1	BiOX (X = Cl, Br, I) photocatalytic nanomaterials: Applications for fuels and
2	environmental management
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12 Abstract

Energy and environmental issues are the major concerns in our contemporary "risk 13 society". As a green technique, photocatalysis has been identified as a promising 14 solution for above-mentioned problems. In recent decade, BiOX (X = Cl, Br, I) 15 photocatalytic nanomaterials have sparked numerous interest as economical and 16 efficient photocatalysts for energy conversion and environmental management. The 17 distinctive physicochemical properties of BiOX nanomaterials, especially their energy 18 band structures and levels as well as relaxed layered nanostructures, should be 19 responsible for the visible-light-driven photocatalytic per 20 mance improvement, which could be utilized in dealing with the global energy e tal challenges. 21 ŵ of DOX i In this review, recent advances for the enhancement 22 tocatalytic activity are detailedly summarized. Furthermore, the applicat spr<u>of</u> X photocatalysts in water 23 splitting and refractory organic pollutaries re al an highlighted to offer guidelines 24 ne for better development in photocatalys Party alarly, no relative reports in previous 25 studies were documented in  $O_2$  n duction as well as heavy metals and air pollutants 26 removal, thus this review presented as a considerable research value. Challenges in the 27 formance BiOX-based photocatalytic systems are also 28 construction of his xponential growth of studies on BiOX photocatalytic discussed. With the 29 nanomaterials, this review provides unique and comprehensive perspectives to design 30 31 BiOX-based photocatalytic systems with superior visible light photocatalytic activity. 32 The knowledge of both the merits and demerits of BiOX photocatalysts are updated and provided as a reference. 33

Keywords: bismuth oxyhalides; photocatalysis; water splitting; CO₂ reduction;
 environmental management

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With the rapid industrialization and urbanization, energy shortages and environmental pollutions have aroused considerable concerns from the world [1-4]. Semiconductor photocatalysis, as one of the most prospective ways to tackle these problems, including hydrogen (H₂) and oxygen (O₂) production from water [5, 6], carbon dioxide (CO₂) reduction to energy-bearing carbon fuels [7, 8] and organic pollutants decomposition [9, 10], has become the focus of study because it is a "green" technology in facing clean energy demand and tackling environmental issues [11].

As far back as 1972, Fujishima and Honda first discove at water can be split 66 into H₂ and O₂ by irradiating a TiO₂ anode connected wit seak cathode via an 67 f into Hy and O₂ under visible external bias, indicating water can be directly dec 68 light irradiation with the assistance of catalysts n then on, great efforts have 69 70 been made in semiconductor [13-17]. Among the traditional p photocatalysts, TiO₂ has been extrasively used as an effective photocatalyst for water 71 splitting and complete organic comminents degradation under ultraviolet (UV) light 72 y induce photons in UV light region which 73 irradiation. Howeve can of approximately acco % of the solar light because of its high band gap energy 74  $(3.0 \sim 3.2 \text{ eV})$  [8, 10, 18]. 75

As for solar light, visible light is easily obtained across the earth, which accounts for about 50%. Thus, considerable attention has been drawn to the research of visiblelight-active photocatalysts [19, 20]. And it has been found that the orbitals of certain pblock metals can hybridize O 2p orbitals to form a better hybridized valence band (VB), such as Ag 4d orbitals in Ag(I), Bi 6s orbitals in Bi(III) and Sn 5s orbitals in Sn(II), enhancing the mobility of photo-generated charge carriers, narrowing their band gaps and promoting the absorption of visible light [6, 21]. Considering of the advantages 83 such as earth abundance, stability, economic and toxicity, bismuth-based (Bi-based) materials are more sustainable photocatalysts; besides, most Bi-based semiconductors 84 have shown efficient photocatalytic activities towards water splitting, CO₂ reduction 85 and harmful pollutants removal under visible light irradiation [22, 23]. On the basis of 86 the above merits, our team have successfully developed some excellent Bi-based 87 visible-light-active photocatalysts, such as Ag/g-C₃N₄/BiVO₄ [14], g-C₃N₄/Bi₂WO₆ 88 [24], Bi/BiOCl/ZnSn(OH)₆ [25] and Ag₃PO₄/Ag/BiVO₄ [26]. As shown in Fig. 1a, an 89 exponential growth of relative publications was reported on Bi-based photocatalysts for 90 energy conversion and environmental management (according SI Web of Science™ 91 from 2006 to 2016). 92 Meanwhile, similar increasing trend in interected with regards to 93

bismuth oxyhalides (BiOX (X = Cl, Br, I)) photo ig. 1b-d). BiOX (X = Cl, 94 at ivs ed) Br, I), as one kind of important Bi-ba ocatalysts, should benefit from their 95 complex band structures and unique la st actures. The band structures of these 96 BiOX are illustrated in Fig. 2,27], he top of the VB and the bottom of the conduction 97 band (CB) are located in the R and Z point, respectively, suggesting they are indirect 98 That is to say the photo-induced electrons on BiOX should 99 band gap semicondu ters pass a certain k-space stance from the VB to arrive in the CB, further to reduce the 100 photo-induced electrons and holes recombination rate [27-29]. All BiOX 101 102 semiconductors possess a tetragonal matlockite structure, as shown in Fig. 3, BiOX displayed relaxed layered structures with [Bi₂O₂] slabs inserting into double halogen 103 atom slabs [30]. The layered structure of BiOX can offer enough space to polarize the 104 105 related atoms and orbitals, which can excite the formation of an internal electric field (IEF) between [Bi₂O₂] and halogen slabs. And because the induced IEF can accelerate 106 the separation and migration of photo-excited electron-hole pairs, the photocatalytic 107

activities of BiOX are improved significantly [27-29, 31]. Throughout the above
analyses, it is reasonable to carry out more investigations on BiOX photocatalysis.

Several reviews about BiOX photocatalytic nanomaterials have been published, 110 but most of them focus on BiOX nanostructures and organic pollutants degradation [30, 111 32, 33]. Nevertheless, the applications of this series of photocatalysts in the fields of 112 fuel production and removal of heavy metals and air pollutants have not been reviewed, 113 which are indispensable fields of the present study. In this review, we sum up the recent 114 strategies for the enhancement of BiOX photocatalytic activity under visible light and 115 their applications in water splitting and degradation of organite of lutants, especially in 116 the fields of CO₂ reduction as well as removal of heavy d i contaminants. 117 This review is finished by the discussion on cruc hat exist in the use of 118 and ntal issues, and giving 119 BiOX nanomaterilas to resolve energy iro suggestions and new directions in con BiO -based photocatalytic systems 120 with high performance. 121

# 122 2. Properties of BiOX nanomatorials

(Br), nd iodine (I) elements are on the same main group, 123 Chlorine (Cl), and BiOI might possess the similar properties. Zhang et al. therefore, BiOCl, 124 [28] first revealed that the Cl 3p states and Bi 6p states respectively constitute the VB 125 and the CB. Furthermore, Zhao et al. [27] proved that both O 2p and X np (n = 3, 4 and 126 5 for X =Cl, Br and I, respectively) states contribute most to the valence band maximum 127 (VBM) while the Bi 6p states dominate the conduction band minimum (CBM). The 128 band gaps of experimental determination for BiOCl, BiOBr, and BiOI are 3.22, 2.64, 129 and 1.77 eV, respectively [34]. Comparatively, their theoretically calculated indirect 130 band gaps are 2.50, 2.10 and 1.59 eV, respectively [27]. The band gaps differences 131 between the experimental and calculated results due to the density-functional theory 132

limitation [35]. Nevertheless, the band gaps decrease with the increase of atomic
number of Cl, Br, and I elements, and their response wavelengths gradually move
toward the visible light region from UV light region.

Many studies have been done to investigate the photocatalytic performance of 136 BiOCl nanomaterials under UV light irradiation [28, 36]. Zhang et al. [28] first 137 introduced the layered BiOCl nanoplates using a hydrolysis approach. And the layered 138 BiOCl nanoplates exhibited much better stability and UV photocatalytic activity 139 towards methyl orange (MO) degradation than TiO₂. Moreover, Jin and co-workers [36] 140 reported that ultrathin BiOCl nanosheets displayed high photocallytic activity for the 141 photoreduction of CO2 into CH4. Besides the surface-to-w 5. i gle-crystalline 142 characteristics and exposed {001} facets, num vacancies of BiOCl 143 nanosheets generated under UV light also contra e excellent photocatalytic 144 activity towards CO2 reduction by promotion adsorption of CO₂ and molecular O₂. 145 However, unmodified BiOCl only expression phot catalytic activity under UV light as a 146 result of its wide band gaps, blocking its more extensive applications. 147

BiOBr photocatalyst was allo widely employed in recent years owing to its 148 relatively narrow bandpar and preferable visible light photocatalytic activity [37, 38]. 149 For example, Zhang t al. [37] successfully prepared 3D flower-like BiOBr 150 microspheres by ethylene glycol (EG) assisting solvothermal method. And high visible 151 152 light photocatalytic activity was observed towards MO degradation because of its intrinsic properties such as narrow band gaps. In addition, Wu et al. [38] utilized {001} 153 facet dominated BiOBr nanosheets to reduce CO₂ under simulated sunlight irradiation. 154 The BiOBr nanosheets exhibited the highest CO production rate of 4.45  $\mu$ mol h⁻¹ g⁻¹, 155 which was mainly ascribed to the large active surface area, effective charge carrier 156 separation and enhanced reduction ability. These results imply that BiOBr has favorable 157

visible-light-driven (VLD) photocatalytic performance, especially after somemodification.

As for BiOI (the narrowest bandgap in three samples), pure BiOI exhibits poor 160 photocatalytic activity due to the inherent rapid electron-hole recombination. An et al. 161 [39] found that BiOI could only degrade rhodamine B (RhB) to N-de-ethylated 162 rhodamine under visible light. In contrast, Long et at. [40] synthesized a novel porous 163 hierarchical BiOI nanostructures at room temperature. And the removal efficiency of 164 RhB was about 98.7% under visible light irradiation by using this novel nanomaterial. 165 sumificantly affect the This result shows that the morphology and structure car 166 photocatalytic performance of BiOI. 167 BiOX nanomaterials display excellent otential for energy 168 vely positive CB position conversion and environmental management, But 169 and weak reduction power can't meet and *f* energy conversion and their 170 photocatalytic efficiency is still unsatis solar light irradiation, which restrict 171 their practical applications (Fig. 4). In order to strengthen the photocatalytic 172 performance of BiOX nanomateria's under solar light irradiation, many strategies have 173 been used to tune the eve gy fund position, boost the sunlight harvesting and promote 174 the separation and trans ortation of photo-induced electron-hole pairs, which contains 175

microstructure modulation, facet and defect control, carbonaceous materialscompounding, heterojunction construction and so on.

# 178 **3.** Strategies for the enhancement of BiOX photocatalytic activity

#### 179 3.1 Microstructure modulation

180 The physical and chemical properties of materials are extremely related to their 181 microstructure, such as size, shape, specific surface area and dimensionality [41, 42]. 182 Among BiOX nanomaterilas, there are one dimensional (1D) nanofibers [43], two

dimensional (2D) nanosheets/nanoplates [44-47] and three dimensional (3D) 183 microspheres/hierarchical nanostructures [37, 48-51]. The 3D assemblies have sparked 184 more interests owing to their distinctive architecture and excellent photocatalytic 185 activity. Zhang et al. [48] successfully synthesized BiOI photocatalyst with flower-like 186 hierarchical structure via direct hydrolysis method at room temperature and first utilized 187 it for photocatalytic reduction of CO₂ to CH₄ under simulated sunlight irradiation. In 188 detail, the total yield of CH₄ over BiOI with flower-like hierarchical structure was 0.198 189  $\mu$ mol h⁻¹ g⁻¹, while the total yield of CH₄ over bulk BiOI and TiO₂ only were 0.085  $\mu$ mol 190  $h^{-1}$  g⁻¹ and 0.015 µmol  $h^{-1}$  g⁻¹, respectively. This work shows that D nanostructure can 191 efficiently enhance the photocatalytic ability of BiOI for 192 Moreover, Zhao et al. [49] synthesized hier microspheres which 193 were almost composed of sphere-like hierarchice st act with the diameter of 2-4 194 um through a solvothermal method wing the lp of sodium dodecyl sulfate (SDS). 195 Meanwhile, 3D flower-like BiOBr catal sts which were nearly made up of 196 ph flower-like structures with the diameter from 3 µm to 5 µm was synthesized without 197 SDS. The Fig. 5 shows the scanning electron microscope (SEM) images of the flower-198 like BiOBr and sphere life BDBr, respectively. Although both of the samples are 3D 199 nanostructure, the photoatalytic degradation efficiency of RhB on sphere-like BiOBr 200 reached about 100% on 30 min under visible light. It was only 85% for flower-like 201 202 BiOBr under identical conditions. This is mainly because the sphere-like BiOBr nanomaterials possess thinner self-assembled nanosheets, smaller nanocrystals and 203 more oxygen vacancies than the flower-like BiOBr, which can provide more active sites 204 205 and promote the direct photoexcitation and indirect dye photosensitization.

206 Hydro/solvothermal treatment is a primary method to construct 3D-structured
207 BiOX because of its high reaction efficiency and simple experimental process [37, 49-

208 51]. The formation mechanism of 3D BiOX assemblies achieved by the hydro/solvothermal reactions usually includes the following three main steps: (i) the 209 formation of BiOX nuclei at the forepart (ii) the growth of 2D nanosheets through a 210 211 dissolution-renucleation process, and (iii) the figuration of 3D BiOX structures from the oriented aggregation of 2D nanoplates under the electrostatic multipole field [50, 212 51]. Overall, the improved photocatalytic activity of 3D nanostructure is attributable to 213 their enhanced light harvesting ability, curtate diffusion pathways, faster separation of 214 photo-excited electron-hole pairs and more reactive spots. 215

216 3.2 Facet and defect control

As a basic feature of crystalline materials, the except facets play an 217 important role in the photocatalytic efficiency sing ccur on the surface 218 cata of BiOX photocatalytic nanomaterials. 219 acets possess different their different geometric and electronic photocatalytic performance because 220 structures [52, 53]. Ye et al. [47] first OCl nanosheets with tunable {001} 221 crystal facets through hydroly ang nolecular precursor  $(Bin(Tu)_x Cl_{3n}, Tu = thiourea)$ . 222 And they discovered that the main r active facets of BiOCl crystals are the {001} facets. 223 atal tic activity could be attributable to the oxygen vacancies The enhanced to 224 formed on the  $\{001\}$  Nets. These oxygen vacancies can generate a defect state lying 225 close to the bottom of the CB over the BiOCl photocatalyst, thus promoting the 226 separation of photo-induced electron-hole pairs and then improving the photocatalytic 227 activity of the BiOCl. 228

To further clarify facet-dependent photocatalytic properties, their group synthesized BiOI nanosheets with exposed active  $\{001\}$  (BiOI-001) and  $\{100\}$  (BiOI-100) crystal facets for CO₂ photoreduction by regulating the hydrothermal reaction time [54]. Under UV-vis irradiation, the production rate of CO and CH₄ over BiOI-001 were

5.18  $\mu$ mol h⁻¹ g⁻¹ and 1.78  $\mu$ mol h⁻¹ g⁻¹, while they were only 1.52  $\mu$ mol h⁻¹ g⁻¹ and 1.50 233 umol h⁻¹ g⁻¹ could be generated by BiOI-100. The differences of IEF and CB position 234 might lead to the photocatalytic activity difference between BiOI-001 and BiOI-100. 235 236 The self-induced IEF of BiOI is perpendicular to {001} facets but parallel to {100} facets, thus the separation and migration of charge carriers are more favorable for BiOI-237 001 due to the shorter diffusion distance. Besides, because the CB level of BiOI-001 is 238 higher than BiOI-100, the BiOI-001 possesses the higher reduction activity [54]. 239 Therefore, both the IEF and CB position are in propitious to the photocatalysis of the 240

241

BiOI-001.

Furthermore, Pan et al. [55] prepared two types t catalysts with 242 exposed active {110} (BiOI-110) and {001} (P al facets by a facile 243 hydrothermal method (Fig. 6). During bisphenov BP degradation, the BiOI-110 244 displayed higher photocatalytic activity the dsorption energy of  $O_2$  on the 245 {110} facets (0.209 eV) was smaller that on the  $\{001\}$  facets (0.656 eV). The 246 results showed that BiOI-110 ould generate more  $\cdot O_2^-$ , thus leading to enhanced visible 247 light photocatalytic activity. Consequently, it can trap more electrons, which promotes 248 f ploto-excited electron-hole pairs and results in generating the separation efficient 249 more reactive oxygen vecies (ROS) related to electrons and holes [55]. In addition, 250 between the two samples, only the BiOI-110 is able to produce •OH because BiOI-110 251 252 has a stronger oxidation potential than BiOI-001. Many other studies introduced the effect of crystal facets on photocatalytic activity of BiOX nanomaterials (Table 1), 253 however, it is still difficult to develop the facets with high reactivity and expound 254 255 underlying reaction mechanisms of different crystal facets [56].

The defects in the exposed facets of semiconductors can also enhance their photocatalytic activity by changing their electronic structures, recombination efficiency of charge carriers and surface properties [64-67]. In previous study, it has been found that the high photocatalytic activity of {001} facets of BiOCl originated from the oxygen vacancies which could improve the separation efficiency of electro-hole pairs.[47] During the CO₂ photoreduction experiment, the oxygen vacancies on BiOCl nanoplates not only improve their trapping capacity for CO₂, but also promote the separation of photo-induced electron-hole pairs, resulting in the considerable CO yield (1.01  $\mu$ mol h⁻¹ g⁻¹) under simulated solar light [68].

Recently, Wang et al. [69] successfully synthesized BiOBr nanosheets with plenty 265 of surface oxygen vacancies on exposed {001} facets by using polybasic carboxylic 266 acids as chelant. In comparison with the pristine BiOBr national **N**O degradation 267 rate over BiOBr nanosheets with surface oxygen 3 times higher than 268 the pristine BiOBr nanosheets. The enhancem from the surface oxygen 269 can vacancies which could trap electrons to radials and leave a large number of 270 holes on the VB consequently. Except oxy en vacancy, Xie et al. [70] found the 271  $V_{Bi}^{\prime\prime\prime}V_{O}V_{Bi}^{\prime\prime\prime}$  triple vacancy as ciate on exposed active {001} facets of atomic scale 272 here triple valancy associates not only strengthen the adsorption 273 BiOCl nanosheets. 7 lecy es through making the {001} facets negatively charged, ability for cationic 274 but also promote the generation of more reductive photo-induced electrons by elevating 275 the CBM position. Therefore, the ultrathin BiOCl nanosheets with  $V_{Bi}^{\prime\prime\prime}V_{O}^{\prime}V_{Bi}^{\prime\prime\prime}$  vacancy 276 associates exhibited 5 times higher solar-light-driven photocatalytic activity than 277 ordinary BiOCl nanoplates for RhB degradation due to the synergetic promotions of 278 improved adsorption ability, effective separation of photo-induced electron-hole pairs 279 and more reductive photo-generated electrons (Fig. 7). 280

However, the oxygen vacancy doesn't always play a positive role in photocatalytic reactions. Chen et al. [71] synthesized BiOCl nanoplates with exposed active {001}

crystal facets through a simple hydrothermal method. Because oxygen vacancy can be 283 easily formed under UV light irradiation, they found that the as-prepared samples 284 exhibited about 3 times higher rate constant (k) for photocatalytic degradation of RhB 285 under visible light (0.034 min⁻¹) than that under UV-vis light irradiation (0.012 min⁻¹). 286 The photosensitization is the main way for BiOCl nanosheets to degrade RhB under 287 visible light irradiation. In contrast, oxygen vacancies are formed on {001} facets of 288 BiOCl nanosheets under UV-vis light irradiation and they can hinder the generation of 289  $\cdot O_2^-$  radicals by trapping photo-induced electrons on the CB of BiOCl. Hence, oxygen 290 vacancies in BiOCl nanosheets here reduce the photocatalytic destadation efficiency of 291 RhB. 292

293 3.3 Carbonaceous materials compounding

Various carbonaceous materials, including 294 rbon nanotubes (CNTs), carbon quantum dots (CQDs) and mportant roles in enhancing 295 olay 🖌 photocatalytic performance of BiO2 erilas. Graphene (usually refers to 296 reduced graphene oxide (RGv)) h 297 s been considered as a good electron collector and transporter in photocatalysis bec use of its high conductivity, excellent electron 298 mobility and large specific surface area [16, 72-74]. Based on those results, RGO/BiOX 299 nanocomposites exhibit significantly enhanced photocatalytic activity [75-77]. 300 Recently, Dong et al. [75] synthesized flower-like BiOCl/RGO nanocomposites to 301 degrade sulfanilamide (SN) under natural sunlight irradiation. And the samples 302 contained 1 wt% RGO showed excellent photocatalytic activity due to the improved 303 electron transfer ability and enhanced visible light absorption, rather than the changes 304 305 of surface area value and band gap.

306 CNTs are used for photocatalysis owing to their excellent ability to conduct 307 electrons [78]. Very recently, CNTs have been used in some CNT/BiOX 308 nanocomposites to increase the separation efficiency of photo-excited electron-hole pairs, and thus enhancing the photocatalytic activity [79-81]. S. Vadivel et al. [79] 309 synthesized multiwall carbon nanotubes (MWCNT)/BiOCl nanocomposites via one 310 step hydrothermal approach. The as-obtained samples showed superior photocatalyic 311 activity in photodegradation of congo red, malachite green and bromophenol blue dyes 312 than pure BiOCl, and the improved photo-generated electron-hole pairs separation 313 314 efficiency was the predominant reason. As new carbonaceous nanomaterials, CQDs have been also extensively applied in photocatalytic applications relied on their superior 315 electron transfer ability [82]. A series of CODs/BiOX r 316 conaterials have been synthesized [83-86], for example, Xia et al. [84] obtained and ODs/BiOX (X =317 io cliquia Cl, Br) nanosheets with different CQDs contents assisted hydrothermal 318 method (Fig. 8). Due to their high visible lig nce, enhanced separation 319 oso efficiency of photo-generated electron rs and lower resistance, the 3 wt% 320 CODs/BiOBr nanosheets exhibited the atalytic efficiency for the degradation 321 imal of RhB, ciprofloxacin (CIP and BPA, However, abovementioned carbonaceous 322 nanomaterials suffer from some d ficiencies, such as complex synthesis method and 323 ar, in easily accessible and low cost carbonaceous material, high cost. Therefore, p 324 has entered people's hid of vision [87, 88]. Li et al. [89] first utilized biochar to 325 produce biochar/BiOX (X = Cl, Br) photocatalysts through a facile in-situ precipitation 326 327 method. And they found that biochar could act as a benign carrier of electrons to promote photocatalytic reactions for BiOBr and photosentisization reactions for BiOCl. 328

329 3.4 Heterojunction construction

Heterojunction construction is the most common strategy to enhance the photocatalytic performance of a single semiconductor, which can accelerate the separation of photo-induced carriers and broaden the wavelength of photo-response for 333 the system [90]. Our team fabricated a Bi/BiOCl/ZnSn(OH)₆ heterojunction and investigated its photocatalytic activity by RhB degradation under visible light 334 irradiation [25]. The photo-degradation rate of RhB over Bi/BiOCl/ZnSn(OH)₆ was 335 about 81 times higher than that of pure ZnSn(OH)₆, demonstrating that the combination 336 of ZnSn(OH)₆ with Bi and BiOCl was an advisable method. The addition of Bi 337 nanoparticles and BiOCl nanosheets not only extend the range of absorption 338 wavelength to visible light from light region, but also promote the separation of charge 339 carriers by the formation of heterojunction among different components. 340

341 In recent work, Li et al. [58] constructed g-C₃N₄/BiO terostructures where nanosized g-C₃N₄ (ng-CN) is loaded in different expose ts  $(\{001\}\)$  and 342 {010}) of BiOCl nanosheets (BOC-001 and BOC f the existence of IEF, 343 cau as shown in Fig. 9, photo-generated electrons tra fin 344 om ng-CN to the reactive site of BiOCl nanosheets had a longer mi istance in BOC-001 than that in BOC-345 se two samples showed significantly 010, leading to the loss of more 346 improved MO and phenol protod gradation ability under visible light, and the ng-347 CN/BOC-010 heteroiunction exhibited better photocatalytic performance than the ng-348 on. This research suggests that the orientation of different CN/BOC-001 heterout 349 exposed facet in semic ductors is a new direction for constructing high-performance 350 heterojunction photocatalysts. Besides, other heterojunction photocatalysts, such as 351 Bi₂O₂CO₃/BiOC1 [91], BiOI/CdS [92], BiOBr/MoS₂ [93], Bi₂WO₆/BiOI [94], 352 BiOBr/ZnFe₂O₄ [95], CoTiO₃/BiOBr [96], BiOC1/TiO₂ [97], Fe₃O₄/BiOI [98], 353 WO₃/BiOI [99] and NaBiO₃/BiOCI [100] have been developed and were confirmed to 354 355 be excellent VLD photocatalysts.

356 *3.5 Other strategies* 

15

Up to date, the limited visible light absorption and short photo-induced electron-357 hole pairs lifetimes are still two major factors restricting the practical application of 358 semiconductor photocatalysts. To strengthen the VLD photocatalytic activity of BiOX 359 photocatalysts, solid solutions, doping and bismuth-rich strategy are also feasible 360 methods. The generation of solid solutions can narrow their energy band gap through 361 lifting the position of VB and/or lowering the position of CB, which can improve their 362 photocatalytic abilities [101]. Until now, a lot of BiOX solid solution photocatalysts 363 with enhanced VLD photocatalytic activities have been prepared, such as  $BiOCl_{1-x}Br_x$ 364 [102], BiOBr_{1-x}I_x [103], BiOCl_{1-x}I_x [104], (BiO)₂(CO₃)_x(I₂)₁, etc. Different from 365 the formation of solid solutions, doping often introduce a e it into the host 366 materials, which leads to dispersed energy level below CB. This can 367 efficient trap photo-generated electrons and decre [106]. Therefore, a series 368 lano of non-metal (e.g., C, N, F) [107-109] Fe, Zn, Sn) [110-112] elements 369 e.g have been doped into BiOX photocal n nomaterials recently and the doped 370 nanomaterials exhibit superio VLI photocatalytic activity than the single sample. The 371 bismuth-rich strategy can uplift the CB potential through changing the bismuth content, 372 hot catalysts is mainly consisted of Bi 6p state [113]. It has because the CB **T**B 373 been reported that BixD₃₁Br₁₀ [113], Bi₄O₅Br₂ [114] and Bi₄O₅BrI [115] all have 374 increased CBM potential as well as photocatalytic reduction enhancement. 375

Owing to those mentioned strategies, the form of BiOX photocatalytic nanomaterials are changed from single materials to modified complex nanomaterials and the VLD photocatalytic capacities of BiOX photocatalysts are greatly improved. These allow BiOX photocatalysts to adapt to a wider range of applications, especially in the fuels preparation from H₂O and CO₂ (Table 2), removal of heavy metals and air pollutants, as described in the following sections.

#### 382 4. BiOX nanomaterials to make fuels from H₂O and CO₂

#### 383 4.1 Photocatalytic hydrogen generation

Photocatalytic water into H₂ and O₂ is perhaps the most urgent task of present 384 research for solving the energy and environmental problems. Although the CB potential 385 386 of BiOX can't satisfy the reduction potential of  $H^+$  to  $H_2$ , recent researches clearly corroborated that H₂ production on BiOX can be achieved by forming heterojunction 387 [120, 126], introducing cocatalysts [117], coupling photosensitizers [116], doping 388 foreign elements [59], tailoring crystal facets [59, 117, 118], utilizing defects [116, 118, 389 119, 127, 128], applying strains [129] and reducing thickn 118, 127, 130]. For 390 example, Ye et al. [118] prepared black ultrathin BiOCl **BiOCl**) which 391 has expanded {001} facet spacing and abundant of 392 (Fig. 10a and b). The expanded facets spacing can strengthen the IF and finally promote the ten 393 ig. 10c show that BU-BiOCl has more separation of photo-induced carriers. Re 394 H₂ production (2.51  $\mu$ mol h⁻¹) then but Bio[1 (0.12  $\mu$ mol h⁻¹) under visible light 395 irradiation. After loading Pt, PU-BiDCl/Pt also displays superior photocatalytic activity 396 for H₂ production (3.96 upol h⁻¹) than bulk BiOCl/Pt (0.18 µmol h⁻¹). These results 397 ncie and expanded {001} facets spacing can improve the indicate that oxygen 398 photocatalytic activity gnificantly, which can be attributed to the enhanced photon 399 400 absorption efficiency and separation efficiency of photo-excited carriers.

Recently, Zhang and co-workers [59] developed BiOCl nanosheets with carbon doped in {001} and {010} facet and applied it to H₂ production with the help of NiO_x co-catalyst and hole scavenger triethanolamine (TEOA). Carbon-doped BiOCl nanosheets with 3 wt% NiO_x loading on {010} facet (BOC-010HC) exhibited the highest photocatalytic H₂ evolution rate (0.42 mmol h⁻¹ g⁻¹) due to the increased optical absorption efficiency and enhanced IEF intensity [59, 119]. However, in this 407 experiment, as a result of the moderate IEF intensity and random distribution of NiO_x, 408 H₂ production rate is still very low [59]. In order to overcome these shortcomings, their 409 team gained oxygen vacancy-rich Bi₁₂O₁₇Cl₂ monolayer nanosheets assembled with 410 metallic MoS₂ monolayers by chemical liquid exfoliation method [119, 131]. Such a 411 Janus bilayer construction endows atomic-level control over carrier separation, 412 transportation and consumption, thus achieving a spectacular photocatalytic H₂ 413 production rate (33 mmol h⁻¹ g⁻¹) under visible light irradiation.

These results definitely demonstrate the feasibility of the BiOX photocatalysts for 414 Although their yield 415 H₂ production under visible light with the help of some strate of hydrogen could not meet the practical production needs of ntial of BiOX 416 nanomaterials for producing H₂ is tremendous j wing aspects. Firstly, 417 their CBM is close to the reduction potential of H The easily lifted to beyond and 418 it. Secondly, the layered structures of R motivate an IEF which is capable of 419 ated electron-hole pairs. Thirdly, their efficient separation and migration of ph 420 en termination feature bring the easy generation of 421 internal strain differences and oxys oxygen vacancies [119, 129]. 422

423 4.2 Photocalarytic exclicition of carbon dioxide

As a result of the creasing use of fossil fuels, CO₂ has caused much attention as 424 a greenhouse gas, and now has been deduced into a serious environmental problem. 425 Converting CO₂ into the energy-bearing carbon fuel sources by photocatalytic reduction 426 is undoubtedly one of the most economical and sustainable methods to reduce levels of 427  $CO_2$  in the atmosphere and solve energy problems [132-134]. However, the application 428 429 of BiOX in the field of CO₂ conversion is very limited due to their relatively positive CB position and weak reduction power. The photocatalytic reduction abilities rely on 430 the CBM position, therefore, some strategies adopted to tune the CBM position of 431

432 BiOX for enhancing the efficiency of CO₂ conversion, such as morphology control [48,

- 433 114], defect effect [68, 122], cocatalyst [121, 123], crystal facet control [38, 54, 124],
- heterojunction [125, 135] and bismuth-rich strategy [114].

In 2016, Kong and co-workers [122] reported an oxygen-deficiency method for 435 BiOBr nanosheets for improved photocatalytic reduction activity. In their study, 436 oxygen-deficient BiOBr nanosheets with oxygen vacancies were fabricated through an 437 ethylene glycol-assisted solvothermal process. The as-prepared BiOBr nanosheets 438 exhibited a huge improvement for CH₄ production under visible light irradiation, 439 obtaining a total yield of 4.86  $\mu$ mol g⁻¹, while the pristine B • only achieved 1.58 440 µmol g⁻¹ of CH₄. Especially, oxygen-deficient BiOBr name 10 y d a 9.58 µmol 441 g⁻¹ of CH₄ formation yield under simulated solar which was 3.2 and 442 adi 5.7 times higher than that of pristine BiOBr and , respectively. 443

Considering that the band gap oxygen-deficient BiOBr nanosheets 444 eV), the enhanced production of fuels (2.70eV) is very close to the pristine Bit 445 could mainly be ascribed to even 1 factors as follows: Firstly, the oxygen-deficient 446 surface highly improves the optical properties of BiOBr and promotes electron-hole 447 inglight absorption; secondly, oxygen vacancies can trap pair generation  $\overline{\bullet}$ 448 photo-induced electron, thus promoting the electron-hole pair separation and 449 restraining the recombination of charge carriers; thirdly, the adsorbed CO₂ molecules 450 451 and oxygen vacancies probably generate unexpected interactions, which can accelerate the interfacial charge transfer [122]. 452

The use of cocatalysts is another significant method to improve the photocatalytic activity of BiOX for the reduction of  $CO_2$  into solar fuels. In 2016, Bai and co-workers [123] prepared a dual-cocatalyst-loaded Au/BiOI/MnOx photocatalyst for  $CO_2$ reduction (Fig. 11a-d). Under UV-vis light irradiation, the CO production rate of

Au/BiOI/MnO_x sample was 42.9  $\mu$ mol h⁻¹ g⁻¹, which was about 7.0 times higher than 457 that of bare BiOI (6.12 µmol h⁻¹ g⁻¹). Under visible light irradiation, the CO production 458 rate increased from 0.51 µmol h⁻¹ g⁻¹ for pure BiOI to 9.76 µmol h⁻¹ g⁻¹ for the 459 Au/BiOI/MnO_x sample (Fig. 11e). Finally, the total yields of CO reached 169 µmol g⁻¹ 460 in the presence of Au/BiOI/MnO_x after 5 h of photocatalytic reaction (Fig. 11f) [123]. 461 This enhancement could be assigned to the cocatalysts including Au and MnO_x because 462 they can't only act as redox-active sites but also improve the separation efficiency of 463 photo-induced charge carriers. Firstly, Au nanoparticles and MnO_x layers are loaded on 464 BiOI nanosheets with photo-excitation. Next, the photo-generated electrons and holes 465 can transfer to the Au and MnO_x respectively and this transfer an restrain the 466 recombination of the photo-excited electron-h the photo-excited 467 electrons can be used for CO₂ reduction. 468 Over past decades, some significat es in  $CO_2$  conversion by using BiOX 469 . However, the relatively low yields photocatalytic nanomaterials have 470

and selectivity of the desired products resulting from the complex processes and
kinetics of CO₂ photoreduction stillninder the practical application. In view of practical
utilization, all the factors (e.g.) excitation, separation and migration of charge carriers,
adsorption of CO₂ and CO₂ reduction kinetics) should be considered and optimized
when designing and synthesizing BiOX photocatalytic nanomaterials for CO₂ reduction.

476 5. BiOX nanomaterials for environmental management

## 477 5.1 Photocatalytic degradation of organic pollutants

In recent years, a lot of effort has been devoted to treating the varied organic pollutants which come from domestic, industrial and medical effluents [136-141]. Various nanomaterials have been extensively applied in the removal of organic pollutants [26, 142-144]. Among them, BiOX nanomaterials have many unusual

properties which endow them excellent photocatalytic activities, such as open layered 482 structures, indirect optical transition and high surface-to-volume ratio [30, 39]. 483 Therefore, BiOX photocatalytic nanomaterials have been widely used for refractory 484 organic pollutants decomposition. For example, Hao et al. [145] synthesized 485 microsphere-like BiOI hierarchical nanomaterial through a one-step solution process at 486 room temperature and utilized it to remove tetracycline hydrochloride (TC). After 2 h 487 visible light irradiation, the TC removal efficiency by BiOI microspheres reached 94%, 488 while only 44% TC could be degraded over the BiOI nanoplatelets, and by comparison, 489 the removal of TC on BiOI microspheres was only 40% in the databases. Several reasons 490 could be concluded for the excellent removal capability A Pio s heres, such as 491 energy band structure, large BET surface area and rfað -volume ratio [145]. 492 The photocatalysis process is considered to ie 1 pathway for the removal 493 of organic pollutants by BiOX nanomat orde to further enhance their ability 494 to photocatalytic degradation of organic llular s under visible light, several strategies 495 have been developed [146-149]. Recently, Di et al. [146] reported that graphene-like 496 boron nitride (BN) modified BDBr flower-like nanomaterials showed satisfing 497 the degradation of CIP, TC and RhB. This enhancement is photocatalytic activity 498 attributed to the decord on of BN, which could improve the visible light harvesting 499 ability and facilitate the separation of photo-generated electron-hole pairs. 500

Especially, constructing efficient BiOX-based nanocomposites for organic pollutants removal often requires the synergetic effect of several systems [33]. Yu et al. [147]demonstrated that Bi/BiOCl heterojunction with oxygen vacancies exhibited outstanding photodegradation activity for dyes and persistent organic pollutants under visible light. This is mainly due to the fact that the abundant oxygen vacancies on BiOCl photocatalyst narrow its band gap to the visible light range and the formed Bi 507 nanoparticles on the BiOCl surface accelerate the transfer of photo-induced electrons from BiOCl to Bi.  $\bullet O_2^-$  and photo-induced holes are proved to be the main active species 508 in this photocatalytic degradation process [147]. The reaction mechanism is shown in 509 Fig. 12, which reveals that organic pollutant molecules can react with active holes on 510 the VB of the BiOCl to form radical ions and then react with  $\cdot O_2^-$  to form the final 511 inorganic products. Moreover, I-BiOCl/I-BiOBr composite combined the merits of I⁻ 512 513 ion doping and BiOCl/BiOCl heterojunction, exhibiting largely enhanced photocatalytic activities for the degradation of MO and phenol under visible light [148]. 514 or notion is the key for The result shows that the synergistic effect of doping and het 515 the excellent photocatalytic activity of the I-BiOCl/I-BiOC 516 In most of reactions that utilize BiOX photoc de organic pollutants, 517 photo-induced holes and •O2⁻ radicals are conbe the dominant reactive cd 518 species [146, 147, 150]. Xiao et al, [1 41 d the photo-induced holes and  $\cdot O_2^-$ 519 radicals played key roles in the **PPA** rated on experiment by BiOI. The photo-520 induced holes of BiOX photor dtaly ts cannot react with H₂O/OH⁻ to form •OH radicals 521 because the standard redox potential of Bi(V)/Bi(III) (+1.59 V) is lower than that of 522 . Bisides, some studies demonstrate that •OH and photo-•OH/OH⁻ (+1.99) 523 induced holes are the **No** primary reactive species in photocatalysis [153]. Gao et al. 524 525 [98] fabricated high-performance 3D hollow magnetic Fe₃O₄/BiOI heterojunction for 526 removal of BPA under visible light. The radical trapping experiments proved that photogenerated holes and •OH were the main active species in the Fe₃O₄/BiOI system. The 527 •OH originated from the reduction of O₂: the photo-generated electrons reacted with 528 529 the adsorbed  $O_2$  to generate  $O_2^-$  and subsequently  $H_2O_2$ ;  $H_2O_2$  reacted with an electron and generated •OH. The detailed photocatalytic process of Fe₃O₄/BiOI system was 530 displayed as below [98]. 531

532 
$$\operatorname{Fe_3O_4/BiOI}(hv) \rightarrow \operatorname{Fe_3O_4/BiOI}(h^+ + e^-)$$
 (1)

533 
$$e^{-} + O_2 \rightarrow \bullet O_2^{-}$$
 (2)

534 
$$2 \cdot O_2^- + 2H^+ \rightarrow O_2 + H_2O_2$$
 (3)

535 
$$H_2O_2 + e^- \rightarrow OH^- + \bullet OH$$
 (4)

BPA + (h⁺, •OH, •O₂⁻)  $\rightarrow$  degradation products  $\rightarrow$  CO₂ + H₂O

(5)

However, many studies have focused on the photocatalytic degradation ability of 537 BiOX nanomaterials, the adsorption ability of BiOX nanomaterials have been neglected 538 to a great extent [146, 148]. To clarify the effect of adsorption in BiOBr photocatalysis, 539 Li and co-workers [154] prepared BiOBr microspheres for the prepared (IBP) removal. 540 In the adsorption process, the IBP and total organic car p bval rate were 541 about 65% and 52%, respectively. While during th 542 process, the removal rate increased slightly, were 80% and 63% accord nall difference of removal 543 Т percentage over IBP between adsorption and 544 ocate ysis reaction indicates that most tion of BiOBr microspheres. This of the removal contribution is 545 demonstrates that the photocatal tic removal efficiency of IBP through BiOBr 546 microspheres is highly adsorptivity dependent. And the better adsorption ability of the 547 so **1** cilitate the higher photocatalytic performance. Besides, prepared catalysts could 548 they found that the ion xchange between bromide ion and dissociated IBP as well as 549 550 the formation of O-Bi-O bond are the primary acting forces during the IBP removal 551 process [154]. Meanwhile, Xu et al. [155] reported that the introduction of TiO₂ nanoparticles could tune the morphology, surface charge property, BET surface area, 552 and hydrophilic property of layered BiOCl nanostructures and hence improve its 553 554 adsorption ability toward Congo red.

555 5.2 *Photocatalytic reduction of heavy metals* 

556 Unlike organic pollutants, heavy metals reduction is a tricky process and tend to

accumulate in organisms and certain heavy metal ions are proved to be toxic or 557 carcinogenic [156, 157]. Conventional technologies for heavy metals removal mainly 558 involve chemical precipitation, ion exchange, biological treatment and physical 559 560 adsorption [158-162]. Compared with these methods, photocatalytic reduction has been regarded as an economic procedure, where the energy consumption was lowest and no 561 secondary pollution could be brought out. The photocatalytic reduction process 562 includes adsorption and reduction of heavy metal ions on the surface of the 563 photocatalysts. Then the reduced metal can be removed by physical and/or chemical 564 methods. Although BiOX nanomaterials as visible light g otocatalysts have been 565 mainly used for photo-degradation of organic pollutant. indicate that 566 they have great potential for photoreduction of he 567

568 M. Qamar and co-workers [163] first ut I for the photocatalytic reduction of Cr(VI) and they found that hibit d higher photocatalytic activity 569 than Degussa P25 for Cr(VI) reduction. 49% Cr(VI) are reduced within short 570 time (30 min) under 355 nm laser rradiation in presence of BiOCl and Degussa P25, 571 respectively. However, the excellent photocatalytic efficiency may be attributed to the 572 laser which is a strong phothromatic and coherent source of light [163]. Therefore, 573 many methods have been applied so as to improve the capacity of BiOX nanomaterials 574 to handle the toxic heavy metal under visible light. 575

Shang et al. [113] reported that BiOBr can be transformed into  $Bi_{24}O_{31}Br_{10}$  with enhanced photocatalytic reduction activity through a bismuth-rich strategy. In the experiment of photocatalytic reduction of Cr (VI) under visible light,  $Bi_{24}O_{31}Br_{10}$ presents the highest ability among  $Bi_2O_3$ , BiOBr and  $Bi_{24}O_{31}Br_{10}$ , and Cr (VI) ions could be completely reduced in 40 min irradiation. Compared with BiOBr,  $Bi_{24}O_{31}Br_{10}$ has uplifted CB level which attributed to the hybridization of Bi 6p states and Br 4s

states. Recently, Bai et al. [115] prepared solid solutions of bismuth-rich Bi₄O₅Br_xI_{2-x} 582 by the molecular precursor method and utilized it for photocatalytic Cr(VI) removal 583 under visible light irradiation. The Cr(VI) removal ratios of Bi₄O₅Br₂, Bi₄O₅BrI and 584 Bi₄O₅I₂ are 47%, 88% and 53%, this means that Bi₄O₅BrI solid solutions exhibit much 585 better photocatalytic reduction ability for Cr(VI) removal than Bi₄O₅Br₂ and Bi₄O₅I₂. 586 This enhancement is ascribed to the higher CB position and faster photo-induced carrier 587 588 separation rates endowed by solid solution strategy and bismuth-rich method [115]. This work indicates that synergistic effect of solid solutions and bismuth-rich could 589 significantly enhance the efficiency of BiOX photocatalysts f (VI) removal. 590 The pH of the initial solution usually affects the of the heavy 591 metals [142]. Very recently, Xu and co-workers ed BN-doped BiOCl 592 nanocomposites with flower-like microsphere st ire ough a facile microwave-593 assisted method for the removal of Cr( ninar s. The FESEM and HRTEM of 594 3a and b, respectively [164]. Under 1% BN/BiOCl composite are displa 595 acidic conditions, the surface of B V/BiOCI adsorbs a great deal of H⁺, which can not 596 only give access to protonation but ilso promote the accumulation of negatively Cr(VI) 597 species such as CDO  $1 \text{HQrO}_4^-$ . Under alkaline conditions, the negative BN/BiOC1 598 surface can only adsort a little Cr(VI) because Cr(VI) species are exist as  $Cr_2O_7^{2-}$ . 599 Moreover, the generated Cr(OH)₃ sediments restrain the photocatalytic activity of 600 601 BN/BiOCl composite by blocking its active sites.

# 602 For acidic Cr(VI) solutions:

603

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
 (6)

604 For alkaline Cr(VI) solutions:

605 
$$Cr_2O_7^{2-} + 7H_2O + 6e^- \rightarrow 2Cr(OH)_3 + 8OH^-$$
 (7)

606 Therefore, at pH 2, the as-prepared 1% BN/BiOCl nanomaterials show the best

607 ability to photocatalytic reduction of Cr(VI) under visible light among all synthesized samples, which is about 2.39 times as high as that of bare BiOCl microspheres (Fig. 608 13c). This could be attributed to the doping of BN, which enhances the adsorption 609 properties of BiOCl, improves the visible light absorption, narrows the band gap and 610 represses the recombination of photo-generated electro-hole pairs. The possible 611 mechanism is depicted in Fig. 13d, under visible light irradiation, the electrons of BiOCl 612 613 excite from the VB to the CB leaving holes in the VB, and then the photo-generated electrons in the VB can be strapped and transferred by BN to convert adsorbed Cr(VI) 614

## 615 to Cr(III) [164].

The adsorption ability for heavy metal ions omaterials in 616 photocatalytic reduction process cannot be ignor [165] discovered that 617 gro flower-like BiOBr nanomaterials can serve as add ints removal of Cr(VI) ions in 618 a wide pH range. Owing to their loose are and big specific surface area, the 619 from microwave irradiation method show a flower-like BiOBr nanostructures obtain 620 satisfactory removal ability fr. Cr(VI) ions. Based on this, their team has developed a 621 series of BiOX nanostructures synt esized by a microwave assisted method in mannitol 622 their, the flower-like hierarchical BiOX nanostructures solution [166]. m 623 exhibited much strong Cr(VI) removal capacity than other BiOX nanostructures, 624 which can be also ascribed to their highly specific surface areas and unique hierarchical 625 626 structures. Compared with flower-like BiOCl and BiOBr nanomaterials, however, flower-like BiOI nanomaterials showed relatively weaker Cr(VI) adsorption efficiency 627 [166]. This could be closely related to their inherent properties, such as BET surface 628 629 area, distribution of surface charge, isoelectric point (IEP) and so on. The IEP of flowerlike BiOCl, BiOBr and BiOI nanomaterials was estimated about 1.9, 2.6 and 0.9, 630 respectively. Thus, the relatively negative IEP of flower-like BiOI nanomaterials may 631

leads to its weak removal ability for negatively Cr(VI) species (HCrO₄⁻ and Cr₂O₇²⁻) [166].

These results highlight the latent capacity of BiOX photocatalytic nanomaterials 634 in photocatalytic removal of heavy metal ions, which is an efficient and energy efficient 635 method for removal of hazardous heavy metal ions. In particular, with the help of some 636 strategies, such as co-catalyst [164], crystal facet control [57, 62, 63], heterojunction 637 [167, 168], bismuth-rich strategy [113, 115] and solid solutions [115], the removal 638 efficiency of heavy metal ions by BiOX nanomaterials under visible light irradiation is 639 greatly enhanced. Progress achieved in this field may 640 h the BiOX-based photocatalytic systems for heavy metal ions removal to a direction. 641

642 5.3 Photocatalytic oxidation of air contaminar

With the deterioration of atmospheric quality 643 po ut on has attracted more and more attention. A number of methods ha :b stablished to purify polluted air, such 644 as physical adsorption, catalysis redox ion and so on [169, 170]. Compared 645 with these techniques, photo atavtic oxidation is of the highest efficiency with 646 recyclable characteristics, and wi hout secondary pollution. Therefore, hierarchical 647 BiOX photocatalistic hand materials as a novel ternary oxide semiconductor are widely 648 used to remove air poll tants due to their distinctive physical, chemical and optical 649 properties, etc. Ai et al. [171] fabricated BiOBr microspheres via a nonaqueous sol-gel 650 method for removal of NO under visible light irradiation. The as-synthesized samples 651 showed superior photocatalytic activity to the Degussa TiO₂ P25 and C doped TiO₂ as 652 well as BiOBr bulk powder. This is mainly due to their suitable band gap and special 653 654 hierarchical structure, which could enhance their absorption efficiency of visible light and accelerate the diffusion of intermediates, respectively. The major reaction steps of 655 this photocatalytic oxidation of NO are displayed by the following equations (8-11) 656

657 [171].

$$NO + 2 \bullet OH \rightarrow NO_2 + H_2O \tag{8}$$

$$NO_2 + \bullet OH \to NO_3^- + H^+$$
(9)

$$NO + NO_2 + H_2O \rightarrow 2HNO_2 \tag{10}$$

 $NO_{x} + \bullet O_{2}^{-} \to NO_{3}^{-}$ (11)

Apart from microstructure modulation, other strategies such as solid solutions [105, 662 172, 173], photosensitization [174], surface metal ion clusters modification [175, 176], 663 heterojunction [177-179], facets and defects controlling [60, 179] and surface plasmon 664 resonance (SPR) [60] have been verified as efficient avenues 665 improve the ability of BiOX photocatalytic nanomaterilas for removal of air poly sible light. For 666 ed P example, Huang and co-workers [175] investig Nght photocatalytic 667 activity of Fe(III)-BiOCl and bare BiOCl by the de n of gaseous acetaldehyde, 668 ÞО and their obtained results demonstration ۰d / the Fe(III)-BiOC1 showed higher 669 photocatalytic performance, as displayed 4a and b. This can be attributed to the 670 Fe(III) clusters fixed on the arfa es of BIOCl, they can promote the separation of 671 photo-induced charge carriers through interfacial charge transfer (IFCT) under visible 672 light illumination and the ve a the centers of redox for the multi-electron reduction 673 reaction of O₂ (Fig. [175]. The electrons in the VB of BiOCl microflowers are 674 induced and migrated to the Fe(III) clusters by the IFCT process under visible light 675 676 illumination. Subsequently the Fe(III) clusters are reduced to the Fe(II) clusters, which can act as the multi-electron redox site for the O₂ reduction and thus are oxidized to the 677 Fe(III) clusters. Meanwhile, the generated holes in the VB of BiOCl can degrade the 678 gaseous acetaldehyde because of their great oxidation power. Moreover, their team 679 discovered that the Rh(III) clusters can also improve the ability of BiOCl for 680 photocatalytic decompose gaseous acetaldehyde [176]. Their work indicates that 681

surface transition metal ion clusters modification could greatly improve the visible light
 photocatalytic capacity of BiOX photocatalysts.

Very recently, Dong et al. developed Bi@BiOCl plasmonic photocatalysts with 684 exposed facets, oxygen defects and plasmonic Bi metal for removal of NO under visible 685 light [60]. In contrast to pure BiOCl and Ag@BiOCl, Bi@BiOCl exhibited enhanced 686 visible light induced photocatalytic oxidation ability for NO. And the Bi@BiOCl with 687 suitable Bi metal concentration and exposed {010} facets (B010-Bi30) displayed the 688 highest photocatalytic activity. This distinct enhancement is due to their improved 689 structure [60]. This 690 separation ability of charge carriers and favorable morpholo work provides a new strategy to construct efficient BiOX for removal of 691 NO using facets, defects and SPR effects. 692

lo 693 However, Dong et al. [180] utilized the Bio incrospheres for removing NO under visible light and they found he generated  $NO_3^-$  could restrict •OH 694 generation through occupying the surface sites of BiOI microspheres. OH⁻ can't 695 e produced because like charges repel each other. be adsorbed again and •OH an't 696 Therefore, NO is directly oxidized to NO₂ by photo-generated holes. Thus, this greatly 697 affects its ability for cata ytic oxidation of NO. **k**ht 698

To overcome this isadvantage, Xia et al. [181] designed a BiOI/Al₂O₃-padded 699 trickling scrubber used for simultaneous removal of SO₂ and NO under visible light 700 701 irradiation. The SO₂ and NO removal efficiencies in this photocatalytic trickling scrubber system can reach 100% and it could be attributed to the fact that the improved 702 gas absorption capacity and massive reactive •OH production. The recycled activity 703 704 tests indicated that this system is stable for long-term continuous elimination of SO₂ and NO [181]. This study demonstrates that the BiOI/Al₂O₃-padded trickling scrubber 705 possess an immense application potential for simultaneous removal of SO₂ and NO. In 706

general, some researches have been done on the treatment of air pollutants with BiOX
photocatalytic nanomaterials, and the results show that the modified BiOX
photocatlysts do have great potential for remove air pollutants.

## 710 6. Conclusion and perspectives

In the past few decades, many advances have been made to use BiOX 711 photocatalytic nanomaterials for addressing energy and environmental challenges. The 712 713 unique properties of BiOX have provided more possibilities to improve their visible 714 light photocatalytic activity. In this review, we summarize the recent studies in the fields of water splitting, reduction of CO₂, removal of environm allutants based on 715 BiOX photocatalytic nanomaterials. Our purposes are to ment research on 716 717 the strategies for the enhancement of BiOX-bas catarythe activities in energy conversion and environmental management give guidelines for future 718 research. Although progresses have be in the field of BiOX photocatalytic 719 720 nanomaterials over recent years, the Bio phetocatalysts which still in experimental stage cannot satisfy the dynamic of practical production applications. Significant 721 he construct on of BiOX-based photocatalytic systems with high 722 challenges remain in n erergy conversion and environmental management. photocatalytic effic 723

First, since BiOX have many different crystal facets, besides the common {001} and {010} facet-dominant BiOX, the facile synthesis of BiOX photocatalysts exposed with other high-performance crystal facets are also essential. In addition, as a result of the difference between crystal facets, the free radicals produced by these crystal facet may be diverse, this requires us to further explore the reaction mechanism between different facets to find the optimal crystal facet.

Second, the IEF intensity originated from the unique layered structure is an
 interesting characteristic of BiOX photocatalysts, however, the study of the effect of

732 IEF on photocatalysis of BiOX is still lacking. Further research should focus on the 733 specific mechanism of photocatalysis under the effect of IEF and the development of 734 strategies for enhancing photoctalytic activities of BiOX-based on the changes of IEF.

735 Third, in future research on the hydrogen production by photocatalytic water splitting based on BiOX nanomaterials, in addition to the in-depth investigation of the 736 reaction mechanisms and development of efficient hydrogen production system, a study 737 of the stability and sustainability of BiOX photocatalysts in practical application should 738 be performed. There are some other difficulties that must be overcome to achieve high 739 pultaneous generation 740 yield of hydrogen and meet practical applications, such as the of  $H_2$  and  $O_2$ , the separation of  $H_2$  and  $O_2$  and the design Ae reactors. 741

Fourth, the products are complex and diverse weakbuse **BOX** photocatalysts to reduce CO₂. In order to obtain single and stable field at vibboe necessary to clarify the reaction mechanism and find the optimal reaction condition. Moreover, the effect of BiOX nanostructures on CO₂ molecules upture should also be discussed.

Fifth, the contaminants management by BiOX nanomaterials now mainly focus on dyes, Cr(VI) and NO. But for complex organic pollutants, especially toxic and refractory pollutants, the relative reports are very deficient. Besides, the abilities of BiOX nanomaterials to tackle cocontamination are still unclear and they need further exploration.

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Fig. 1 Increasing interest in bismuth-based photocatal sets and ofsmuth oxyhalides. The charts display the total number of publications per year bout (a) bismuth-based photocatalysis, (b) BiOCl photocatalysis, (c) BiORr photocatalysis and (d) BiOI photocatalysis.





**Fig. 2** Band structures of BiOX: (a) BiOCl crystals, (b) BiOBr crystals and (c) BiOI crystals (reprinted with permission from ref. 27. Copyright (2012) Elsevier).





Fig. 3 Layered structure models of BiOCl: (a) three-dimensional spatial structure, (b) {110}
crystal facets and (c) {001} crystal facets (reprinted with permission from ref. 30. Copyright
(2014) The Royal Society of Chemistry).





Fig. 4 Band positions of BiOX and redox potentials of different species in photocatalysis.





Fig. 5 SEM images of (a) flower-like BiOBr and (b) sphere-like BiOBr (reprinted with permission from ref. 49. Copyright (2015) Elsevier).





**Fig. 6** (a) TEM, (b) HRTEM and (c) SAED images of BiOI-110. (d) TEM, (e) HRTEM and (f) SAED images of BiOI-001 (reprinted with permission from ref. 55. Copyright (2015) American Chemical Society).





Fig. 7 Effect of BiOCl V^m_{Bi}V_ÖV^m_{Bi} formation on photocatalytic activity (reprinted with permission from ref. 70. Copyright (2013) American Chemical Society).







1017Fig. 9 Photocatalytic reaction mechanism of (a) ng-CN/BOC-001 and (b) ng-CN/BOC-0101018(reprinted with permission from ref. 58. Copyright (2015) The Royal Society of Chemistry).









MnOx. (e) Rates of Fig. 11 TEM images of (a) Au/BiOI, (b) MnOx/BiOI, (c and d) Au 1026 products over BiOI, Au/BiOI/MnOx, Au/BiOI, and MnOx/BiOI und 1027 hţ 1028 inset displays the corresponding rates of products under visible l f) CO yields on 1029 BiOI, Au/BiOI/MnOx, Au/BiOI, and MnOx/BiOI for 5 h up radiation (reprinted with permission from ref. 123. Copyright (2016) f Chemistry). 1030 1031





 Fig. 12 Photocatalytic mechanism diagram of oxygen vacancies modified Bi/BiOCl heterojunction photocatalysts under visible light irradiation (reprinted with permission from ref. 147. Copyright (2014) The Royal Society of Chemistry).

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1038Fig. 13 (a) FESEM and (b) HRTEM of 1% BN/BiOC composite. (b) Vr(VI) photocatalytic1039reduction over different photocatalysts under visible light pradiction. (c) The possible mechanism1040of the Cr(VI) photoreduction over the 1% BN/BiOCl compared required with permission from1041ref. 164. Copyright 2016. Ency rf.





- 1044Fig. 14 Concentration of gaseous acetaldehyde on (a) BiOCl and the Feldt + DCCl under visible1045light irradiation. (c) Diagram of the photo-induced electrons separation and migration in the1046Fe(III)-BiOCl under visible light irradiation (reprinted with the mission from ref. 175. Copyright1047(2015) Elsevier).

Examples	Exposed facets	Synthetic methods	Facets control	Photocatalytic results	Ref.
BiOCl SCNSs	80% {001} facets 73% {010} facets	Hydrothermal	рН	Degradation efficiency of MO is 99% (UV, 45min) and 10% (Vis, 180min) Degradation efficiency of MO is 59% (UV, 45min) and 33% (Vis, 180min)	[44]
BiOCl NSs	0, 71%, 75% and 87% {001} facets	Hydrothermal	Feed ratios	Degradation efficiency of RhB is 9.6%, 33.6%, 48.1% and 81.1% (UV, 32min)	[47]
Ag-BiOCl SCNSs	71% {001} facets 77% {010} facets	microwave-assisted solvothermal (EG)	-	Removal efficiency of a V2, and NaPCP are 65% and 63% (Vis, 180min) Removal efficiency of CVV and VaPCP are 86% and 80% (Vis, 180min)	[57]
g-C3N4/BiOCl	{001} facets {010} facets	Hydrothermal	рН	Degradation effectively of 2 O and 2 are 65% and 40% (Vis, 150min) Degradation efficient are 10 Para phenol are 94% and 54% (Vis, 150min)	[58]
C-doped BiOCl/NiOx	{001} facets {010} facets	Hydrothermal and impregnation method	рН	Photocatalyte the evolution rate is 0.24 mmol $h^{-1}$ g ⁻¹ (Vis) Photocatalyte $H_2$ evolution rate is 0.42 mmol $h^{-1}$ g ⁻¹ (Vis)	[59]
Bi@BiOCl	{001} facets {010} facets	Hydrothermal	рН	Rep wal afficie sector NO is 35% (Vis, 30min) Rep warene hey of NO is 50% (Vis, 30min)	[60]
BiOBr NSs	{001} facets	Hydrothermal	рН	) production rate is 4.45 $\mu mol \ h^{-1} \ g^{-1}$ (UV-Vis, 2h)	[38]
BiOBr NSs	{001} facets	Combustion	Amount of MH4Br	Ughest degradation efficiency of RhB is 91.6% (Vis, 120min)	[45]
BiOBr NSs	94% {001} facets	Hydrolysis	Temperature and solvent	Degradation efficiency of RhB is 100% (Vis, 60min)	[46]
BiOBr NSs	{102} facets {001} facets	Hydrothermal	Temperatu and solvent	Degradation efficiency of RhB is 100% (Vis, 16min) Degradation efficiency of RhB is 80% (Vis, 16min)	[61]
BiOBr	{001} facets {110} facets	Hydrolysis Hydrothermal		Removal efficiency of Cr(VI) is 40% (Vis, 50min) Removal efficiency of Cr(VI) is 100% (Vis, 50min)	[62]
BiOI NSs	{001} facets {100} facets	Hydrothermal	Time	Production rate of CO and CH ₄ are 5.18 $\mu$ mol h ⁻¹ g ⁻¹ and 1.78 $\mu$ mol h ⁻¹ g ⁻¹ (UV-Vis) Production rate of CO and CH ₄ are 1.52 $\mu$ mol h ⁻¹ g ⁻¹ and 1.50 $\mu$ mol h ⁻¹ g ⁻¹ (UV-Vis)	[54]
BiOI MCSs	{001} facets {110} facets	Hydrothermal	Time	Degradation efficiency of BPA is 52%, TOC value decreased by 44% (Vis, 5h) Degradation efficiency of BPA is 95%, TOC value decreased by 95% (Vis, 5h)	[55]
BiOI MCSs	{001} facets	Solvothermal	-	Removal efficiency of RhB and Cr(VI) are 99% and 100% (Vis)	[63]

Table 1 Effects of exposed crystal facets on photocatalytic activity of BiOX nanomaterials

SCNSs: single-crystalline nanosheets; NSs: nanosheets; MCSs: microspheres.

Photocatalytic applications	Examples	Synthetic methods	Light	Photocatalytic activity	Ref.
Water splitting to H ₂	Carbon-doped BiOCl/NiO _X	Hydrothermal carbonization, thermal-induced doping and impregnation	500 W Xe lamp	$0.42 \text{ mmol } h^{-1} \text{ g}^{-1} \text{ H}_2$	[59]
	BiOCl/CuPc	Solvothermal synthesis(EG)	500 W Xe lamp	20 μmol h ⁻¹ g ⁻¹ H ₂	[116]
	BiOCl@Au/MnOx	Hydrothermal synthesis and photodeposition	500 W Xe lamp	66 μmol h ⁻¹ g ⁻¹ H ₂	[117]
	BU-BiOCl/Pt	Solvothermal synthesis (glycerol)	300 W Xe lamp λ 200m	79.2 μmol h ⁻¹ g ⁻¹ H ₂	[118]
	$Bi_{12}O_{17}Cl_2/MoS_2$	Chemical liquid exfoliation	300 W Xe lamp .≫20r	33 mmol h ⁻¹ g ⁻¹ H ₂	[119]
	BiOBr/a-Fe ₂ O ₃ /Pt	Hydrothermal synthesis	300 W Xe / (n ) > -20 ar	.08 μmol h ⁻¹ g ⁻¹ H ₂	[120]
Reduction of CO ₂ to fuels	Oxygen-deficient BiOCl nanoplates	Solvothermal synthesis(EG)	500 - Xe lan p	1.01 µmol h ⁻¹ g ⁻¹ CO, 0.15 µmol h ⁻¹ g ⁻¹ CH ₄	[68]
	BiOBr-001 nanosheets	Hydrothermal synthesis	200 Weitenp	4.45 μmol h ⁻¹ g ⁻¹ CO	[38]
	BiOBr	Solvothermal synthesis (ethanol)	305 Xeenmp $\lambda > 400$ nm	$1.68 \ \mu mol \ h^{-1} \ g^{-1} \ CO, \ 0.17 \ \mu mol \ h^{-1} \ g^{-1} \ CH_4$	[114]
	Ultrathin BiOBr	Solvothermal synthesis (ethanol)	200 W Xe mp 400 nm	2.67 µmol h-1 g-1 CO, 0.16 µmol h-1 g-1 CH ₄	[114]
	Bi ₄ O ₅ Br ₂ microspheres	Solvothermal synthesis (glycerol) and hydroxsis	$00 \text{ W Xe amp } \lambda > 400 \text{ nm}$	2.73 $\mu mol \; h^{\text{-1}} \; g^{\text{-1}} \; CO, 2.04 \; \mu mol \; h^{\text{-1}} \; g^{\text{-1}} \; CH_4$	[114]
	Bi ₂ O ₄ /BiOBr	Hydrothermal synthesis	◆ 300 W / e lamp	2.60 $\mu mol \; h^{\text{-1}} \; g^{\text{-1}} \; CO, \; 1.85 \; \mu mol \; h^{\text{-1}} \; g^{\text{-1}} \; CH_4$	[121]
	Oxygen-deficient BiOBr	Solvothermal synthesis(EG)	500 W Xe lamp 500 W Xe lamp λ > 400 nm	0.96 μmol h ⁻¹ g ⁻¹ CH ₄ 0.49 μmol h ⁻¹ g ⁻¹ CH ₄	[122]
	BiOI-001 nanosheets	Solvothermal synthesis (ethnol)	300 W Xe lamp	5.18 $\mu mol \ h^{\text{-1}} \ g^{\text{-1}}$ CO, 1.78 $\mu mol \ h^{\text{-1}} \ g^{\text{-1}}$ CH ₄	[54]
	BiOI-100 nanosheets	Solvothermal synthesis (ethan )	300 W Xe lamp	$1.52~\mu mol~h^{1}~g^{1}$ CO, $1.50~\mu mol~h^{1}~g^{1}$ CH_4	[54]
	Au/BiOI/MnO _X	Photochoosition	300 W Xe lamp 300 W Xe lamp λ > 420 nm	42.9 µmol h-1 g-1 CO, 1.36 µmol h-1 g-1 CH ₄ 9.76 µmol h-1 g-1 CO, 0.39 µmol h-1 g-1 CH ₄	[123]
	Few-layered BiOI	Solvotian LontheshiEG)	300 W Xe lamp $\lambda >$ 420 nm 300 W Xe lamp $\lambda >$ 700 nm	4.10 $\mu mol\ h^{-1}\ g^{-1}\ CO,\ 0.42\ \mu mol\ h^{-1}\ g^{-1}\ CH_4$ 0.80 $\mu mol\ h^{-1}\ g^{-1}\ CH_4$	[124]
	BiOI/g-C ₃ N ₄	Deposition	300 W Xe lamp $\lambda > 400 \text{ nm}$	3.45 $\mu mol~h^{1}~g^{1}$ CO, 0.16 $\mu mol~h^{1}~g^{1}$ CH4, 0.37 $\mu mol~h^{1}~g^{1}$ H_2	[125]

Table 2 Recent studies on BiOX (X=Cl, Br, I) photocatalytic nanomaterials used for fuels preparation from H₂O and CO₂