Substitution Boosts Charge Separation for High Solar-Driven Photocatalytic Performance

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Supporting Information

ABSTRACT: Bandgap engineering of photocatalysts is a common approach to achieving high effective utilization of solar resource. However, the difficulty in achieving bandgap narrowing and high activity simultaneously seems to be irreconcilable via the traditional modification pathway. Herein, we have substituted iodine for a fraction of bromine atoms in BiOBr to overcome this restriction and provided some deep-seated insights into how the substitution boosts the photocatalytic properties. The substituted $\text{BiOBr}_{0.75}\text{I}_{0.25}$ exhibited exceptional photoactivity, with photon-to-current conversion efficiency approximately 6 times greater than TiO_2 in UV region, and more than 10 times higher than BiOBr or BiOI in visible-light region. We found that the substitution narrowed the bandgap, facilitated the diffusion of electron with small effective mass, as well as induced oxygen vacancies on $[\text{Bi}_2\text{O}_2]^{2+}$ layers. By virtue of the stronger dipole moments produced, the enhancement of intrinsic electric fields between $[\text{Bi}_2\text{O}_2]^{2+}$ and halogen slabs was achieved in $\text{BiOBr}_{0.75}\text{I}_{0.25}$; thereby the distance the photogenerated electron could diffuse was sufficient to inhibit the recombination. Our findings not only shed light on the potential properties of hybrid-halide photocatalysts but also provide a strategy for developing high efficiency catalysts.

KEYWORDS: BiOBr, iodine, substitution, vacancy, photoactivity

INTRODUCTION

Photocatalysts provide significant potential for the conversion of solar radiation to chemical energy.^{1–3} Different approaches for narrowing the bandgap have developed into an active pursuit by researchers aimed at gathering solar energy.^{4,5} Doping, a common method for the modification of nanomaterials, is traditionally considered to be of crucial and scientific significance in materials science.⁶ Unfortunately, the difficulty of simultaneously achieving bandgap narrowing and high photoactivity seems to be irreconcilable. Although some success has been reported in achieving visible light activity by using dopants, the charge carrier trapping and recombination sites induced in the bulk have negative effects on photochemical activity.^{7,8}

As the layered ternary semiconductors, bismuth oxyhalides (BiOX , $X = \text{Cl}$, Br , and I) with $[\text{Bi}_2\text{O}_2]^{2+}$ slabs sandwiched between halogen atom slabs have drawn extensive attention due to their superior photocatalytic performance, in some cases surpassing that of TiO_2 in UV region.^{9–11} However, in contrast

to some other Bi-based semiconductors (such as BiVO_4 , Bi_2WO_6 , and BiFeO_3),^{12,13} lower visible-light activities of the BiOX need to be enhanced for satisfying practical applications. In BiOX crystals, the valence band is comprised of X np and O 2p states, while the conduction band minimum (CBM) is dominated by Bi 6p states. The BiOX crystals may be vested in O 2p and X np to Bi 6p, a p-to-p charge-transfer type, and the bandgap can also be derived using the charge-transfer energy minus the valence-bandwidth.¹⁴ The charge-transfer energy is proportional to the Pauling electronegativity of X atom (3.16, 2.96, and 2.66 for Cl, Br, and I, respectively), which shows an apparent trend of the bandgap narrowing with the X atomic number. Hence, there are numerous reports on the preparation of BiOBr or BiOI that have good visible-light photoactivity.^{15,16}

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Figure 1. Characterizations of $\text{BiOBr}_{0.75}\text{I}_{0.25}$ sample. (a) SEM of the $\text{BiOBr}_{0.75}\text{I}_{0.25}$. Scale bar, 500 nm. (b) STEM image of the single $\text{BiOBr}_{0.75}\text{I}_{0.25}$ nanosphere. Scale bar, 100 nm. Inset: Magnified HAADF-STEM image of the $\text{BiOBr}_{0.75}\text{I}_{0.25}$ shell along with [010] direction, demonstrating the iodine is well distributed in the bromine host sites. Scale bar, 0.5 nm. (c) The large area STEM-EDS mapping corresponding to the red dash quadrate in (b). (d) XRD patterns, (e) the Bi L-edge extended EXAFS oscillation, and (f) corresponding Fourier transform (FT) for the BiOBr , BiOI , and $\text{BiOBr}_{0.75}\text{I}_{0.25}$.

Additionally, the intrinsic electric fields due to the dipole moments between the $[\text{Bi}_2\text{O}_2]^{2+}$ layer and the anionic halogen atoms also determine the separation of photogenerated charge carriers.^{17,18} With increasing halogen atomic number, the covalent bond between the Bi and X atoms is strengthened, which promotes the internal electric fields through an increase in the dipole moments; thereby the photogenerated charge carriers are separated effectively.¹⁹ Notably, in recently reported organic–inorganic mixed-halide perovskites, notwithstanding the coexistence of other elusive factors, remarkably enhanced photovoltaic performances have been indeed observed resulting from substitution.^{20,21} This has prompted us to hypothesize that the homogeneous substitution with foreign halogen atoms in BiOX would be feasible to achieve a strong intrinsic electric field for long charge diffusion length.

Meanwhile, during the process of pursuing optimized internal dipole moments, a few dangling bonds will be simultaneously created in the covalently bonded layers when

strengthening the covalent bonding effect between bismuth and halogen atoms, resulting in vacancies in the crystal.²² Defects, as active sites where the charge carriers can be effectively separated,^{23,24} have been recently reported to narrow the band gap as well.²⁵ Thus, the defect bismuth oxy-hybrid-halides have the potential to reconcile the apparent contradiction between bandgap narrowing and performance, and to provide an ideal platform to attain a comprehensive understanding of correlations between the structure, defects, and properties.

Herein, we report a detailed investigation on the substitution of iodine for bromine in BiOBr to optimize the performance through compositional tuning. The $\text{BiOBr}_{0.75}\text{I}_{0.25}$ exhibited exceptional photoactivity, with photon-to-current conversion efficiency approximately 6 times greater than TiO_2 in the UV region, and more than 10 times higher than BiOBr or BiOI in the visible-light region. On the basis of the results of X-ray absorption fine structure (XAFS) spectra, positron annihilation lifetime spectra (PAS), and electron paramagnetic resonance

(EPR) spectra in association with theoretical calculations, the relationships between substitution, vacancies, and enhanced activity were analyzed thoroughly.

RESULTS AND DISCUSSION

The substitution of iodine atoms into the BiOBr crystal should have the best potential for the preparation of highly efficient

Figure 2. Theoretical calculation on the effect of substituted iodine numbers on BiOBr. (a) Computational optical absorption for the different substitution iodine atoms into BiOBr. From density functional theory (DFT) calculations, pure BiOBr possesses a bandgap of 2.82 eV. With increase in the substituted numbers, the bandgap decreased from the 2.52 eV in the two-iodine-atom substitution to 1.90 eV in pure BiOI. (b) The effective mass approximation with various degrees of iodine atom substitution. The bold solid line is the ratio of m^* (hole) to m^* (electron), for quantitative analysis of the separation efficiency.

Figure 3. Mott–Schottky plots of BiOBr, BiOI, and BiOBr_{0.75}I_{0.25} electrodes measured at 1000 Hz.

photocatalysts. Here, we achieve this by applying a facile solvothermal method (see [Experimental Section](#)). In contrast to the morphology range from flake to solid sphere with addition of different amounts of precursors ([Figure S1](#)), regular spheres with porous structure assembled from numerous smooth and flower-like nanoshells were observed in the case of Bi:Br:I ratio of 1.0:1.5:1.5 ([Figure 1a](#)), similar to BiOBr and BiOI. The sphere was further observed by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) ([Figure 1b](#)). Generally, the detector in HAADF gathers electrons that change high-angle scattering, the signal intensity of which is directly proportional to the atomic number, Z .^{26,27} Therefore, the sharp contrast in the image enables the identification of the Bi ($Z = 83$), Br ($Z = 35$), and I ($Z = 53$) ions in shells.²⁸ As shown in the inset in [Figure 1b](#), the brightest spots symbolize Bi atoms, spots with the darkness represent Br atoms, and the spots with intermediate darkness stand for the I atoms, which are well-distributed in the Br host sites. Uniform distribution of Bi, O, Br, and I was observed throughout the structure ([Figure 1c](#)). The elemental composition of the sample was analyzed via energy dispersive X-ray spectroscopy (EDX). The Bi:Br:I atomic ratio was around 1.0:0.75:0.25, which was further confirmed through the ion chromatography (IC) and inductively coupled plasma optical emission spectrometry (ICP-OES). Moreover, on the basis of calculated reaction enthalpy ([Figure S2](#)), a stable bismuth oxy-hybrid-halide structure could be achieved by random substitution of iodine atoms into the BiOBr crystal. XRD pattern confirms that the sample has a tetragonal matlockite crystal structure ([Figure 1d](#)), representing a layered structure with $[\text{Bi}_2\text{O}_2]^{2+}$ interleaved between halogen atoms slabs.²⁹ Meanwhile, in contrast to BET surface areas of 45.8 and 42.6 $\text{m}^2 \text{g}^{-1}$ of BiOBr and BiOI, a decreased value of 29.2 $\text{m}^2 \text{g}^{-1}$ was observed in BiOBr_{0.75}I_{0.25} after iodine substitution ([Figure S3](#)).

Extended X-ray absorption fine structure spectroscopy (EXAFS) measurements were performed to study the arrangement of atoms around the photoabsorber.³⁰ The Bi L-edge oscillation curve for BiOBr/I displays a remarkable difference in comparison with those of unsubstituted BiOBr and BiOI ([Figure 1e](#)), indicating the different local atomic arrangements in the catalysts.³¹ Fourier transform (FT) curves present three peaks in the range from 1 to 4 Å, corresponding to Bi–O, Bi–Br, and Bi–I distances, respectively. The FT curve of BiOBr shows the Bi–Br coordination with a main peak at 2.80 Å, whereas the peak is shifted to higher R by 0.08 Å in BiOBr/I. The high- R shift of the Bi–Br peak that resulted from the elongated distance between Bi and Br ([Table S1](#)) was due, most probably, to the electrostatic repulsion induced by the iodine with a smaller charge-to-mass ratio in BiOBr/I ([Figure S4](#)). On the contrary, the Bi–I coordination is almost the same as that in BiOI. Thus, on the basis of the coordination information and the fitted distance between Bi and halogen atoms, the atom distributions in BiOBr/I were established ([Figure S5](#)). Hence, we denoted the material as BiOBr_{0.75}I_{0.25}.

On the basis of the as-identified atom arrangements in BiOBr_{0.75}I_{0.25}, first-principle calculations were first performed to evaluate the effect of substitution on the band gap energy. BiOBr possesses a bandgap of 2.82 eV ([Figure 2a](#)). The substitution of iodine atoms for 25% the bromine in the BiOBr crystal results in a sharp down-shift of Bi 6p orbitals to VBM, decreasing the bandgap to 2.52 eV ([Figure S6a](#)). Further, carrier mobility, characterizing how rapidly an electron can

Figure 4. Formation of oxygen vacancies on BiOBr_{0.75}I_{0.25}. (a) The HRTEM image of [Bi₂O₂]²⁺ layers ([001] direction), confirming the existence of defects on the layer. Scale bar, 2 nm. Inset: Annular bright-field and dark-field STEM imaging in the white dash quadrate for visualizing atomic arrangements in the covalence layers (blue and red balls represent bismuth and oxygen atom, respectively). The white arrowhead in the dark-field STEM image indicates the shift of the bismuth atom, which might have resulted from the deficiency of oxygen atom on layer. (b) Positron annihilation lifetime spectra (PAS) with lifetime parameters (table inset), and (c) low temperature (70 K) EPR spectra of BiOBr, BiOI, and BiOBr_{0.75}I_{0.25}, respectively.

transfer through materials under field, was investigated using effective mass approximation, to evaluate the effect of substitution on photoinduced carrier separation efficiency.^{32,33} In a semiconductor, the movement of electron takes place in a periodic potential, different from its motion in vacuum, and the effective mass (m^*) is a quantity that is applied to simplify the band structure by constructing an analogy to the behavior of a free particle with the same mass.³⁴ A particle with small effective mass means will have low inertia and high carrier mobility (μ) based on the formulas:

$$\mu = \frac{e\tau_s}{m^*} \quad (1)$$

where e and τ_s are electron charge and mean scattering time, respectively. Remarkably, BiOBr_{0.75}I_{0.25} exhibits the smallest m_e^* (electron) and the largest m_h^* (hole) among all of the compositions studied (Figure 2b), which suggests that the electron in the iodine-substituted material has the highest mobility. Moreover, iodine has a substantially larger radius than that of the atom it is replacing; thereby the equilibrium positions of the unsubstituted atoms nearby are shifted away from the original sites. Thus, the dipole moment for BiOBr_{0.75}I_{0.25} increased to 2.98 D, with respect to the values of 1.70 and 2.45 D for BiOBr and BiOI. The enhanced intrinsic electric field due to the promoted dipole moment could facilitate the diffusion of the small effective mass m_e^* to the trap sites, leaving the heavy hole at its original (VBM), which would effectively decrease their recombination probability.³⁵

Mott–Schottky plots were constructed to determine the carrier density of BiOBr, BiOI, and BiOBr_{0.75}I_{0.25}, respectively. The observed positive slopes indicate the n-type nature of BiOX samples (Figure 3).^{36,37} The carrier density could be determined by the relation:

$$N_d = \left(\frac{2}{e\epsilon\epsilon_0} \right) \left(\frac{dC^{-2}}{dV} \right)^{-1} \quad (2)$$

where N_d is the number of donors, ϵ is the dielectric constant, e is the electron charge, and ϵ_0 is vacuum permittivity. Notably, BiOBr_{0.75}I_{0.25} exhibits an order of magnitude higher carrier density than BiOBr and BiOI (carrier densities for BiOBr, BiOI, and BiOBr_{0.75}I_{0.25} were evaluated as 1.25×10^{18} , 1.38×10^{18} , and 1.29×10^{19} , respectively). In addition, flat-band potential of BiOBr_{0.75}I_{0.25} was negatively shifted, which depressed charge carriers' recombination by enhancing band bending at interface.³⁸ Meanwhile, conduction band edges of n-type BiOX can be obtained from the following equation:

$$V_{CB} = U_{fb} - \frac{K_B T}{q} \ln \left(\frac{N_D}{N_C} \right) \quad (3)$$

in which N_C is the density of states in CB; q is unsigned charge of an electron. In contrast to the DOS result for defect-free BiOBr_{0.75}I_{0.25}, negative shifted CB in the Mott–Schottky plot was due to the presence of transition state induced by oxygen vacancies, which was in good agreement with the theoretical calculations as well.

Figure 5. (a) High-resolution XPS scans for Bi 4f, and (b) the first-order derivative of Bi L-edge XANES measurements for BiOBr, BiOI, and BiOBr_{0.75}I_{0.25}, respectively.

As discussed above, the substitution of iodine atoms into the BiOBr crystal could improve the carrier density because of the large electron mobility. Remarkably, in some domains, a distorted lattice can be observed in $[\text{Bi}_2\text{O}_2]^{2+}$ layers (Figure 4a). Such lattice dislocation is usually derived from atom deficiency. It should also be noted that the oxygen vacancies can be regarded as electron donor species.^{39,40} To ascertain this, the nature of the defects was first studied by PAS. Figure 4b depicts the three types of positron annihilation measurements for the BiOX, and the table inset shows lifetime components of the two positrons, τ_1 and τ_2 , with the corresponding intensities I_1 and I_2 , respectively. Normally, τ_1 was derived from the defects with small-size in bulk, while τ_2 results from positrons trapped by defects with larger size on surface.⁴¹ According to the theoretically calculated lifetime of positrons, the short τ_1 around 189 ps could be assigned to positron annihilation as trapped at the oxygen defects, while the other component (τ_2) around 460 ps was attributed to larger vacancy clusters on surface. Moreover, further information on the concentration of the vacancies could be gained from the relative intensity (I). In comparison with the values of 0.45 and 0.71 of BiOBr and BiOI, respectively, the I_1/I_2 value of BiOBr_{0.75}I_{0.25} increased to 2.12, indicating a higher concentration of defects after iodine substitution.

The underlying mechanism of the oxygen vacancy formation is, in fact, closely related to the generation of reduced states of bismuth with iodine substitution, and depended on the synthetic process as well. As observed in the electronic density

distribution (Figure S6), the local atomic arrangement in BiOBr_{0.75}I_{0.25} strengthens the covalent interaction between the bismuth and halogen atoms, resulting in remarkable variations in the electronic landscape around the Bi atoms. The enhancing covalency can also be quantitatively noticed according to effective ionic valence, which is the variance between Mulliken charge and primitive ionic charge in the compound. The average Mulliken charge of halogen atoms in BiOBr_{0.75}I_{0.25} decreased to -0.22 with respect to that of -0.43 and -0.33 in BiOBr and BiOI, respectively; the corresponding effective ionic valence increased from 0.57 and 0.67 to 0.78 (the primitive ionic charge of a halogen ion is -1.00). The greater value in BiOBr_{0.75}I_{0.25} means a higher level of covalent interaction between the halogen elements and bismuth atoms. The binding energy of Bi 4f in the BiOBr_{0.75}I_{0.25} is red-shifted by 0.5 eV (Figure 5a), and the absorption edge energy of Bi species in first-order derivative of Bi L-edge XANES is red-shifted by 0.3 eV with respect to unsubstituted BiOBr and BiOI (Figure 5b), implying the presence of low valence state bismuth species. Moreover, during the solvothermal synthetic process, the Bi atoms possess inadequate oxygen as bonding partners to accommodate the valence variation. EPR spectra were then performed to gain more information on the BiOBr_{0.75}I_{0.25}. As shown in Figure 4c, both BiOBr and BiOI have a weak signal at $g = 2.003$. On the contrary, BiOBr_{0.75}I_{0.25} exhibits obvious EPR signal at $g = 2.003$, indexing to the low-valence Bi atoms with dangling bonds located in the $[\text{Bi}_2\text{O}_2]^{2+}$ layers,⁴² bringing about a high concentration of oxygen vacancies (OVs) in the crystal.^{43,44}

The existence of OVs in the semiconductor greatly changes the Bader charges, band structure, partial density of states (PDOS), total density of states (TDOS), and frontier molecular orbitals (Figure 6). As above-mentioned, the substitution of iodine atoms into BiOBr decreased the bandgap by 0.30 eV. To further investigate the electron density contour maps, it must be noted that Bi 6p and X np states generated another high-density region in the presence of OVs, resulting in a sharp downshift of localized Bi 6p states and moderate downshift of the X np states, further narrowing the bandgap by 0.26 eV. This trend is consistent with the UV/vis diffuse reflection data (Figure S8). In addition, newly hybridized states between the Bi 6p and X-np states created a transition energy band between CBM and VBM, which was also conducive to photon absorption. The occupied states near the Fermi level could be considered to consist of isolated and localized states, which were mainly due to the existence of reduced Bi species. The presence of the transition states will facilitate electron diffusion by the polaron hopping mechanism.⁴⁵ Moreover, in contrast to defect-free material, the observed k -vector (crystal momentum) in the Brillouin zone for CB and VBM is different in the defected BiOBr_{0.75}I_{0.25}, indicating that it is of an indirect bandgap semiconductor. Hence, the recombination efficiency of as-generated electron–hole pairs is far slower than that in the defect-free material.

Further examination of electron density distribution demonstrated that the covalent interactions were strengthened between the halogen slabs and Bi atoms in the defect BiOBr_{0.75}I_{0.25}; thereby the dipole moment increased to 3.38 D. Additionally, the variation in electronic structures induced by the OVs implies that the electron-donor species can also serve as a dopant to enhance the electron mobility. According to the effective mass approximation, the electron effective mass was decreased by a factor of 1.5 in contrast to defect-free

Figure 6. Band structure and density of electronic states of defect-free BiOBr_{0.75}I_{0.25} (top) and the defected one (bottom). Inset: The electron density contour maps for the LUMO and HOMO, respectively.

material. The small effective mass with high mobility would effectively diffuse in the enhanced intrinsic electric fields, thereby inhibiting recombination.

The photon-to-current conversion efficiency of BiOBr_{0.75}I_{0.25} was investigated by using the photocurrent action spectra and included the state-of-the-art TiO₂ catalyst for comparison. Figure 7a shows that BiOBr has the lowest photocurrent, BiOI has an intermediate photon-to-current efficiency, and BiOBr_{0.75}I_{0.25} achieves much higher photocurrent than BiOBr, BiOI, and BiOBr_aI_b with other Br:I ratios in the UV–visible -light regions (Figure S8). The superior photoactivity of BiOBr_{0.75}I_{0.25} is reasonably speculated to originate from its high carrier mobility, density, and the enhanced dipole moments. It must be noted that the maximum photocurrent of BiOBr_{0.75}I_{0.25} was approximately 6 times greater than P25 TiO₂ toward light region from 330 to 350 nm. In addition, chronoamperometric technique was applied for evaluating the photoresponse of catalysts. Upon power excitation, photocatalysts exhibited instantaneous photocurrents, which then sharply reverted to steady state after the light was turned off. BiOBr_{0.75}I_{0.25}, with

the highest carrier mobility, exhibits a photocurrent density of 620 $\mu\text{A cm}^{-2}$ under AM 1.5, which is more than 10 times higher than BiOBr and BiOI (Figure 7b). A similar tendency is also observed under visible-light irradiation (Figure 7c).

The charge-transfer properties of the photocatalysts were further measured by means of electrochemical impedance spectrum (EIS) measurements. We selected equivalent circuit (EC) (Figure 7d, inset), which has been evidenced to be suitable in fitting Bi-based semiconductors, to fit the parameters in different electrochemical processes. Similar to the role of surface state reported in former literature,^{46–48} bulk defect crystals were here emphasized in EC model, which can not only trap holes from the valence band (R_{trapping}), but similarly influence the transfer of holes from solid interface to the donor species in solution, as defined by $R_{\text{ct,trap}}$. As shown in Figure 7d, the electrical resistance of BiOBr_{0.75}I_{0.25} was much smaller than that of BiOBr and BiOI in the dark as indicated by smaller impedance arc radius, which was undoubtedly attributed to the existence of OV with high concentration after substitution. Under light illumination, the smaller charge-transfer resistance

Figure 7. Photoelectrochemical properties. (a) The photon-to-current conversion efficiencies of BiOBr, BiOI, and BiOBr_{0.75}I_{0.25} measured using photocurrent action spectra in UV and visible light, and photoresponse recorded by chronoamperometry at +0.5 V in (b) solar or (c) visible light irradiation, respectively. (d) Nyquist plots for the electrochemical impedance spectroscopy (EIS) obtained from 0.1 Hz to 100 kHz in dark and light (AM 1.5) irradiation (inset) with an inserted equivalent circuit for fitting the data, where C_d is the double-layer capacitance, R_s is electrolyte resistance, $R_{trapping}$ represents the resistance during the process of trapping carriers by surface states, C_{trap} represents the amount of active sites in surface states, and $R_{ct,trap}$ is the value of charge-transfer resistance.

($R_{ct, trap}$) on the surface of BiOBr_{0.75}I_{0.25} resulted from the enhanced diffusion of electrons with high mobility (Table S2). Meanwhile, the C_{trap} value, which reflects the quantity of trapped carriers in surface states, was $4.9 \times 10^{-4} \text{ F cm}^{-2}$ in BiOBr_{0.75}I_{0.25}, in sharp contrast to the values of 6.1×10^{-5} and $4.7 \times 10^{-5} \text{ F cm}^{-2}$ in BiOI and BiOBr. The increase in C_{trap} is ascribed to the larger quantities of photoinduced holes on the surface.

Moreover, the photocatalytic performance of the BiOX materials was evaluated. First, with UV light (200–400 nm) irradiation, the red-color of Rhodamine (RB) was totally degraded by BiOBr_{0.75}I_{0.25} within 5 min, whereas 20 min was needed with TiO₂. Under visible light, pseudo-first-order kinetics was fitted well in degradations, and the apparent rate constant (k) of 1.2 min^{-1} was calculated for BiOBr_{0.75}I_{0.25}, which was in sharp contrast to that of 0.32 and 0.067 min^{-1} with BiOI and BiOBr (Figure 8a). In contrast to BiVO₄, a state-of-the-art Bi-based material for photocatalytic splitting water, defect-rich BiOBr_{0.75}I_{0.25} catalyst exhibited the higher photocatalytic efficiency to the colored chemicals.⁴⁹ Meanwhile, due to the suitable iodine substitution as well as the as-induced active oxygen vacancies, degradation efficiency for RB under the same light irradiation outperformed other BiOBr_aI_b samples reported before.⁵⁰ Furthermore, EPR spectra followed by radical-trapping were carried out to gain deep insights into

reactions.⁵¹ An intensity ratio of 1:2:2:1 in 4-fold characteristic peak was observed for DMPO-•OH adduct in BiOBr.²⁹ Notably, a seven-line spectrum characteristic signal with higher intensity was observed for the BiOBr_{0.75}I_{0.25} (Figure 8b). The results show that the reaction of the excited electrons or holes with oxygen in aqueous suspension is able to generate a significant amount of oxidant as shown by the formation of 5,5-dimethyl 1-2-pyrrolidone-*N*-oxyl (DMPOX).⁵² In addition, the photogenerated charge carriers participated in the photocatalytic reaction directly, which was confirmed by the photocatalytic oxidation of Bisphenol A (BPA), and reduction of Cr^{VI} in neutral conditions. BPA, which has been reported to cause adverse effects on aquatic organisms,⁵³ was chosen as a probe to assess the role of holes in degradation.⁵⁴ Under solar light, the degradation rate constant (k) is 0.19 min^{-1} in BiOBr_{0.75}I_{0.25}, which is approximately 7 times that of TiO₂, indicating the direct attack by a high concentration of holes (Figure 8c). Meanwhile, the reduction of Cr^{VI} was completed in 30 min with BiOBr_{0.75}I_{0.25} at a rate constant 0.056 min^{-1} , while negligible H₂O₂ was detected, implying that the Cr^{VI} was reduced by these photogenerated electrons (Figure 8d). The photoactivities of BiOBr_{0.75}I_{0.25} over 10 consecutive cycles for three contaminants containing solutions are shown in Figure S10. A decreased catalytic efficacy after 10 cycles can be observed in the RB- and Cr^{VI}-containing solutions, which were

Figure 8. Photocatalytic performances. (a) Photocatalytic degradation of RB (20 mg L⁻¹) with 0.02 g of BiOBr_{0.75}I_{0.25} or P25 TiO₂ under UV light (left), and degradation of RB (10 mg L⁻¹) at a load of 0.02 g of BiOBr, BiOI, BiOBr_{0.75}I_{0.25}, or P25 TiO₂ catalysts under visible light (right). (b) EPR spectra for BiOBr, BiOI, and BiOBr_{0.75}I_{0.25} in DMPO-containing solutions under solar light irradiation. (c) Photocatalytic oxidation of BPA and (d) reduction of Cr^{VI} at neutral pH condition under solar light irradiation.

due to a strong adsorptive effect with RB, and deposition of as-reduced Cr^{III} on surface in neutral condition. The photocatalytic degradation to BPA in the 10th almost remained the same as the first time. Overall, the observed stability was an important attribution for practical application of BiOBr_{0.75}I_{0.25} to environmental remediation.

CONCLUSIONS

In summary, we here prepared oxygen-vacancy-rich bismuth oxy-hybrid-halide photocatalysts by substitution of iodine atoms into BiOBr crystal, which was confirmed by quantitative analysis of the corresponding EXAFS regions. Results of experimental observations and theoretical calculations showed that the iodine substitution narrowed the bandgap, promoted the carrier mobility, and could be regarded as a prerequisite for the formation of oxygen vacancies. The photocatalytic experiments showed that the vacancy-rich structure constructed by substitution reconciled the apparent contradiction between bandgap narrowing and high activity; striking enhancements were achieved in photon-to-current conversion efficiency in both UV and visible-light regions. The results led to a greater mechanistic understanding of the synergistic effect in hybrid-halide photocatalysts, for example, in hybrid-halide perovskite solar cells.⁵⁵ The relationships among the structure, defects, and enhanced properties will provide a theoretical foundation for the design of a highly efficient catalyst.

EXPERIMENTAL SECTION

Materials Synthesis. 2.0 g of polyvinylpyrrolidone (PVP) ($M_w = 30\,000$) (Aldrich) was added to 40 mL of hot ethylene glycol (70 °C) to obtain a homogeneous solution, and then 1 mmol of Bi(NO₃)₃·5H₂O (Alfa) was carefully dissolved in 2 min. Meanwhile, 1.5 mmol of

Table 1. Reaction Details and Ratios of the As-Obtained Bi–Br–I in the BiOBr_aI_b

Bi(NO ₃) ₃ (mmol)	KBr (mmol)	KI (mmol)	Bi:Br:I	temp/°C
1.00	0.00	1.50	1:0:1	150
1.00	0.50	0.50	1:0.65:0.12	150
1.00	0.50	1.5	1:0.25:0.72	150
1.00	1.00	1.00	1:0.45:0.48	160
1.00	1.25	1.50	1:0.70:0.22	160
1.00	1.50	0.00	1:1:0	160

KBr was added under ultrasound, and subsequently 1.5 mmol of KI was added into the reaction mixture. The mixture was then kept in a Teflon-lined autoclave (filled to 80% of its entire capacity), which was sealed and placed in an electric oven at 160 °C for 12 h. When the Teflon-lined autoclave was allowed to cool at room temperature, pale-yellow precipitate was filtered. The washing procedure was repeated several times with distilled water and absolute ethanol.

Additionally, for preparing samples with different substitution levels, the procedures were the same as for the BiOBr_{0.75}I_{0.25} except that the amounts of halogen precursors and reaction temperatures were adjusted accordingly (Table 1).

Characterizations for Bismuth Oxyhalides. The particle size, composition, and crystal structure of the sample were characterized by powder X-ray diffraction (XRD) (PANalytical Inc.) equipped with Cu K α irradiation. Morphologies of the samples were observed by Zeiss field emission scanning electron microscopy (FESEM). Transmission electron microscopy (TEM) was measured using a high-resolution JEM-ARM200F TEM/STEM for exploring the information on structure and lattice. X-ray photoelectron spectroscopy (XPS) was conducted in a PHI5000 Versa Probe system (Physical Electronics, MN) using monochromatic Al K α radiation (225 W, 15 mA, 15 kV), and the binding energy was calibrated with internal standard by use of C 1s peak at 284.80 eV. To explore light absorbance and emission behavior, UV–visible absorption spectra were recorded in diffuse

reflection mode (UV2401/2, Shimadzu, Japan). Positron annihilation lifetime spectra (PAS) measurements were performed via a fast–slow coincident method. X-ray absorption fine structure spectroscopy (XAFS) for Bi L-edge was carried out at the Shanghai Synchrotron Radiation Facility (SSRF) on beamline BL14W1.

Photoelectrochemical Measurements. A two-electrode configuration system was used for photocurrent action spectra,⁵⁶ where catalysts were covered on FTO glasses by the surgical-blade method applied as a working electrode (a glass rod was applied to roll the pastes containing 0.2 g of powder and 0.5 mL of ethanol on FTO) in 0.2 M KCl electrolyte; a platinum wire with high purity served as a counter electrode. Light source was a 300 W xenon lamp equipped with a monochromator, and PEC cell with an illumination area of 0.12 cm² was illuminated from the FTO side. A lock-in amplifier synchronized with light chopper (monochromatic illuminating intensity was evaluated about 15 $\mu\text{W}/\text{cm}^2$) was applied for recording the current signal. P25 TiO₂-coated photoelectrode was first applied as the control. Photoelectrochemical properties were measured in a standard three-electrode configuration using a Princeton Versa STAT 3 electrochemical workstation, with BiOX electrodes as photoanodes; Pt wire and an Ag/AgCl electrode were applied as counter and reference electrodes in KCl electrolyte, respectively. The light was from an AM 1.5 solar power system, whose wavelength below 420 nm was removed to achieve visible light by an optical filter.

Photocatalytic Test. Photocatalytic effectiveness was investigated by oxidation of Rhodamine B (RB), Bisphenol A (BPA), and the reduction of Cr^{VI} in an initial concentration of 10 mg L⁻¹. Specifically, 20 mg of catalyst was added to 50 mL of solution containing the above chemicals. Before light irradiation, to attain adsorptive equilibrium, mixtures were mixed in the dark about 60 min. After a predetermined time, samples were withdrawn for analyzing the concentration of the chemicals. In cycle runs, the photocatalytic reaction was 5, 20, and 30 min for RB, BPA, and Cr^{VI}, respectively. The concentration of RB was detected by UV/vis spectrophotometry (UV2401/2, Shimadzu). Residual concentration of BPA was determined via an Agilent high performance liquid chromatography (HPLC) system through a C18 column. For BPA, the mobile phase was the mixture of methanol and ultrapure water with a volume ratio of 30:70. Hexavalent chromium was detected at 540 nm via the 1,5-diphenylcarbazid analytical method following the AFNOR standard NFT 90-043.⁵⁷ H₂O₂ was analyzed spectrophotometrically at 400 nm applying potassium titanium oxalate solution.⁵⁸

Computational Details for Bismuth Oxyhalides. All of the calculations were conducted by the Vienna ab initio simulation package (VASP), and the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional within the generalized gradient approximation (GGA) was employed.⁵⁹ The cutoff energy for basis set was set to 450 eV. Brillouin zone was sampled with a $4 \times 4 \times 4$ *k*-mesh of Monkhorst–Park scheme.⁶⁰ When treating valence-core interactions with 5, 6, and 7 valence electrons for Bi, O, and X (X = Br, I), the projector augmented-wave method (PAW) was used. Structures were relaxed until residual force on atomic individual was less than 0.01 eV/Å. The BiOX are a sort of layered compounds with *P4/nmm* space group. BiOX were composed by [Bi₂O₂]²⁺ layers and two sheets of X-ions arranged in a sandwiched way. In this work, a $2 \times 2 \times 1$ supercell was applied for all calculations.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b08676.

Experimental details, partial results of calculations, and some characterizations (PDF)

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Notes

The authors declare no competing financial interest.

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