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## Achieving selective photocatalytic $\text{CO}_2$ reduction to CO on bismuth tantalum oxyhalogen nanoplates<sup>†</sup>

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The photocatalytic conversion of carbon dioxide to fuels presents great promise for storing renewable energy and alleviating global warming. Herein, using the visible-light-responsive semiconductor bismuth tantalum oxyhalogen ( $\text{Bi}_4\text{TaO}_8\text{X}$ , X = Cl, Br) with suitable band structures, we realize the photocatalytic reduction of  $\text{CO}_2$  to selectively produce CO under visible light without introducing any sacrificial reagents. An isotope-labeling experiment clearly demonstrated that the produced CO originated from  $\text{CO}_2$  and, additionally, continuous water oxidation for  $\text{O}_2$  evolution was also detected during photocatalytic  $\text{CO}_2$  reduction. Further introducing crystal morphology modulation to prepare well-defined nanocrystals enables great enhancement of the photogenerated charge separation performance compared to that of irregular nanoparticles. Moreover, surface modification of the silver nanoparticles deployed as the  $\text{CO}_2$  reduction cocatalyst evidently facilitates the generation of intermediate species to promote the surface catalytic reaction. This work not only presents a potential semiconductor candidate for photocatalytic  $\text{CO}_2$  reduction, but it also provides a feasible strategy for designing artificial photosynthetic systems *via* combining morphology tailoring and suitable cocatalysts.

Artificial photosynthesis mimicking the process in green plants to realize the conversion and storage of solar energy and atmospheric  $\text{CO}_2$  gas into high-value-added carbon-containing compounds is of profound fundamental importance for coping with global warming and energy problems.<sup>1–3</sup> However, the photocatalytic conversion of abundant  $\text{CO}_2$  using  $\text{H}_2\text{O}$  as a proton source offers both promise and challenges, especially given the relatively inert nature of  $\text{CO}_2$  molecules and the multi-electron reaction process.<sup>4,5</sup> Although the use of semiconductor

based photocatalysts for photocatalytic  $\text{CO}_2$  reduction has received increasing attention since the first pioneering work in 1978,<sup>6</sup> the progress has been limited by poor charge separation and sluggish reaction kinetics. To achieve the  $\text{CO}_2$  reduction reaction using  $\text{H}_2\text{O}$  as the proton source, the photogenerated charges in semiconductors must separate, transfer to the surface, and then react with the absorbed molecules, giving rise to the photoassisted splitting of  $\text{H}_2\text{O}$  to release oxygen and produce carbon-containing compounds. Additionally, the thermodynamic requirements necessitate semiconductor photocatalysts with suitable band positions to ensure that the photoexcited electrons and holes are endowed with sufficient energy to reduce  $\text{CO}_2$  and oxidize  $\text{H}_2\text{O}$  simultaneously.<sup>7</sup>

The challenges in photocatalytic  $\text{CO}_2$  conversion include not only the difficult activation of  $\text{CO}_2$  and the sophisticated reaction kinetics, but also the notoriously fast recombination and deficient separation of the photogenerated charge carriers of the photocatalysts.<sup>2</sup> Endeavors in the past few decades have resulted in the development of strategies including surface decoration of suitable cocatalysts, size control, and surface defect engineering of stoichiometric photocatalysts to promote the efficiency and selectivity of photocatalytic  $\text{CO}_2$  reduction.<sup>8–10</sup> For instance, the decoration of an atomic-cobalt-based cocatalyst on  $\text{W}_{18}\text{O}_{49}$  nanowires enabled the acceleration of the electron transport and modified the energy configuration, resulting in impressive CO generation.<sup>11</sup> It was reported that the assembly of a  $\text{BiOBr}$  photocatalyst with abundant oxygen vacancies could tailor the electronic band structure and capture photoinduced carriers to benefit the separation and stabilize the intermediates to reduce the activation energy barrier.<sup>12</sup> Although progress has been made, the overwhelming majority of published reports so far have concentrated on  $\text{CO}_2$  reduction in the presence of various easily oxidized reagents including alcohols or amines to donate electrons, producing carbon-containing products at the cost of these sacrificial reagents. Even in the overall reduction of  $\text{CO}_2$  using  $\text{H}_2\text{O}$  as the sole proton source, the detection of water oxidation is scarcely considered, despite the nonnegligible significance of water oxidation in photosynthesis.<sup>13</sup> The water

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oxidation reaction to evolve oxygen or hydroxyl radicals in parallel with the  $\text{CO}_2$  reduction reaction is recognized as the bottleneck, with a sluggish kinetics and complex proton-coupled electron transfer process.<sup>14</sup> Moreover, the detection of oxygen is even harder given the fact that the evolved oxygen and hydroxyl radicals tend to be adsorbed on the surface of photocatalysts and to oxidize the  $\text{CO}_2$ -reduced intermediates and interrupt the reduction; consequently, few reported works have referred to the oxidation reaction so far. Reliable detection of water oxidation was reported on a  $\text{SiC}@\text{MoS}_2$  Z-scheme photocatalyst that could achieve the overall conversion of  $\text{CO}_2$  with  $\text{H}_2\text{O}$  and yielded  $\text{CH}_4$  and a stoichiometric ratio of  $\text{O}_2$  at the same time.<sup>15</sup> A fundamental reason for the challenging nature of the water oxidation reaction in the overall photocatalytic reduction of  $\text{CO}_2$  is the relatively inferior photocatalytic water oxidation ability of many semiconductors in terms of thermodynamics and kinetics.

Bismuth tantalum oxygen halogen ( $\text{Bi}_4\text{TaO}_8\text{X}$ ,  $\text{X} = \text{Cl, Br}$ ) is a class of typical Sillén–Aurivillius compounds with layered perovskite structures that have excellent light harvesting properties.<sup>16</sup> We previously reported the fabrication of a series of  $\text{Bi}_4\text{TaO}_8\text{X}$  photocatalysts that are able to achieve photocatalytic hydrogen reduction and the oxygen evolution reaction, especially their decent performance in photocatalytic water oxidation under the irradiation of visible light.<sup>17,18</sup> Furthermore, the intrinsic layered structure makes it feasible to achieve morphology tuning as well as efficient photogenerated charge separation. Although  $\text{Bi}_4\text{TaO}_8\text{X}$  photocatalysts possess unique crystalline structures and water oxidation capabilities, little research has focused on this series of materials to date, except one previous study on the conversion of  $\text{CO}_2$  to  $\text{CH}_4$  over this semiconductor, which did not mention the detection of water oxidation during the process.<sup>19</sup> This shows the need for further insight into the exploration of photocatalytic  $\text{CO}_2$  reduction on these promising materials.

Herein, we report that the selective photocatalytic conversion of  $\text{CO}_2$  to CO can be realized on visible-light-responsive bismuth tantalum oxygen halogen under visible light irradiation, and that the oxidation of water to  $\text{O}_2$  can also be detected simultaneously. Two determining factors, morphology regulation, which significantly tunes the photogenerated charge separation process, and surface decoration of a silver cocatalyst, which promotes the absorption and generation of intermediates, together result in a great enhancement in photocatalytic  $\text{CO}_2$  reduction, thereby providing a feasible strategy to assemble efficient photocatalysts for the photoassisted reduction of  $\text{CO}_2$  into valuable chemicals.

The crystalline structure of bismuth tantalum oxygen halogen ( $\text{Bi}_4\text{TaO}_8\text{X}$ ,  $\text{X} = \text{Cl, Br}$ ) is shown in Fig. 1a. It is composed of slices of  $[\text{Bi}_2\text{O}_2]$  and layers of  $[\text{TaO}_6]$  octahedra, intercalated with halogen atoms. The intrinsic layered structure is expected to form two-dimensional morphologies, which exhibit superiority in photogenerated charge separation and transfer in photocatalysis.<sup>20,21</sup> The  $\text{Bi}_4\text{TaO}_8\text{X}$  was verified to have a band gap of approximately 2.6 eV with the conduction band and valence band located at approximately  $-0.9$  and  $1.7$  eV vs. NHE ( $\text{pH} = 7$ ), respectively, which could meet the

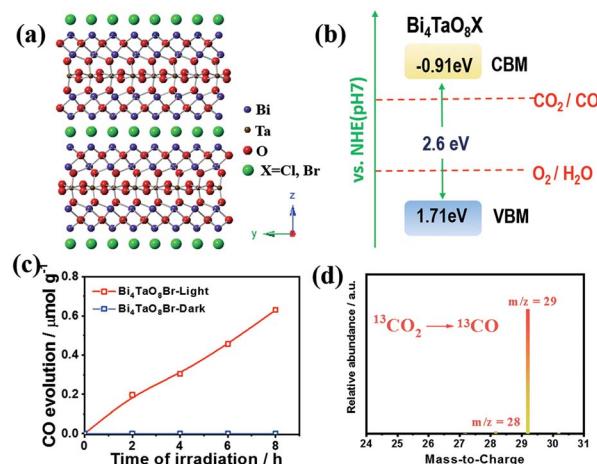


Fig. 1 (a) The crystal structure of  $\text{Bi}_4\text{TaO}_8\text{X}$  ( $\text{X} = \text{Cl, Br}$ ). (b) A schematic illustration of the band structure of  $\text{Bi}_4\text{TaO}_8\text{X}$  ( $\text{X} = \text{Cl, Br}$ ). (c) The time course of photocatalytic  $\text{CO}_2$  reduction on  $\text{Bi}_4\text{TaO}_8\text{Br}$ . (d) GC-MS analysis of the generated CO using  $^{13}\text{CO}_2$  as the feedstock.

thermodynamic requirements for water oxidation and the reduction of  $\text{CO}_2$  to multiple products including CO (Fig. 1b). Notably,  $\text{Bi}_4\text{TaO}_8\text{X}$  demonstrated good photocatalytic water oxidation capability under visible light irradiation, making it a candidate for the photocatalytic overall  $\text{CO}_2$  conversion reaction.

$\text{Bi}_4\text{TaO}_8\text{X}$  ( $\text{X} = \text{Cl, Br}$ ) was synthesized *via* a traditional solid-state reaction, in which stoichiometric amounts of the precursors  $\text{Bi}_2\text{O}_3$ ,  $\text{Ta}_2\text{O}_5$ , and  $\text{BiOX}$  were mixed and sealed in a vacuum quartz tube, followed by calcination at  $973\text{ K}$  for 14 hours. Using the as-prepared  $\text{Bi}_4\text{TaO}_8\text{Br}$  as the photocatalyst, we found that surprisingly, photocatalytic  $\text{CO}_2$  reduction could be realized in the presence of  $\text{H}_2\text{O}$  without introducing any sacrificial reagents, and CO was observed as the sole product with a selectivity of 100% and no other products being detected (Fig. 1c). To directly track the origin of the produced CO, an isotope labelling experiment using  $^{13}\text{CO}_2$  as the input was performed. As shown in Fig. 1d, the result of gas chromatography–mass spectrometry (GC-MS) analysis showed the production of  $^{13}\text{CO}$ , clearly evidencing that CO originated from the input  $^{13}\text{CO}_2$ , although the photocatalytic activity was not high. Considering that the activity may be limited by the poor charge separation and transfer for  $\text{Bi}_4\text{TaO}_8\text{Br}$ , flux treatment was utilized in the preparation process, and the corresponding sample was labelled as  $\text{Bi}_4\text{TaO}_8\text{Br-F}$ . As shown in Fig. 2a and b, unlike the irregular  $\text{Bi}_4\text{TaO}_8\text{Br}$  nanoparticles,  $\text{Bi}_4\text{TaO}_8\text{Br-F}$  exhibits a nanoplate morphology with a diameter of  $\sim 500\text{ nm}$  (Fig. S1†). XRD patterns of the two samples were consistent with the standard card for the pure phase and showed negligible differences between each other (Fig. S2†). Raman spectra were also collected, and no obvious variation was observed between the spectrum of the  $\text{Bi}_4\text{TaO}_8\text{Br}$  nanoparticles and that of the nanoplates, indicating no changes in the phase or bonding situation during the process of flux treatment (Fig. S3†). UV-visible spectra also depicted a comparable result in the light absorption range (Fig. S4†). However, as shown in Fig. 2c, when

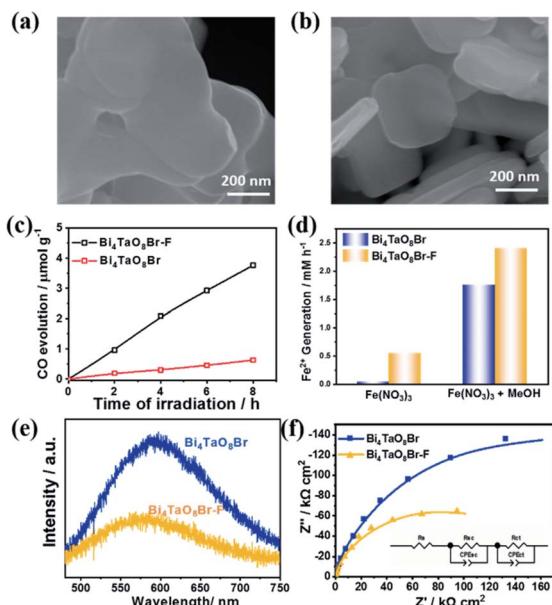


Fig. 2 (a and b) SEM images of Bi<sub>4</sub>TaO<sub>8</sub>Br and Bi<sub>4</sub>TaO<sub>8</sub>Br-F. (c) The time course of photocatalytic CO<sub>2</sub> reduction on Bi<sub>4</sub>TaO<sub>8</sub>Br and Bi<sub>4</sub>TaO<sub>8</sub>Br-F. (d) Photocatalytic reactions on Bi<sub>4</sub>TaO<sub>8</sub>Br and Bi<sub>4</sub>TaO<sub>8</sub>Br-F in the presence of Fe(NO<sub>3</sub>)<sub>3</sub> and CH<sub>3</sub>OH. (e) Steady photoluminescence (PL) spectra of Bi<sub>4</sub>TaO<sub>8</sub>Br and Bi<sub>4</sub>TaO<sub>8</sub>Br-F at room temperature. (f) Electrochemical impedance spectra (EIS) of Bi<sub>4</sub>TaO<sub>8</sub>Br and Bi<sub>4</sub>TaO<sub>8</sub>Br-F and the corresponding equivalent circuit.

the photocatalytic CO<sub>2</sub> reduction was conducted under light irradiation, the photocatalytic activity of the flux-treated Bi<sub>4</sub>TaO<sub>8</sub>Br nanoplates obviously showed enhanced photocatalytic reduction of CO<sub>2</sub> to CO compared to the Bi<sub>4</sub>TaO<sub>8</sub>Br nanoparticles.

To determine the influence of flux treatment on the photo-generated charge separation, both electron-consuming and hole-consuming reagents were introduced. It was assumed that both charge-consuming reactions were kinetically fast enough. We chose the photocatalytic conversion of Fe<sup>3+</sup> to Fe<sup>2+</sup> to probe the electrons and the oxidation of CH<sub>3</sub>OH molecules for capturing holes; the conversion of Fe<sup>3+</sup> to Fe<sup>2+</sup> can be used as an index for activity evaluation. As demonstrated in Fig. 2d, Bi<sub>4</sub>TaO<sub>8</sub>Br-F exhibited superior Fe<sup>3+</sup> conversion performance in the presence of CH<sub>3</sub>OH as a result of the high activity of the oxidation half-reaction. The enhancement compared to Bi<sub>4</sub>TaO<sub>8</sub>Br implies that the charge separation efficiency of Bi<sub>4</sub>TaO<sub>8</sub>Br-F is higher than that of Bi<sub>4</sub>TaO<sub>8</sub>Br synthesized without flux treatment. Additionally, the water oxidation on the surface of Bi<sub>4</sub>TaO<sub>8</sub>Br-F is superior to that of Bi<sub>4</sub>TaO<sub>8</sub>Br in view of its higher conversion activity without CH<sub>3</sub>OH. Correspondingly, the steady photoluminescence (PL) spectrum of Bi<sub>4</sub>TaO<sub>8</sub>Br-F exhibits a significantly decreased intensity of radiative recombination compared to that of Bi<sub>4</sub>TaO<sub>8</sub>Br, implying more inhibited recombination over the same period (Fig. 2e). In addition, electrochemical impedance spectra (EIS) were also carried out to evaluate the charge separation properties for Bi<sub>4</sub>TaO<sub>8</sub>Br and Bi<sub>4</sub>TaO<sub>8</sub>Br-F. As can be seen in Fig. 2f, the fitting results showed smaller resistance values for Bi<sub>4</sub>TaO<sub>8</sub>Br-F in

both the space charge region and the process of charge transfer from the semiconductor to the surface reactants compared to those of Bi<sub>4</sub>TaO<sub>8</sub>Br (Fig. S5†), indicating better charge separation and transfer properties in Bi<sub>4</sub>TaO<sub>8</sub>Br-F. Moreover, the charge separation efficiency calculated from the *J*-*V* curves in the presence of the hole acceptor further demonstrated the enhanced photogenerated charge separation in Bi<sub>4</sub>TaO<sub>8</sub>Br-F, which parallels the EIS and PL results (Fig. S6†). Similar results were also obtained for Bi<sub>4</sub>TaO<sub>8</sub>Cl and Bi<sub>4</sub>TaO<sub>8</sub>Cl-F (Fig. S7–S9†). The above results demonstrate that flux treatment greatly improves the photogenerated charge separation properties of Bi<sub>4</sub>TaO<sub>8</sub>X (X = Cl, Br).

As mentioned above, even if the photogenerated charge separation is satisfactory, the photocatalytic CO<sub>2</sub> reaction is limited by the poor surface catalytic reaction. To promote the photocatalytic conversion of CO<sub>2</sub> to CO, different kinds of surface cocatalysts (namely, Au, Ag, Pd, Ir, Rh and Cu) were loaded on the surface of Bi<sub>4</sub>TaO<sub>8</sub>Br-F, given its robust performance in electrocatalytic CO<sub>2</sub> reduction.<sup>22,23</sup> As shown in Fig. 3a, decoration with Au, Ag and Pd resulted in enhanced CO evolution compared to that of bare Bi<sub>4</sub>TaO<sub>8</sub>Br-F, while the others cocatalysts resulted in negative effects, which might be attributed to the mismatch between the semiconductor and the cocatalysts. Surprisingly, Ag was found to be the best cocatalyst for photocatalytic CO<sub>2</sub> reduction on Bi<sub>4</sub>TaO<sub>8</sub>Br-F, and further optimization of the loading amount demonstrated a plateau in the CO evolution at a weight of 1%. Various oxide-based cocatalysts, namely, MnO<sub>x</sub>, CoO<sub>x</sub>, ZnO<sub>2</sub>, ZrO<sub>2</sub>, and MgO were also preliminarily introduced; unfortunately, none of these could work yet (Fig. S10 & S11†). Photocatalytic stability testing of Ag–Bi<sub>4</sub>TaO<sub>8</sub>Br-F was also carried out for more than three cycles with each reaction cycle being 4 hours (Fig. 3c). The result suggests that Ag–Bi<sub>4</sub>TaO<sub>8</sub>Br-F is able to realize the stable conversion of CO<sub>2</sub> to CO, and only a slight decrease was observed after three cycling tests. Furthermore, the water oxidation product was also tracked during the photocatalytic CO<sub>2</sub> reduction *via* a linkage with an online gas detection system. As expected, the appearance of an obvious O<sub>2</sub> peak was observed *via* GC, and the intensity of the signal gradually increased with the reaction time, as shown in Fig. 3d. Although the amount of O<sub>2</sub> is still very low and the production of CO could not be analysed simultaneously, the significant O<sub>2</sub> peak strongly verified that the water oxidation half-reaction proceeded, which means the overall photocatalytic CO<sub>2</sub> reduction with H<sub>2</sub>O could indeed take place on the semiconductor Ag–Bi<sub>4</sub>TaO<sub>8</sub>Br-F. Notably, given the low solubility of CO<sub>2</sub> in water, all the photocatalytic experiments were conducted in a saturated KHCO<sub>3</sub> solution; the photocatalytic performance in pure water was also demonstrated in Fig. S12†.

The roles of the Ag cocatalyst in the photocatalytic reaction were then investigated to better understand the reaction mechanism. As can be seen in Fig. 4a, Ag nanoparticles with diameters of ~5–20 nm were dispersed on the surface of the Bi<sub>4</sub>TaO<sub>8</sub>Br-F nanoplates (Fig. S13 & S14†). High-resolution transmission electron microscopy (HRTEM) provided great insight into the surface microstructure of Ag-loaded Bi<sub>4</sub>TaO<sub>8</sub>Br-F, as shown in Fig. 4b. The clear lattice fringes indicate the good

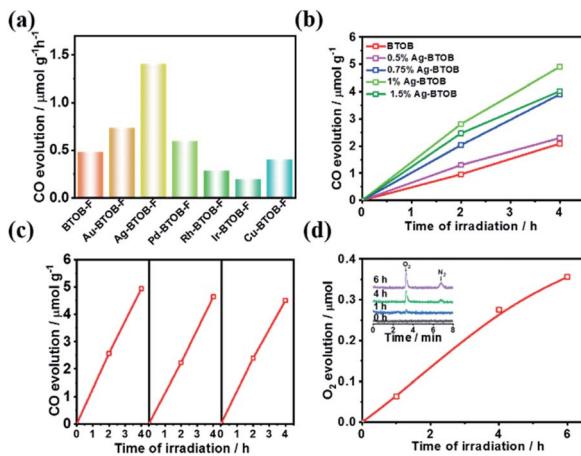


Fig. 3 (a) The photocatalytic activity of  $\text{CO}_2$  reduction on  $\text{Bi}_4\text{TaO}_8\text{Br}-\text{F}$  loaded with different cocatalysts. (b) The time courses of photocatalytic  $\text{CO}_2$  reduction on  $\text{Bi}_4\text{TaO}_8\text{Br}-\text{F}$  loaded with different amounts of Ag. (c) Cycling tests of photocatalytic  $\text{CO}_2$  reduction on Ag- $\text{Bi}_4\text{TaO}_8\text{Br}-\text{F}$ . (d) The time course of oxygen evolution during photocatalytic  $\text{CO}_2$  reduction on Ag- $\text{Bi}_4\text{TaO}_8\text{Br}-\text{F}$  under UV light irradiation; inset: GC signals of  $\text{O}_2$  and  $\text{N}_2$  after different reaction times.

crystallinity of both the cocatalyst and the semiconductor, where the lattice spacing of 0.233 nm is consistent with the (111) lattice plane of metallic Ag, while the observed lattice distance of 0.381 nm corresponds well with the (110) facet of  $\text{Bi}_4\text{TaO}_8\text{Br}$ . The Ag nanoparticles were in intimate contact with the semiconductor, which is conducive to better synergy. In addition, the chemical states of the Ag cocatalyst as well as the interaction between Ag and  $\text{Bi}_4\text{TaO}_8\text{Br}-\text{F}$  were investigated using XPS (X-ray photoelectron spectroscopy) (Fig. 4c). The XPS spectra of Bi, Ta and O showed slight shifts to higher bonding energy, which could be due to electron transfer from  $\text{Bi}_4\text{TaO}_8\text{Br}$  to Ag, implying intimate contact between  $\text{Bi}_4\text{TaO}_8\text{Br}$  and Ag (Fig. S15†).<sup>24</sup> In addition, the fine spectrum of Ag showed the coexistence of peaks at 373.8 and 367.8 eV, which is due to spin-orbit splitting according to the literature, indicating the presence of the metallic state of  $\text{Ag}^0$ , which agrees well with the HRTEM analysis.<sup>25,26</sup> The Ag nanoparticles on the surface show some aggregation after the cycling reaction, and the structural characterizations of Ag- $\text{Bi}_4\text{TaO}_8\text{Br}-\text{F}$  after the photocatalytic reactions indicate that it maintained similar phase and chemical states on the surface to the fresh material (Fig. S16–S18†). Furthermore, the influence of Ag on the  $\text{CO}_2$  absorption was also investigated, as shown in Fig. 4d, in which surface loading of the Ag cocatalyst resulted in obviously enhanced absorption of  $\text{CO}_2$  molecules compared to pristine  $\text{Bi}_4\text{TaO}_8\text{Br}$ , implying that the Ag on the surface could facilitate the process of  $\text{CO}_2$  absorption.

To explore the possible mechanism of  $\text{CO}_2$  conversion on  $\text{Bi}_4\text{TaO}_8\text{Br}$ , *in situ* Fourier Transform Infrared Spectrum (FTIR) was utilized to provide decisive evidence regarding the intermediate products and reaction pathways. Significant  $\text{CO}_2$  adsorption could be observed from the vibrational mode of (C=O) at 2295 and 2380  $\text{cm}^{-1}$  (Fig. S19†). As shown in Fig. 4e and f, various carbon-containing reaction intermediates, including

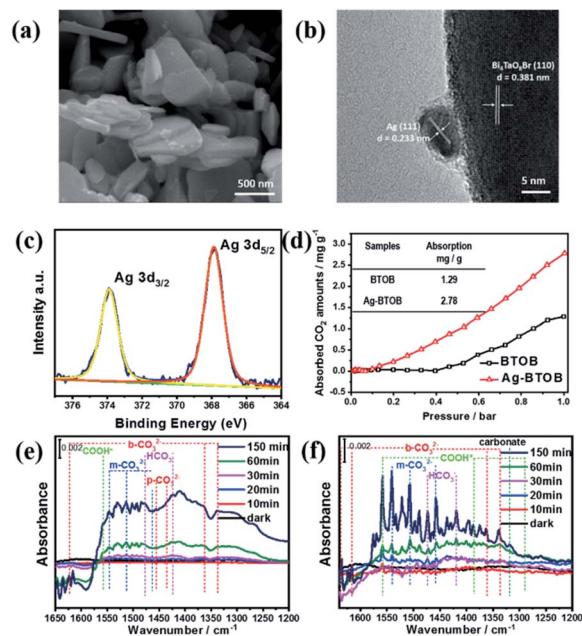
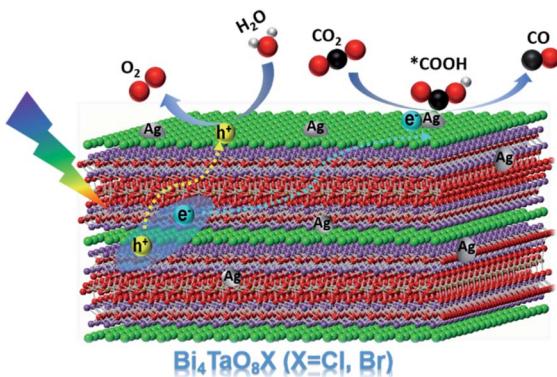


Fig. 4 (a and b) SEM and HRTEM image of  $\text{Bi}_4\text{TaO}_8\text{Br}-\text{F}$  loaded with Ag. (c) The XPS fine spectrum of silver in Ag- $\text{Bi}_4\text{TaO}_8\text{Br}-\text{F}$ . (d) The absorption curves of  $\text{CO}_2$  on  $\text{Bi}_4\text{TaO}_8\text{Br}-\text{F}$  and Ag- $\text{Bi}_4\text{TaO}_8\text{Br}-\text{F}$  at room temperature. (e and f) *In situ* FTIR spectra of photocatalytic  $\text{CO}_2$  reduction on  $\text{Bi}_4\text{TaO}_8\text{Br}-\text{F}$  and Ag- $\text{Bi}_4\text{TaO}_8\text{Br}-\text{F}$ .

bicarbonate ( $\text{HCO}_3^-$ , 1473 and 1419  $\text{cm}^{-1}$ ), bidentate carbonate (b- $\text{CO}_3^{2-}$ , 1338, 1363, 1616, and 1635  $\text{cm}^{-1}$ ), and monodentate carbonate (m- $\text{CO}_3^{2-}$ , 1558, 1541, 1508 and 1457  $\text{cm}^{-1}$ ) corresponding to adsorbed  $\text{CO}_2$  species were detected during the photocatalytic reaction, and all of these species gradually increased as the reaction proceeded. Compared to bare  $\text{Bi}_4\text{TaO}_8\text{Br}-\text{F}$ , the Ag-loaded  $\text{Bi}_4\text{TaO}_8\text{Br}-\text{F}$  demonstrated signals with stronger intensities within the same period, which could be attributed to the more intensive of  $\text{CO}_2$  absorption ability and activation on Ag- $\text{Bi}_4\text{TaO}_8\text{Br}-\text{F}$ . Additionally, the peaks located at 1588, 1386 and 1288  $\text{cm}^{-1}$  were assigned to the symmetric and antisymmetric OCO vibrations and C=O stretching of \*COOH, respectively,<sup>27,28</sup> which is consistent with previous experimental and theoretical studies claiming that the conversion of  $\text{CO}_2$  to CO usually proceeds *via* a \*COOH intermediate coordinated to the catalyst surface.<sup>29,30</sup> As depicted in Fig. 4e and f, the Ag-loaded  $\text{Bi}_4\text{TaO}_8\text{Br}-\text{F}$  showed more significant surface intermediate signals compared to bare  $\text{Bi}_4\text{TaO}_8\text{Br}-\text{F}$ , which further certifies that the surface assembled with the Ag cocatalyst is favourable for  $\text{CO}_2$  activation (\*COOH formation), thus promoting the overall conversion of  $\text{CO}_2$  to CO.

Based on the above results, a plausible mechanism for the photocatalytic conversion of  $\text{CO}_2$  to CO on Ag- $\text{Bi}_4\text{TaO}_8\text{Br}-\text{F}$  was proposed (Scheme 1).  $\text{Bi}_4\text{TaO}_8\text{Br}$  was irradiated under visible light to generate electrons and holes with high energy, which could effectively separate and transfer to the surface due to the layer-structured properties with superior charge separation capability. The reduction of  $\text{CO}_2$  to CO on the surface usually consists of two elementary steps, the first of which is the reductive adsorption of  $\text{CO}_2$  on the catalyst surface involving



**Scheme 1** The proposed mechanism of photocatalytic  $\text{CO}_2$  reduction to CO on  $\text{Bi}_4\text{TaO}_8\text{X}$ .

a proton-coupled electron transfer process to form a  $^*\text{COOH}$  intermediate, where  $^*$  indicates the corresponding adsorption states of surface species. The adsorbed  $^*\text{COOH}$  intermediate is further reduced to  $^*\text{CO}$  *via* a concerted electron–proton transfer, and then desorbed from the catalyst surface. Ag has been shown to be an ideal electrocatalyst endowed with an appropriate adsorption strength for the key intermediate  $^*\text{COOH}$ ,<sup>31–33</sup> and the cocatalyst on the surface with a relatively low Fermi level has also been proven to be capable of electron trapping and to further enhance the photogenerated charge separation,<sup>34</sup> which is assumed to promote the reduction of  $\text{CO}_2$  to CO. Given the capability of  $\text{Bi}_4\text{TaO}_8\text{Br}$  for photocatalytic water oxidation, the water oxidation half-reaction to consume photogenerated holes is expected to take place on the surface of  $\text{Bi}_4\text{TaO}_8\text{Br}$ . Ultimately, the loading of the Ag cocatalyst promotes the  $\text{CO}_2$  reduction reaction on the surface, combined with morphology tuning, which promotes the process of photogenerated charge separation and transport, contributes to the realization of overall photocatalytic  $\text{CO}_2$  conversion on the  $\text{Bi}_4\text{TaO}_8\text{Br}$  photocatalyst.

## Conclusions

In conclusion, we have presented the achievement of the photocatalytic reduction of  $\text{CO}_2$  to CO on the semiconductor  $\text{Bi}_4\text{TaO}_8\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) using  $\text{H}_2\text{O}$  as the electron donor under visible light irradiation. During the photocatalytic reduction of  $\text{CO}_2$  by the photogenerated electrons, the oxidation of  $\text{H}_2\text{O}$  to  $\text{O}_2$  by photogenerated holes takes place simultaneously. Through the morphology modulation, the flux-treated nanoplates demonstrate greatly enhanced charge separation and transfer properties compared to irregular nanoparticles. Further decoration with the cocatalyst Ag was proven to be favourable for the adsorption and activation of  $\text{CO}_2$  and the generation of key intermediates, further promoting the overall  $\text{CO}_2$  reduction reaction. This work not only presents a potential semiconductor candidate for photocatalytic  $\text{CO}_2$  reduction, but also provides a feasible strategy combining morphology tailoring and appropriate cocatalysts in the hope of designing and recreating efficiently implemented artificial photosynthetic systems.

## Conflicts of interest

There are no conflicts to declare.

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