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## Ferroelectric polarization and thin-layered structure synergistically promoting CO<sub>2</sub> photoreduction of Bi<sub>2</sub>MoO<sub>6</sub>

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**ABSTRACT**: Photocatalytic  $CO_2$  reduction for producing solar fuels is promising but severely restricted by the fast recombination of photogenerated electrons and holes and insufficient reactive sites of photocatalysts. Formation of internal electric field is an effective route for facilitating the charge separation, and two-dimensional structure construction is beneficial to increasing catalytic sites. Herein, ultrathin Bi<sub>2</sub>MoO<sub>6</sub> nanosheets with strong ferroelectricity were prepared by a combined CTAB-assisted hydrothermal and corona poling post-treatment process for synergistically improving the  $CO_2$  photoreduction activity. Without sacrificial agents and co-catalysts, the polarized Bi<sub>2</sub>MoO<sub>6</sub> ultrathin nanosheets demonstrate a remarkable CO<sub>2</sub> reduction activity for CO production with a rate of 14.38 µmol g<sup>-1</sup> h<sup>-1</sup> in the gas-solid system, over 10 times enhancement than the bulk Bi<sub>2</sub>MoO<sub>6</sub>. The combined strategies considerably promote the separation of the photogenerated electrons and holes and enrich the reactive sites for  $CO_2$  adsorption, which co-boost the photocatalytic  $CO_2$  reduction performance of Bi<sub>2</sub>MoO<sub>6</sub>. In addition, a synergistically-enhanced effect between corona poling and thin-layered structure was disclosed. This work provides corona poling as an efficient route for promoting charge separation of particulate photocatalysts, and offers new insights into synergistically improving the CO<sub>2</sub> photoreduction activity.

*Keywords:* Bi<sub>2</sub>MoO<sub>6</sub>, ultrathin structure, ferroelectric polarization, charge separation, CO<sub>2</sub> reduction.

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#### 1. Introduction

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With the rapid development of technology, more and more energy is required to meet the needs of human life and activities.<sup>1,2</sup> As the massive consumption of fossil energy, the issues of energy depletion and environmental pollution are becoming increasingly serious, which now many researchers are paying extensive attention to.<sup>3,4,5</sup> Semiconductor-based photocatalysis has emerged as one of the most promising ways to solve the above problems. In particular, the photocatalytic CO<sub>2</sub> reduction shows huge potentials for converting CO<sub>2</sub> into carbon-containing solar fuels.<sup>6,7</sup> However, the low charge separation and insufficient reactive sites seriously impairs the photocatalytic CO<sub>2</sub> reduction performance of semiconductors.<sup>8</sup>

Internal electric field has received wide spread attention due to the large potential in driving the directional movement of the photogenerated charge carriers.<sup>9</sup> For example, the carrier separation efficiency and photocatalytic ability of BiOI can be enhanced by optimizing crystal structure to increase the internal electric field.<sup>10</sup> As a new type of electric field, polarization electric field was recently regarded as an efficient approach to inhibit the charge recombination.<sup>11-15</sup> Due to the spontaneous or piezo- polarization, there will generate the positive and negative polarized charges at the two ends of the polar materials, which offers a strong driving force to drive the photogenerated electrons and holes to separate and transport along opposite directions. Our group reported that the macroscopic polarization enhancement can considerably strengthen the bulk charge separation of BiOIO<sub>3</sub>, which largely improves its photocatalytic activity for production of reactive oxygen species and CO<sub>2</sub> reduction.<sup>11,12</sup> Besides, it was also

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demonstrated that the annealing post-treatment causes the increased ferroelectric polarization of SrBi4Ti4O15 nanosheets, thus resulting in high charge separation and prominent photocatalytic CO2 reduction activity.<sup>14</sup> In addition, it has been reported that fabrication of two-dimensional (2D) thin-layered structure was capable of exposing more unsaturated atoms as surface catalytic sites, thus enhancing the photocatalytic activity.<sup>16</sup> For instance, the construction of 2D ultrathin structure of Bi<sub>2</sub>WO<sub>6</sub> was revealed to provide a large amount of reactive sites for improving the CO<sub>2</sub> reduction activity.<sup>17</sup>

Among the numerous semiconductors, bismuth-based photocatalytic materials are considered to be excellent candidates because of their inherent physical and chemical properties.<sup>18</sup> As a typical Aurivillius-phase compound, Bi<sub>2</sub>MoO<sub>6</sub> has attracted substantial attentions in the field of photocatalysis due to its layered crystal structure and moderate band gap,<sup>19</sup> which has been widely surveyed for degradation of pollutants<sup>20,21</sup>, oxygen evolution<sup>22</sup>, nitrogen fixation<sup>23</sup> and reduction of CO<sub>2</sub> to solar fuels<sup>24,25</sup>. Bi<sub>2</sub>MoO<sub>6</sub> is structurally composed of alternating (Bi<sub>2</sub>O<sub>2</sub>)<sup>2+</sup> and perovskitetype (MoO<sub>4</sub>)<sup>2-</sup> layers, and oxygen atoms are shared between the layers.<sup>26,27</sup> The internal electric field formed between (Bi<sub>2</sub>O<sub>2</sub>)<sup>2+</sup> and (MoO<sub>4</sub>)<sup>2-</sup> layers in Bi<sub>2</sub>MoO<sub>6</sub> can effectively separate the photogenerated charge carriers.<sup>28</sup> Owing to the unique layered structure of Bi<sub>2</sub>MoO<sub>6</sub>, it is very conducive to the formation of nanosheets, and the thickness can be regulated from dozens of layers to an atomic layer. More importantly, Bi<sub>2</sub>MoO<sub>6</sub> is a typical ferroelectric belonging to the Bi<sub>2</sub>WO<sub>6</sub> family with the asymmetric space group of *Pna2*,<sup>29</sup> and thus the ferroelectric polarization field in Bi<sub>2</sub>MoO<sub>6</sub> may be employed as

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the driving force to restrain the charge recombination. Besides, the ferroelectric  $^{101039/D017A02102D}$  polarization of Bi<sub>2</sub>MoO<sub>6</sub> can be enhanced by applying an external electric field, which may further promote the charge separation. However, the influence of ferroelectricity on the photocatalytic activity of Bi<sub>2</sub>MoO<sub>6</sub> has not been investigated so far to the best of our knowledge.

In this work, we first prepared ultrathin Bi<sub>2</sub>MoO<sub>6</sub> nanosheets by a CTAB-assisted hydrothermal process, and then employed the corona poling post-treatment to enhance the ferroelectricity of Bi<sub>2</sub>MoO<sub>6</sub>. It was found that the corona poling and formation of thin-layered structure greatly enhance the separation and transfer of photogenerated charge carriers and CO<sub>2</sub> adsorption, which co-promote the photocatalytic CO<sub>2</sub> reduction performance. The ultrathin Bi<sub>2</sub>MoO<sub>6</sub> nanosheets treated by corona poling demonstrate a highly enhanced CO<sub>2</sub> reduction activity into CO with a production rate of 14.38 μmol g<sup>-1</sup> h<sup>-1</sup>, over 10 times higher than that of the bulk Bi<sub>2</sub>MoO<sub>6</sub> sample. Besides, the microstructure, chemical states and ferroelectricity were investigated in detail to elucidate the photocatalytic mechanism.

#### 2. Experimental section

#### 2.1 Sample preparation and poling treatment

2.1.1 Synthesis of ultrathin Bi<sub>2</sub>MoO<sub>6</sub> (BMO-U)

All chemicals were of analytic grade and were used without further treatment. The ultrathin  $Bi_2MoO_6$  nanosheets were synthesized by a typical hydrothermal method. 1.940 g of  $Bi(NO_3)_3 \cdot 5H_2O$  was added in 30 ml of distilled water containing 10% molar ratio of CTAB. After sufficient ultrasonic stirring for 30 min, 0.484 g of

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 $Na_2MoO_4 \cdot 2H_2O$  was added into the mixture solution followed by continuous ultrasonic stirring for 30 minutes, and then the mixture was transferred into a 50 ml Teflon-lined autoclave. The autoclave was heated in an oven at 180 °C for 20 h. After cooling down to room temperature, the obtained products were collected by centrifugation and washed with hot distilled water and absolute ethanol for ten times. The resulting products were dried at 80 °C for 12 h, and denoted as BMO-U. Bulk Bi<sub>2</sub>MoO<sub>6</sub> was synthesized according the same preparation procedure without the addition of CTAB, and the as-obtained products were named as BMO.

2.1.2 Corona poling

A self-made instrument was employed to exert corona poling on the photocatalysts. 150 mg of the as-prepared BMO and BMO-U was put into the mold, and then the voltage of the instrument was increased to achieve an electric field of 20 kV/cm. Afterwards, the samples were treated under this electric field for 30 min. The asobtained polarized BMO-U and BMO were denoted as BMO-U-P and BMO-P, respectively.

#### 2.2 Characterization

X-ray powder diffraction (XRD) test was used to survey the phases of photocatalysts on an XRD powder diffraction instrument with monochromatized Cu Ka radiation (1 = 1.5406 nm) at 40 kV and 40 mA at room temperature. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were conducted to investigate the morphologies and microstructures of the series of Bi<sub>2</sub>MoO<sub>6</sub> samples with using a JEM-2100 electron microscopy (JEOL, Japan), and

energy dispersive spectroscopy (EDS) attached to the TEM was used to examine the Display attached to the TEM was used to examine the composition of the products at the same time. Nitrogen adsorption BET method was utilized to characterize the specific surface area of the samples on a Micromeritics 3020 instrument. X-ray photoelectron spectroscopies (XPS, ESCALAB 250Xi) were conducted to analyze the surface elemental composition and states of the samples. UV–vis diffuse reflectance spectra (DRS) were recorded on a Cary 5000 (America Varian) spectrophotometer to determine the light absorption properties of the samples. The

4600 fluorescence spectrophotometer.

#### 2.3 Photocatalytic CO<sub>2</sub> reduction measurement

The photocatalytic CO<sub>2</sub> reduction activities of the as-obtained Bi<sub>2</sub>MoO<sub>6</sub> samples were assessed in a gas-solid reaction system with a closed quartz reactor (PerfectLight, China) of 500 ml in volume. 10 mg of the photocatalyst was put in a petri dish with an area of about 28 cm<sup>2</sup> containing a small amount of distilled water. The above mixture was dispersed sufficiently by ultrasonic treatment, and then the petri dish was put into an oven for drying. After that, the above petri dish was put in the reaction cell with a triangular bracket. 1.7 g of NaHCO<sub>3</sub> was placed in the bottom of the reaction cell, followed by sealing and vacuum treatment. Then, 15 ml of H<sub>2</sub>SO<sub>4</sub> (0.7 M) was injected into the cell to produce CO<sub>2</sub> gas via the reaction between NaHCO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. At every 1 h, 1 ml of generated gas was taken by a syringe and then qualitatively analyzed by the gas chromatograph. The production yield was calculated on the basis of a calibration curve. The blank test was conducted without adding NaHCO<sub>3</sub> or with purging argon in

photoluminescence (PL) spectra of the samples were measured by using a Hitachi F-

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the reaction cell.

#### 2.4 Photoelectrochemical measurement

The electrochemical impedance spectroscope (EIS) and Mott-Schottky plots were measured on an electrochemical analyzer (CHI660E, Shanghai) equipped with a standard three-electrode system. Ag/AgCl (saturated KCl) electrode and platinum (Pt) wire are employed as the reference electrode and the counter electrode, respectively. With respect to the preparation of working electrodes, 10 mg of BMO series of samples was dispersed in 1 ml of ethanol. Subsequently, the obtained suspension liquid was dropped on the indium tin oxide glass (25 mm × 40 mm) and then dried at 70 °C for 12 h in an oven. 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution was used as the electrolyte solution, and a 300 W Xe lamp was used as the light source.

#### 2.5 Ferroelectric property measurements

The ferroelectric property of the series of BMO samples was measured on a ferroelectric tester (AixACCT, TF Analyzer 2000, Germany). The samples were firstly pressed in a tablet (~10 mm in diameter and ~1.10 mm in thickness), and then were annealed at 250 °C for 3 h and the silver paste was applied to both sides of the tablets. Afterwards, the samples were treated under an electric field of 150 kV/cm at 1000 Hz. An atomic force microscopy (AFM) combined with Kelvin probe force microscopy (KPFM) (Bruker Multimode 8) was used to provide the KPFM images. The samples were dispersed in absolute ethanol and then dropped on a silicon wafer to form a thin film.

#### 3. Results and discussion

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#### 3.1 Characterization of photocatalysts

The morphology, phase and crystal structure of the series of Bi<sub>2</sub>MoO<sub>6</sub> samples were studied. Figure 1a shows the XRD patterns. All the samples show diffraction peaks at 10.8°, 23.4°, 28.2°, 32.5°, 33.1°, 35.9°, 46.6°, 47.1°, 55.5°, 56.2° and 58.4°, corresponding to the (020), (111), (131), (200), (060), (151), (202), (260), (331), (191) and (262) planes of  $Bi_2MoO_6$  (JCPDS No. 21-0102), respectively. Compared with the bulk BMO sample, no extra peaks were detected in the XRD spectra of BMO-U, BMO-P and BMO-U-P, which demonstrates that the introduction of CTAB and corona poling do not change the crystalline phase of Bi<sub>2</sub>MoO<sub>6</sub>.<sup>30</sup> The diffraction peak intensity ratio of the (131)/(200) crystal planes of BMO is about 3.57, which is higher than that of BMO-U ( $\Box$ 3.18). The decrease in this peak intensity ratio may indicate the presence of selective growth of specific facet of Bi<sub>2</sub>MoO<sub>6</sub> by the addition of CTAB. From the XRD data, it was found that the lattice parameters were altered in BMO-U, BMO-P and BMO-U-P, which indicates the distortion of crystal lattice and stronger polarization in these samples (Table S1). The unit cell parameters for a, b and c axis of BMO-U-P are changed by 0.161%, 0.028% and -0.104% compared to that of BMO, respectively, which suggest that the crystal lattices undergo larger prolongation along a axis and compression along c axis.



Figure 1. (a) XRD patterns of the BMO, BMO-P, BMO-U and BMO-U-P samples. (b) TEM, (c) HRTEM (inset: the SAED pattern) and (d) EDS elemental mapping of the BMO-U-P sample. (e) AFM image of BMO-U-P and (f) the corresponding height profile.

TEM image shows the nanosheet morphology of the as-prepared BMO-U-P (Figure 1b), revealing a lamellar structure. Figure 1c shows the HRTEM image of the BMO-U-P nanosheet, and the legible interplanar lattice with a space of 0.275 and 0.274 nm corresponds well with the (200) and (002) planes of Bi<sub>2</sub>MoO<sub>6</sub>, suggesting the exposure of {020} facet. The selected area electron diffraction (SAED) pattern (inset of Fig. 1c) further clearly reveals the single crystalline nature of the BMO-U-P nanosheet. The elemental mapping shows that Bi, Mo, O are evenly distributed in BMO-U-P (Figure 1d). The thickness of as-obtained series samples was measured by the AFM, and the results were shown in Figure 1e, 1f and S2. The thickness of BMO and BMO-P is

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approximately 40 nm, while that of BMO-U and BMO-U-P is about 3  $\text{nm}^{10}\text{The}^{10}\text$ 

XPS is used to characterize the surface element composition and chemical state of BMO, BMO-P, BMO-U and BMO-U-P.<sup>31</sup> All the XPS survey spectra clearly demonstrated the existence of Bi, Mo, and O in all samples (Figure 2a). The C 1s peak is because of the widespread presence of carbon in the environment.<sup>32</sup> Figure 2b-d show the high-resolution XPS of Bi 4f, Mo 3d, and O 1s, respectively. The Bi 4f spectrum exhibits two peaks located at 164.67 and 159.37 eV, resulting from the spin-orbit splitting of Bi 4f<sub>5/2</sub> and Bi 4f<sub>7/2</sub>, respectively (Figure 2b). Similarly, the Mo 3d spectrum also shows two peaks at 235.80 and 232.63 eV, which are attributed to the Mo  $3d_{3/2}$  and Mo  $3d_{5/2}$ , respectively (Figure 2c). The O 1s peak is divided into two peaks at 531.73 and 530.17 eV, corresponding to the surface adsorbed -OH and lattice oxygen atom, respectively (Figure 2d). In comparison with BMO and BMO-U, it can be clearly seen that the binding energies of Bi 4f, Mo 3d and O 1s peaks shift slightly to a lower position in BMO-P and BMO-U-P, which demonstrates that the corona poling changes the coordination environments of these atoms. It provides an obvious evidence for the presence of lattice distortion due to the strong external electric field, confirming the successful ferroelectric polarization.<sup>18,33</sup> Moreover, the binding energies of the Bi 4f, Mo 3d and O 1s in BMO-U-P show larger right-shifts than that in BMO-P, indicating

that the ultrathin structure may enhance the lattice distortion under external <sup>Det 101039/DOTA02102D</sup> field. The XPS results clearly disclose that corona poling causes the lattice distortion of Bi<sub>2</sub>MoO<sub>6</sub>, and a larger distortion occurs in ultrathin Bi<sub>2</sub>MoO<sub>6</sub> nanosheets.



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Figure 2. (a) XPS survey spectra and the high-resolution XPS spectra of (b) Bi 4f, (c) Mo 3d and (d) O 1s of the BMO, BMO-P, BMO-U and BMO-U-P samples.

UV-vis DRS were measured to compare the light absorption property of BMO, BMO-P, BMO-U and BMO-U-P.<sup>34</sup> Figure 3a and 3b show the UV–vis DRS spectra of the samples and their bandgap energy level from the plots  $(\alpha hv)^{1/2}$  estimated by the energy of absorbed light, respectively.<sup>35</sup> From the steep absorption edge of the spectra, not the impurity level, there are relationships between the visible light absorption and the intrinsic band transition.<sup>36,37</sup> Compared to BMO and BMO-P, the light absorption edges of BMO-U and BMO-U-P shift from 489 nm to 478 nm (a magnified view of the

absorption edge is shown in the inset of Figure 3a), revealing that the thin-layered structure causes the blue shift of absorption edge, and the polarization treatment has no effect on the light absorption properties of the samples. The formula was used to determine the band gap  $(Eg)^{38}$ :

$$\alpha h v = A (h v - E_g)^{n/2}$$
<sup>(1)</sup>

and the a, v, h and Eg correspond to coefficient, light frequency, Planck constant and band gap energy, respectively, and the A is a constant. The band gap of BMO-U and BMO-U-P was estimated to be 2.32 eV, which is slightly wider than that of BMO and BMO-P (2.30 eV) (Figure 3b).

The band gap level plays a very important role in understanding the photocatalytic activity because the redox reaction types of a semiconductor are determined by the valence band (E<sub>VB</sub>) and conduction band (E<sub>CB</sub>) positions.<sup>39</sup> In order to determine the flat band potential (E<sub>fb</sub>) of BMO, BMO-P, BMO-U and BMO-U-P, the Mott-Schottky plots were measured under three different frequencies (500, 800 and 1000 Hz) as shown in Figure 3c, 3d, S3a and S3b.40 At the given different test frequencies, it is obvious that three tangents of the Mott-Schottky curves intersect at the same point on the X axis. And the E<sub>th</sub> of BMO, BMO-P, BMO-U and BMO-U-P was determined to be -0.61, -0.61, -0.65 and -0.65 eV (versus to Ag/AgCl electrode), respectively. Thus versus to a standard hydrogen electrode (NHE), the E<sub>fb</sub> of BMO, BMO-P, BMO-U and BMO-U-P was -0.41, -0.41, -0.45 and -0.45 eV, respectively.<sup>41</sup> It indicates that the polarization treatment does not change the position of the energy band. The series of BMO samples are obvious n-type semiconductors, because of the positive slopes of the Mott-Schottky

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curves.<sup>42</sup> In general, for n-type semiconductors, the  $E_{CB}$  position is about  $0.1 \stackrel{\text{DO}}{=} 0.3 \stackrel{\text{View Article Online}}{=} 0.3 \stackrel{\text{View Article Online}}{=}$ 

$$E_{VB} = E_{CB} + E_g \tag{2}$$

the VB position of BMO, BMO-P, BMO-U and BMO-U-P is calculated to be 1.79, 1.79, 1.77 and 1.77 eV, respectively. As it is well known, there is a close relationship between the photoreduction ability and CB position for a semiconductor, and electrons on a more negative CB potential show a stronger driving force for reduction.  $^{45,46}$  Thus, BMO-U and BMO-U-P have a stronger CO<sub>2</sub> reductive ability.



Figure 3. (a) UV–vis absorption spectra of a series of BMO samples and (b) the corresponding Tauc plots. The Mott-Schottky plots of the (c) BMO and (d) BMO-U-P

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under three different frequencies.

#### 3.2 Photocatalytic activity for CO<sub>2</sub> reduction

The photocatalytic activity of BMO, BMO-P, BMO-U and BMO-U-P was investigated by CO<sub>2</sub> reduction under simulated solar irradiation in a gas-solid system. As demonstrated in Figure 4a, BMO shows the poorest CO<sub>2</sub> photoreduction performance among all the samples with a CO production of only 5.45 µmol g<sup>-1</sup> within 4 h. Both BMO-P and BMO-U samples exhibit improved photocatalytic performance, and the CO production reaches 22.06 and 16.34 µmol g<sup>-1</sup>, respectively. BMO-U-P displays the highest photocatalytic CO<sub>2</sub> reduction performance with a CO production of 57.51 µmol g<sup>-1</sup> within 4 h. Figure 4b shows the corresponding CO production rate of these samples. The CO evolution rate of the BMO-U-P sample is 14.38 µmol g<sup>-1</sup> h<sup>-1</sup>, which is over 10 times higher than that of BMO (1.36  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup>). This outstanding CO evolution rate is also higher than that of most of the previously reported bismuthbased catalysts, such as  $Bi_{24}O_{31}Cl_{10}$ -OV (0.90 µmol g<sup>-1</sup>h<sup>-1</sup>), BiOI (5.18 µmol g<sup>-1</sup>h<sup>-1</sup>), and even some other state-of-the-art photocatalysts, such as Mg-In LDH (4.00 µmol g-<sup>1</sup>h<sup>-1</sup>) (detailed comparison with more photocatalyts are shown in Table S2).<sup>47-49</sup> The control experiments of the BMO-U-P sample under different conditions were shown in Figure 4c. It can be clearly seen that there is no CO detected in the darkness or without photocatalyst, which demonstrates the necessity of both light and photocatalyst. A slight of CO was detected over the BMO-U-P sample under simulated solar irradiation in an Ar atmosphere. It is understandable that trace of organics were attached on the surface though the samples were alternately washed with anhydrous ethanol and hot

/iew Article Online distilled water. Figure 4d shows the results of CO<sub>2</sub> reduction of BMO-U-P for three cycles. It can be seen that the CO production still maintains 44.36 µmol g<sup>-1</sup> after three cycles, revealing the good stability of BMO-U-P.



Figure 4. (a) Photocatalytic CO production and (b) production rate of the BMO, BMO-P, BMO-U and BMO-U-P samples under simulated sunlight. (c) CO production rate of the BMO-U-P sample under different conditions or without catalyst. (d) Cycling experiment of the BMO-U-P sample.

#### 3.3 Mechanism investigation on the enhanced photocatalytic activity

Due to ferroelectric polarization, a strong polarization electric field will be formed between the two sides of BMO-U-P nanosheets, which can provide a stronger driving force for improving the separation and transfer efficiency of photogenerated charge

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carriers.<sup>50-53</sup> The surface potential of the samples was investigated by AFM and KPFM.<sup>57D0TA02102D</sup> Figure 5 shows the AFM topographic and KPFM potential images of the as-obtained samples, where the black and red lines represent for their thickness and surface potential, respectively. For more accurate comparison, the samples with the similar stacking thickness (31-33 nm) were selected for potential difference measurement, as shown by the height plots (the black lines) in Figure 5c, f, i and l. As revealed by the red lines, the potential difference of BMO, BMO-P, BMO-U and BMO-U-P is measured to be 28.25, 43.82, 56.02, and 108.25 mV, respectively. Thus, BMO-U-P has the largest surface potential difference, which indicates its strongest internal electric field, thus resulting in substantially strengthened separation and transfer efficiencies of photogenerated charge carriers.<sup>54</sup>

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Figure 5. (a, d, g, j) AFM topographic images, (b, e, h, k) KPFM potential images and (c, f, i, l) the corresponding height curves (black lines) and surface ferroelectric potential (red lines) of BMO, BMO-P, BMO-U, BMO-U-P, respectively.

The polarization-electric field hysteresis curves of the as-obtained samples were measured to study the importance role of ferroelectricity in improving the photocatalytic performance (Figure 6a). When an electric field of  $-150\Box 150 \text{ kV/cm}$  was applied, both the saturation polarization (Ps) and remnant polarization (Pr) display an order of BMO < BMO-P < BMO-U < BMO-U-P. BMO-P and BMO-U-P show

larger Ps and Pr than their non-polarized counterparts (BMO and BMO-U), which may be due to that corona poling causes the aligned arrangement of ferroelectric domains, thus enhancing the ferroelectricity, as confirmed by the surface potential difference of BMO-P and BMO-U-P (Figure 5). It was worth noting that the ferroelectricity of BMO-U is stronger than that of BMO-P, which may be attributed to that the fabrication of ultrathin structure increases the asymmetry of the structural units in Bi<sub>2</sub>MoO<sub>6</sub>. As shown in Table S1, the lattice parameter a of BMO-U has prolonged to be 5.49556 Å from 5.48338 Å for BMO, which clearly proves that lattice distortion has occurred in BMO-U. It can be explained as that the construction of thin-layer structure causes the absence of a large amount of surface atoms, which results in larger lattice distortion, contributing to enhanced spontaneous polarization of BMO-U. The same phenomenon was also observed for the ultra-thin SrTiO<sub>3</sub> material.<sup>55</sup> It was also confirmed by the above XPS analysis that the largest shift in binding energy was observed for BMO-U-P. Based on the above analysis, it can be inferred that the microstructure change of ferroelectric materials also affects their ferroelectric properties. Due to the synergistic effect of thin-layered structure and corona poling, BMO-U-P shows the strongest ferroelectricity, consistent with KPFM observation.

To investigate the relationship between ferroelectric properties and charge separation, PL was used to study the charge recombination rate in Bi<sub>2</sub>MoO<sub>6</sub> series samples.<sup>56</sup> The recombination efficiency of photogenerated electrons and holes is demonstrated by the intensity of the PL emission peak, and a lower PL emission intensity means a lower recombination rate. Figure 6b displays that BMO shows the highest emission intensity

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at the emission peak position of approximately 480 nm, which matches well<sup>DOJ</sup> with its optical band gap. It should be noted that the emission intensity of BMO-P and BMO-U is significantly lower than that of the BMO, which indicates that both corona poling treatment and fabrication of ultrathin structure can reduce the recombination rate of photogenerated charge carriers. Evidently, BMO-U-P demonstrates the weakest emission intensity among all the samples, revealing its lowest recombination rate of photogenerated electrons and holes.



Figure 6. (a) Electric hysteresis loop, (b) PL spectra, (c) EIS spectra and (d)  $CO_2$ adsorption isotherms of BMO, BMO-P, BMO-U and BMO-U-P.

Electrochemical impedance spectroscopy (EIS) can indicate the migration and transfer of photogenerated charge carriers in semiconductors, in which the arc can

reflects the interface layer resistance at the surface of electrode.<sup>57</sup> Figure 6c shows the Nyquist plots of BMO, BMO-P, BMO-U and BMO-U-P under irradiation of simulated sunlight. It can be seen that the arc radius of BMO-P, BMO-U and BMO-U-P electrodes is all smaller than that of BMO, which indicates that the charge transfer rate can be increased by corona poling and fabrication of ultrathin structure. The smallest arc radius was observed for BMO-U-P, suggesting the fastest charge transfer efficiency.

It is well known that difference in CO<sub>2</sub> adsorption capability has an impact on the photocatalytic CO<sub>2</sub> reduction activity. Figure 6d shows the CO<sub>2</sub> adsorption isotherms of BMO, BMO-P, BMO-U and BMO-U-P. Compared to BMO and BMO-P, the thinlayered structure in BMO-U and BMO-U-P greatly enhanced the CO<sub>2</sub> adsorption, which is due to exposure of more surface reactive sites. It has been reported that the photoreduction reaction mainly occurs on the {020} crystal plane of the Bi<sub>2</sub>MoO<sub>6</sub>.<sup>58</sup> From Figure 1c, the exposed facet of the as-prepared BMO-U-P sample is {020} facet. Thus, the large exposure proportion of {020} facet in BMO-U-P is beneficial for increasing the surface catalytic sites for CO reduction. In addition, the polarized samples (BMO-P and BMO-U-P) also show slightly higher CO<sub>2</sub> adsorption ability than un-polarized counterparts. It may be because the corona poling results in the lattice distortion and asymmetric distribution of surface charges, benefiting the CO<sub>2</sub> adsorption.

Based on the above analyses, the mechanisms for substantially boosted charge separation and  $CO_2$  reduction reaction over BMO-U-P were proposed, as illustrated in Figure 7. Under the strong polarization electric field, the photogenerated electrons and

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holes are promptly separated and transferred to opposite directions along a or c axis. The thin-layered structure is also favorable for the fast migration of charge carriers from bulk phase to surface of BMO-U-P. Moreover, the surface reactive sites on the top facets were enriched, which greatly benefits CO<sub>2</sub> adsorption and activation. Especially, the ferroelectric polarization and thin-layered structure take a synergistic part in promoting the above advantages, thus co-boosting the CO<sub>2</sub> photoreduction activity of Bi<sub>2</sub>MoO<sub>6</sub>.



Figure 7. The schematic illustration for charge separation mechanism and  $CO_2$ reduction reaction over BMO-U-P.

#### 4. Conclusion

In conclusion, ultrathin Bi<sub>2</sub>MoO<sub>6</sub> nanosheets with strengthened ferroelectricity were synthesized by a one-step hydrothermal reaction with the addition of CTAB followed

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by corona poling. Corona poling induces the formation of strong polarized electric field  $^{(1)}$   $^{(1)}$   $^{(1)}$   $^{(1)}$   $^{(1)}$   $^{(2)}$   $^{(1)}$   $^{(2)}$   $^{$ 

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Corona poling for establishing polarization electric field and fabrication of two-dimensional structure was demonstrated as an efficient strategy for promoting charge separation and enriching catalytic sites, synergistically boosting  $CO_2$  photoreduction activity.