Bismuth-rich Bi₄O₅X₂ (X= Br, and I) nanosheets with dominant {1 0 1} facets exposure for photocatalytic H₂ evolution. *Chem. Eng. J.* **2016**, *304*, 454-460. DOI: 10.1016/j.cej.2016.06.100
115. Bai, Y.; Ye, L.; Chen, T.; Wang, L.; Shi, X.; Zhang, X.; Chen, D., Facet-dependent photocatalytic N₂ fixation of bismuth-rich Bi₅O₇I nanosheets. *ACS Appl. Mater. Interfaces* **2016**, *8*, (41), 27661-27668. DOI: 10.1021/acsami.6b08129
116. Zhang, L.; Han, Z.; Wang, W.; Li, X.; Su, Y.; Jiang, D.; Lei, X.; Sun, S., Solar-Light-Driven Pure Water Splitting with Ultrathin BiOCl Nanosheets. *Chemistry* **2015**, *21*, (50), 18089-94. DOI: 10.1002/chem.201503778
117. Kong, X. Y.; Lee, W. C.; Ong, W. J.; Chai, S. P.; Mohamed, A. R., Oxygen-Deficient BiOBr as a Highly Stable Photocatalyst for Efficient CO₂ Reduction into Renewable Carbon-Neutral Fuels. *ChemCatChem* **2016**, *8*, (19), 3074-3081. DOI: 10.1002/cctc.201600782
118. Ye, L.; Wang, H.; Jin, X.; Su, Y.; Wang, D.; Xie, H.; Liu, X.; Liu, X., Synthesis of olive-green few-layered BiOI for efficient photoreduction of CO₂ into solar fuels under visible/near-infrared light. *Sol. Energy Mater Sol. Cells* **2016**, *144*, 732-739. DOI: 10.1016/j.solmat.2015.10.022
119. Ma, Z.; Li, P.; Ye, L.; Zhou, Y.; Su, F.; Ding, C.; Xie, H.; Bai, Y.; Wong, P. K., Oxygen vacancies induced exciton dissociation of flexible BiOCl nanosheets for effective photocatalytic CO₂ conversion. *J. Mater. Chem. A* **2017**, *5*, (47), 24995-25004. DOI: 10.1039/C7TA08766G
120. Bi, Y.; Wang, Y.; Dong, X.; Zheng, N.; Ma, H.; Zhang, X., Efficient solar-driven conversion of nitrogen to ammonia in pure water via hydrogenated bismuth oxybromide. *RSC Adv.* **2018**, *8*, (39), 21871-21878. DOI: 10.1039/C8RA02483A
121. Si, H. Y.; Mao, C. J.; Xie, Y. M.; Sun, X.G.; Zhao, J. J.; Zhou, N.; Wang, J. Q.; Feng, W. J.; Li, Y. T., P-N depleted bulk BiOBr/ α -Fe₂O₃ heterojunctions applied for unbiased solar water splitting. *Dalton Trans.* **2017**, *46*, (1), 200-206. DOI: 10.1039/C6DT03683J

For Table of Contents Use Only

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