1. Introduction

Over the past few years, photocatalytic water splitting has attracted much attention owing to its potential to produce clean and sustainable energy.\(^1\) However, the conversion efficiency of photocatalysts has often been limited by poor light absorption and low charge separation as well as unsatisfactory light stability.\(^2\) To overcome these challenges, strategies such as band gap engineering, micro/nanoengineering, co-catalyst engineering, surface engineering and interface engineering have been explored to ameliorate the drawbacks of the currently developed photocatalysts and photoelectrochemical cells.\(^7,3\) Compared with pure photocatalysts, photoelectrochemical cells have much higher energy conversion efficiency because the external electric field can effectively separate light-exited electron–hole pairs, manipulate redox reactions and ease the separation of gaseous production.\(^4\) As the most important components of photoelectrochemical cells, highly efficient and stable semiconductor photoelectrodes have been extensively studied. Nevertheless, due to the limitations of chemical synthesis technology and material feasibility, these photoelectrodes have still limitations to a certain extent in terms of energy conversion efficiency which needs to be improved by these methods.

In some photocatalysts, the space charge region and built-in electrical field \(E_{in}\) near the interface are the major driving forces for the separation of photogenerated electron–hole pairs.\(^5,7\) Generally, a complicated strategy is employed to form the heterojunction; however, the space charge region usually exists near the interface and only takes up a small part of the entire photocatalyst. In contrast to the \(E_{in}\) near the interface, the depolarization electric field of ferroelectric polarization \(E_{FE}\) extends across the entire volume of the film or bulk material, effectively separating the electron–hole pairs and driving them toward their respective electrodes.\(^5,9\) Being similar to the external electric field of photoelectrochemical cells, this \(E_{FE}\) can also adjust the chemical potential and surface band bending of photoelectrodes based on ferroelectric materials, thereby allowing tailoring the photoelectrochemical performance.\(^10,12\) Due to these fascinating features, ferroelectric metal oxides have been intensively studied either as the sole harvesting materials, such as BiFeO\(_3\),\(^11,13,14\) Bi\(_3\)FeCrO\(_6\),\(^15,16\) KNbO\(_3\),\(^18\) BaTiO\(_3\),\(^17\) or in hybrid systems, as exemplified by the Au/BiFeO\(_3\) heterostructure,\(^18\) BiFeO\(_3\)/BiVO\(_4\) photoanode,\(^19\) and TiO\(_2\)/BaTiO\(_3\) photoanode,\(^20\) which have greatly enhanced photocatalytic or photoelectrochemical activities through appropriate manipulation of ferroelectric polarization.

Bi\(_2\)MoO\(_6\) is the simplest \((n = 1)\) member of the large family of layered perovskite-related compounds with the general formula \((\text{Bi}_2\text{O}_3)(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})\).\(^21\) At room temperature, Bi\(_2\)MoO\(_6\)
has the $P_{2\bar{1}}ab$ Aurivillius structure which allows the macroscopic ferroelectric polarization in theory.\textsuperscript{22,23} In addition, Bi$_2$MoO$_6$ is one of the most studied materials in photocatalytic and photoelectrochemical fields, exhibiting remarkable photocatalytic and photochemical properties in dye degradation and water splitting, respectively.\textsuperscript{24,25} However, the rapid combination of electron–hole pairs generated by light irradiation is still one of the major limitations of Bi$_2$MoO$_6$ for energy conversion efficiency.\textsuperscript{24,26} Various modification strategies such as morphology control,\textsuperscript{27} doping\textsuperscript{28,29} and semiconductor combination\textsuperscript{30,31} have been developed to improve the photocatalytic or photoelectrochemical activities of Bi$_2$MoO$_6$. However, to our knowledge, there have been no reports on the macroscopic polarization of Bi$_2$MoO$_6$ observed in experiments and the effect of ferroelectric regulation on photoelectrochemical properties until now.

In this work, Bi$_2$MoO$_6$ nanopillars with large surface areas were prepared on an ITO-coated glass substrate. The ferroelectric polarization orientation toward ITO greatly enhances the photoelectrochemical properties of the Bi$_2$MoO$_6$ photoanode. $E_{FR}$ leads to the efficient separation of photogenerated carriers and a 28% enhanced photocurrent density, i.e. 250 $\mu$A cm$^{-2}$ at 1.23 V vs. reversible hydrogen electrode (RHE).

2. Experimental

2.1. Material preparation

The Bi$_2$MoO$_6$ nanopillars were grown on the ITO-coated glass substrate via a pulsed laser deposition technique using a Bi$_2$MoO$_6$ target. A Bi$_2$MoO$_6$ target with 5% Bi excessively compensating for the evaporation of the Bi element was sintered at 670 °C by conventional solid state reactions. Prior to the deposition of Bi$_2$MoO$_6$ nanopillars, the ITO-coated glass substrates were washed in acetone, ethanol and deionized water each for 30 min to remove impurities. The deposition chamber was initially evacuated to a base pressure of 10$^{-3}$ Pa. The distance between the target and the substrate was set to 6.5 cm. The deposition process was carried out at a substrate temperature of 480 °C and an oxygen pressure of 15 Pa, with a KrF excimer laser operated at a laser repetition rate of 2 Hz and a laser energy of 45 mJ. After the deposition, the samples were post-annealed at 480 °C in situ for 30 min in 1000 Pa of O$_2$ atmosphere.

2.2. Characterization

Cross-sectional images of the samples were observed with a field emission scanning electron microscope (SEM, FEI Quanta 250F). The XRD patterns were characterized with a Bruker D8 diffractometer equipped with a Cu-Kα radiation source. The crystal structure was also characterized by transmission electron microscopy (TEM, FEI Tecnai G2 F20 S-Twin). X-ray photoelectron spectroscopy (XPS) spectra were recorded with an X-ray photoelectron spectrometer (Thermo Scientific K-Alpha+). The ultraviolet-visible (UV–Vis) spectrum was recorded using a UV–Vis spectrophotometer (Shimadzu Co.), Polarization versus electric field ($P-E$) hysteresis loops were measured at 1000 Hz with a commercial ferroelectric tester (Radiant precision multiferroic II). The morphology and piezoelectric force microscopy (PFM) images were observed with a commercial atomic force microscope (AFM, Bruker Multimode 8) and the conductive tip (Bruker MESP-RC).

2.3. Photoelectrochemical measurements

All photoelectrochemical measurements were performed on an electrochemical workstation (CH Instruments Inc., CHI 660E) in a three-electrode configuration using a Bi$_2$MoO$_6$ sample as the working electrode, a Pt foil as the counter electrode, and saturated Ag/AgCl as the reference electrode. Na$_2$SO$_4$ solution (pH = 6.8) with 0.5 M concentration was used as the electrolyte. AM 1.5 G simulated solar light illumination (100 mW cm$^{-2}$) was obtained from a 350 xenon lamp solar simulator coupled with an AM 1.5 G filter (NBet). All electrodes were illuminated from the front side with an active area of 1 cm$^2$.

Before the measurements, the light intensity was calibrated with a light power meter. The conversion between the potentials vs. Ag/AgCl and vs. RHE was performed using the following equations:

\[ E(\text{vs. RHE}) = E(\text{vs. Ag/AgCl}) + E_{\text{Ag/AgCl}} + 0.0591 \times \text{pH} \]

where $E_{\text{Ag/AgCl}}$ is 0.1976 V at 25 °C. During a typical $J-V$ measurement, linear sweep voltammetry (LSV) was conducted at a scan rate of 30 mV s$^{-1}$. H$_2$ gas was collected with an air-tight three-electrode photoelectrochemical cell in the 0.5 M Na$_2$SO$_4$ and 0.2 M Na$_2$SO$_3$ aqueous solution where Na$_2$SO$_3$ is used as the hole scavenger, and then the H$_2$ amount was measured with a gas chromatograph (PerkinElmer Clarus 580 GC). Electrochemical impedance spectroscopy (EIS) was performed with an AC voltage amplitude of 5 mV and a frequency range of 0.1–100 kHz under AM 1.5 G illumination. The Mott–Schottky plots were recorded at 1 kHz in the dark.

3. Results and discussion

Fig. 1a shows the schematic diagram of the geometry and crystal structure of Bi$_2$MoO$_6$ nanopillars. Bi$_2$MoO$_6$ unit cells are composed of [Bi$_2$O$_3$]$^{2+}$ slices linked with a corner-sharing structure of MoO$_6$ octahedra.\textsuperscript{21,24} The layered configuration facilitates good electron conductivity and influences the visible light photo-absorption.\textsuperscript{24} When a dense Bi$_2$MoO$_6$ target was sputtered by the pulsed laser with a focused spot diameter of ∼0.5 mm, the Bi$_2$MoO$_6$ film with a flat surface was also grown on the ITO-coated glass substrate at 480 °C. When the focused spot diameter increases from ∼0.5 mm to ∼2 mm while other conditions are unchangeable, the generated ions have a weaker kinetic energy and a shorter diffusion length on the substrate which just allows the island growth mode at 480 °C. A decrease in the kinetic energy of the ablated particles from the target plays a significant role in forming nanopillars. In addition, increasing the oxygen pressure and target–substrate distance can also create favorable conditions for the growth of
The corresponding crystal structure is investigated by X-ray diffraction (Fig. 1b). All the diffraction peaks of the Bi$_2$MoO$_6$ nanopillars can be readily indexed to $\gamma$-Bi$_2$MoO$_6$ (JCPDS No. 21-0101), indicating the high purity of the prepared nanopillars. Most importantly, [200] oriented crystal grains account for the majority according to the XRD patterns.

These Bi$_2$MoO$_6$ nanopillars have a special columnar structure with a large specific surface which is beneficial for enhancing photoelectrochemical performance. Fig. 1c and d display the SEM images of the as-prepared Bi$_2$MoO$_6$ nanopillars, providing a direct view of the section and surface morphology. The Bi$_2$MoO$_6$ nanopillars with a height of 290 nm and a diameter of 100–200 nm are uniformly distributed on the ITO-coated glass substrate. Furthermore, the columnar structure of these Bi$_2$MoO$_6$ nanopillars is also observed in the cross-sectional TEM image (Fig. S1†). The root-mean-square roughness ($R_q$) of the Bi$_2$MoO$_6$ nanopillars is 31.8 nm, while the $R_q$ of the ITO film and the flat Bi$_2$MoO$_6$ film is 3.9 nm and 9.5 nm according to the surface image characterized by AFM (Fig. S2†). The larger specific surface areas of this morphology can greatly increase the electrochemically active area. At the same time, the nanopillars with a columnar structure shorten the distance of charge transport and reduce the recombination of electron–hole pairs, which is beneficial to water splitting.

The energy-band gap ($E_g$) of Bi$_2$MoO$_6$ was analyzed according to the UV–Vis diffuse reflectance spectrum (Fig. 2a) and was calculated according to the Tauc plot:35

$$ahv = A(hv - E_g)^{n/2}$$

where $a$, $h\nu$, and $A$ are the absorption coefficient, photon energy, and a constant, respectively. Meanwhile, $n$ is determined by the type of optical transition in the semiconductor ($n = 1$ for a direct transition, $n = 4$ for an indirect transition). For Bi$_2$MoO$_6$, the $n$ value is 1 and $E_g$ is approximately 2.78 eV which are close to previously reported values.34,36

The chemical states of the elements in the Bi$_2$MoO$_6$ nanopillars are identified according to XPS spectra. The XPS survey spectrum (Fig. S3†) reveals the coexistence of Bi, Mo and O elements, and there are no other impurity peaks. The high-resolution XPS spectra of each element are shown in Fig. 2b–d. Two strong peaks in the Bi 4f region at 159.0 eV and 164.3 eV are assigned to Bi 4f$_{7/2}$ and Bi 4f$_{5/2}$, confirming the presence of Bi$^{3+}$ species (Fig. 2b).36 Besides, there are two characteristic peaks at 232.4 eV and 235.5 eV (Fig. 2c), corresponding to Mo 3d$_{3/2}$ and Mo 3d$_{5/2}$ states of Mo$^{6+}$ in Bi$_2$MoO$_6$, respectively. Furthermore, the two peaks at 529.9 eV and 531.9 eV for the O 1s spectra belong to lattice oxygen and oxygen vacancies in the...
The differences between the Fermi level ($E_F$) and the valence band maximum ($E_v$) were determined by the intercepts of the extrapolated lines for the spectra near the Fermi edge, which is obtained as 1.88 eV (Fig. 2e). The band structure of Bi$_2$MoO$_6$ is achieved in Fig. 2f which indicates the n type semiconductor being consistent with previous reports.

Both P–E hysteresis loops and PFM images confirm the ferroelectric polarization switching of Bi$_2$MoO$_6$ nanopillars. As shown in Fig. 3a, a remanent polarization ($P_r$) of 1.2 μC cm$^{-2}$ is observed in the P–E loop of the (00) Bi$_2$MoO$_6$ single-crystal film on the Nb:SrTiO$_3$ substrate, and an unsaturated P–E loop is observed in Bi$_2$MoO$_6$ nanopillars due to a larger leakage current especially at grain boundaries. This study proves that Bi$_2$MoO$_6$ is a typical ferroelectric semiconductor. Furthermore, the morphology and ferroelectricity of a 3 × 3 μm$^2$ region are characterized using a AFM with PFM mode. Bi$_2$MoO$_6$ nanopillars are the columnar crystal grains with average diameters of 150–200 nm according to the three-dimensional AFM morphology (Fig. 3b). The polarization toward ITO (downward polarization, dark color) was introduced by the tip with 10 V scanning upon a 2 × 2 μm$^2$ region (Fig. 3c), and then the polarization against ITO (upward polarization, bright color) was introduced again by the tip with −10 V bias scanning upon the central 1 × 1 μm$^2$ region (Fig. 3d). The stable polarizations toward and against the ITO bottom electrode prove the ferroelectric polarization switching of Bi$_2$MoO$_6$ nanopillars again. The ferroelectricity originates from the non-centrosymmetric crystal structure. Bi$_2$MoO$_6$ belongs to the family of bismuth-layered compounds (i.e. Aurivillius family) which is composed of bismuth-oxygen (Bi$_2$O$_2$) and perovskite-like octahedral layers. Ferroelectric ordering in most multi-layer Aurivillius phases typically leads to a transition from a tetragonal (4/mmm) to a polar orthorhombic structure. The distorted MoO$_6$ octahedra are related to the existence of spontaneous polarization in the crystal. Bi$_2$MoO$_6$ is an orthorhombic ferroelectric phase at room temperature and it transforms into an orthorhombic paraelectric phase at a Curie temperature of 604 °C according to previous studies.

The polarization toward ITO significantly enhances the photocurrent density to 250 μA cm$^{-2}$ at 1.23 V vs. RHE. Photocurrent density versus potential ($J$–$V$) curves of the Bi$_2$MoO$_6$ photoanode were recorded to study the role of ferroelectric polarization in photoelectrochemical water splitting. As shown in Fig. 4a, the very low $J$ in the dark indicates a small amount of electrocatalytic water splitting even at 1.6 V vs. RHE which far exceeds the water splitting potential. The as-grown sample exhibits a $J$ of ∼195 μA cm$^{-2}$ at 1.23 V vs. RHE with an onset potential ($V'_*_{on}$) of 0.63 V, where $V'_*_{on}$ is the potential at the intersection point of potential-axis and the tangent at the maximum slope of photocurrent. This $J$ is 129% higher than the $J$ of the flat Bi$_2$MoO$_6$ film under the same characteristic conditions (Fig. S4†). To fully pole the Bi$_2$MoO$_6$ nanopillars for macroscopic polarization, a piece of dust-free cloth impregnated with ionic liquid (1-ethyl-3-methylimidazolium

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**Fig. 2** (a) UV–Vis diffuse reflectance spectra of the Bi$_2$MoO$_6$ nanopillars. XPS spectra of (b) Bi 4f, (c) Mo 3d, (d) O 1s and (e) valence band. (f) Energy-band diagram.
bis(trifluoromethanesulfonyl)imide) was used to contact the surface of Bi$_2$MoO$_6$ nanopillars, and then a flat piece of aluminum foil on the ionic liquid was used as the top electrode to provide a uniform electric field (Fig. S5†). The 5 V pulsed voltage was applied on aluminum foil for 5 min to fully pole Bi$_2$MoO$_6$ nanopillars. Polarization switching is realized by 5 V according to the corresponding PFM image (Fig. S6†). After that, the sample was ultrasonically cleaned in ethanol and deionized water to remove the ionic liquid for further photoelectrochemical measurements. There is an enhanced $J$ of $\sim 250 \mu$A cm$^{-2}$ for the Bi$_2$MoO$_6$ nanopillar photoanode with the macroscopic polarization toward ITO (positive poling), which is 28% enhancement compared with the as-grown Bi$_2$MoO$_6$ nanopillars without macroscopic polarization. Such $J$ is much higher than those of the photocurrent density of Bi$_2$MoO$_6$ photoanodes reported in previous literature (Table S1†). Besides, a negative shift in the $V'_{on}$ $\approx$ 65 mV suggests that polarization switching changes band alignment and tunes the charge separation as well as the charge transfer efficiency. The produced H$_2$ gas was analyzed using gas chromatography. The as-grown Bi$_2$MoO$_6$ photoanode and that with polarization toward ITO produced the H$_2$ gas with a rate of 4.08 $\mu$mol cm$^{-2}$ and 5.61 $\mu$mol cm$^{-2}$ per hour which further confirmed the improved photoelectrochemical performance of the photoanode by appropriate manipulation of the ferroelectric polarization (Fig. S7†). However, the Bi$_2$MoO$_6$ photoanode with the polarization against ITO (negative poling) exhibits a $J$ of 182 $\mu$A cm$^{-2}$ which is slightly lower than that of the origin Bi$_2$MoO$_6$ nanopillars. In addition, the minor standard deviation of photocurrent shows good stability and repeatability for different Bi$_2$MoO$_6$ nanopillar photoanodes which were prepared, subjected to polarization poling and characterized under the same conditions (Fig. S8†). Fig. 4b shows the $J$–$V$ curves under chopped light illumination. The rapid photoresponse was observed during the light on/off state. The obvious spikes at low potential (<1 V) are ascribed to the rapid recombination of photogenerated carriers under light illumination. The chronoamperometry ($J$–$t$) measurements under chopped light illumination at 1.23 V vs. RHE were performed to further study the instantaneous photoresponse (Fig. 4c), whose results are consistent with those of the $J$–$V$ measurements. In a word, the $J$–$V$ measurements show that a 28% increase of photocurrent has been realized by tuning the ferroelectric polarization.

To gain more insight into the suppression of charge recombination, the transient photocurrent curve was recorded by chronoamperometry to investigate charge recombination (inset in Fig. 4d). A normalized parameter (i.e., $D$) is intro-
duced from the J-time (J–t) curve to determine the charge recombination,\textsuperscript{16,45}

\[ D = \frac{I_t - I_{st}}{I_{in} - I_{st}} \]

where \( I_t \), \( I_{st} \) and \( I_{in} \) are the time-dependent, the steady-state photocurrent and the initial photocurrent, respectively. The normalized plots of ln(\( D \)) as a function of time are displayed in Fig. 4d. The transient time constant (i.e., Time) is defined as the time at ln(\( D \)) = −1. Time is estimated as 13 s, 32 s and 9 s for the as-grown sample and that with polarization toward ITO and against ITO, which confirms the suppression of charge recombination when polarization is toward ITO. Furthermore, the charge transfer efficiency (\( \eta_{\text{trans}} \)) of origin Bi\(_2\)MoO\(_6\) nanopillars is just 38\% at 1 V (vs. RHE), and that of the Bi\(_2\)MoO\(_6\) with polarization toward ITO significantly increases to 56\% (Fig. S9\textsuperscript{†}). The increase of Time and \( \eta_{\text{trans}} \) proves that the \( E_{\text{FE}} \) of the macroscopic polarization toward ITO remarkably enhances the separation efficiency of light-excited electron–hole pairs. However, all the samples still suffer photocorrosion to some extent under long-term illumination due to the surface-accumulated holes, and the photoelectrochemical photocurrent decreases about 34–38\% at 1.23 V vs. RHE within 8000 s (Fig. S10\textsuperscript{†}). Nevertheless, the photocurrent of the sample with polarization toward ITO at 1.23 V vs. RHE is still 30\% higher than that of the pristine sample, indicating the good stability of ferroelectric polarization during this photoelectrochemical process.

The dependence of the band structure on polarization can elucidate the enhanced charge separation of Bi\(_2\)MoO\(_6\) nanopillars discussed above (Fig. 5). At first, when Bi\(_2\)MoO\(_6\) is immersed in the electrolyte, the light-excited electrons transfer from the Bi\(_2\)MoO\(_6\) to the electrolyte due to the difference between the Bi\(_2\)MoO\(_6\) work function and electrochemical potential of the electrolyte, leading to upward band bending and a significant space charge region width on the surface of Bi\(_2\)MoO\(_6\), as shown in Fig. 5a. After Bi\(_2\)MoO\(_6\) nanopillars are positively poled, the macroscopic ferroelectric polarization toward ITO induces negative (positive) bound charges at the Bi\(_2\)MoO\(_6\)/electrolyte (Bi\(_2\)MoO\(_6\)/ITO) interface, as shown in Fig. 5b. As a result, the high \( E_{\text{FE}} \) increases the magnitude of upward (downward) band bending toward the Bi\(_2\)MoO\(_6\)/electrolyte (Bi\(_2\)MoO\(_6\)/ITO) interface, producing a wider space charge region at the Bi\(_2\)MoO\(_6\)/electrolyte and Bi\(_2\)MoO\(_6\)/ITO interface side. Due to the favorable band bending, the photo-generated electron–hole pairs in the bulk Bi\(_2\)MoO\(_6\) will be sep-
arated effectively by the $E_{FE}$, leading to an enhanced photoelectrochemical performance. However, the situation is reversed when the polarization against ITO is induced in Bi$_2$MoO$_6$ nanopillars (Fig. 5c). The downward band bending at the Bi$_2$MoO$_6$/electrolyte interface and upward band bending at the Bi$_2$MoO$_6$/ITO interface will hinder the transfer of photogenerated electrons to the ITO bottom electrode and photogenerated holes to the electrolyte, which is against the water oxidation reaction in the electrolyte.

Mott–Schottky plots support the charge transfer mechanism and validate the effect of ferroelectric polarization on the improved photoelectrochemical performance of the Bi$_2$MoO$_6$ photoanode. The flat-band potential ($V_{fb}$) is obtained from the Mott–Schottky equation,$^{46}$

$$\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 N_d} \left( V - V_{fb} \right) - \frac{kT}{e}$$

where $C$ represents capacitance at the semiconductor/electrolyte interface, $\varepsilon$ is the electronic charge, $\varepsilon_0$ is the permittivity of vacuum, $\varepsilon$ is dielectric constant of Bi$_2$MoO$_6$ (i.e., 37.5),$^{47}$ $N_d$ is the majority charge-carrier concentration in the semiconductor, $V$ is the applied potential, $V_{fb}$ is the flat-band potential, $k$ is Boltzmann’s constant, and $T$ is the temperature. The $V_{fb}$ is determined from the $x$ intercept by extrapolating the linear fit of the $1/C^2$ vs. $V$ plot. A positive slope in the $1/C^2$ vs. $V$ plots confirms the n-type conductivity of Bi$_2$MoO$_6$, which is consistent with the previous band structure according to the XPS result. Considering that $kT/e$ is calculated to be 0.026 V at 300 K, the $V_{fb}$ of the as-grown Bi$_2$MoO$_6$ photoanode is calculated to be 0.42 V, 0.32 V and 0.44 V (vs. RHE) for the as-grown Bi$_2$MoO$_6$ nanopillars and those with polarization toward ITO and against ITO, respectively (Fig. 6a). A negative shift in the flat-band potential for the sample with polarization toward ITO confirms the enhancement in the upward band bending. Such band bending evolution increases the space charge region width, enhances the separation efficiency of the photogenerated charge carriers and accelerates the transfer of the charge carriers for the photoelectrochemical water-splitting reaction. On the other hand, the positive shift of $V_{fb}$ suggests a reduction of band bending and the downward band bending will hinder the transfer of carriers in the photoanode.$^{48}$ In addition, the $N_d$ is estimated to be $1.75 \times 10^{19}$ cm$^{-3}$ according to the slope of the linear fit of the Mott–Schottky plot for the as-grown sample. For the Bi$_2$MoO$_6$ nanopillars with polarization toward ITO, the $N_d$ is estimated to be $6.40 \times 10^{19}$ cm$^{-3}$. Oxygen vacancies introduced by the charge injection may be one of the reasons for the increasing carrier concentration.$^{49}$ Such increase can shift the Fermi level of Bi$_2$MoO$_6$ toward the conduction band, introduce a more significant band bending at the Bi$_2$MoO$_6$/electrolyte interface and further facilitate charge separation and transportation at the interface.$^{50}$

Electrochemical impedance spectroscopy supports that ferroelectric polarization tunes the charge-transfer efficiency at the Bi$_2$MoO$_6$/electrolyte interface. There is a reduced charge transfer resistance at the interface between Bi$_2$MoO$_6$ and the electrolyte for the Bi$_2$MoO$_6$ nanopillars with polarization toward ITO due to the shorter radius of the circular arc compared to the as-grown Bi$_2$MoO$_6$ nanopillars without macroscopic polarization.$^{10,48,51}$ However, the larger charge transfer resistance in the sample with polarization against ITO will degrade the photoelectrochemical performance which is consistent with photoelectrochemical measurements. The results indicate that the polarization toward ITO and the corresponding $E_{FE}$ can indeed enhance the interface charge transfer efficiency of the Bi$_2$MoO$_6$ nanopillars.

**Fig. 5** Schematic diagrams of the energy band structure of ferroelectric Bi$_2$MoO$_6$ (a) without macroscopic polarization, and with macroscopic polarization (b) toward and (c) against the ITO bottom electrode.
4. Conclusions

In summary, Bi₂MoO₆ nanopillars with large surface areas were grown on the ITO-coated glass substrate by a pulsed laser deposition technique through optimizing growth conditions. The ferroelectric polarization switching of Bi₂MoO₆ nanopillars is confirmed by $P$–$E$ loops and PFM images. The macroscopic polarization orientation toward the ITO electrode was successfully induced by a special poling method with an ionic liquid as the top electrode. Such polarization increases the magnitude of band bending, thus promoting the separation efficiency of light-excited electron–hole pairs and enhancing holes’ extraction, and offers more carriers for the water oxidation reaction. As a result, the Bi₂MoO₆ nanopillars with the polarization toward ITO show a 28% enhanced photocurrent density of $250 \mu A \, cm^{-2}$ at $1.23 \, V$ vs. RHE compared with the origin nanopillars without macroscopic polarization. This work gives inspiration for the development of new and highly efficient photoelectrochemical devices with ferroelectric nanopillars.

Conflicts of interest

There are no conflicts of interest to declare.

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