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Supporting Information for

Efficient Charge Separation between Bi_2MoO_6 Nanosheets and ZnO Nanowires for Enhanced Photoelectrochemical Properties

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Experimental Section

1. Materials and Instruments

All chemicals were analytical grade and used directly without any further purification. They were purchased from Sinopharm Group Chemical Reagent Co. Ltd. China. Deionized water with a resistivity of 18.25 MΩ.cm was used in all reactions. Indium-tin oxide (ITO) coated glasses were purchased from Zhuhai Kaivo Electronic Components Co., Ltd. China.

Morphology and structure of the samples was observed by field emission scanning electron microscope (JEOL-JSM6701F, Japan) at an accelerating voltage of 5 kV. The crystalline structure of the products was identified by X-ray diffraction analysis (XRD, Rigaku RINT-2000) using Cu Kα radiation at 40 keV and 40 mA. The element composition was detected by X-ray photoelectron spectroscope (XPS, ESCALAB 250Xi). UV-visible diffuse reflectance spectra were taken on a UV-2550 (Shimadzu) spectrometer. The photoluminescence(PL) spectra were detected with an F-7000 spectrofluorometer (Hitachi High-Technologies, Tokyo, Japan) using a 325 nm line.

2. Preparation of ZnO nanowire arrays

As reported in our previous work, in a typical procedure[1,2], 1.0 M ZnO sol was prepared first: 4.3900g zinc acetate dehydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$] was dissolved in 20mL ethylene glycol monomethyl ether [$CH_3O\text{-}CH_2\text{-}CH_2OH$], and then an equal mole number of diethanolamine (DEA) was added in. After that, painting the as-prepared sol on an ITO coated glasses substrate ($10 \times 50 \times 1 mm^3$) using a vacuum spin coater (VTC-100) followed with a pretreatment temperature of 200℃ three times. After that, the as-prepared ITO was calcined in a muffle furnace at 350℃ for 30 min in air to obtain the ZnO seed layer. Then the as-prepared ZnO seed layer with the coating side facedown was placed in a 100mL Telflon liner stainless-steel autoclave at a certain angle which contained 0.04M zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) and 0.04M hexamethylene tetraamine (HMT) to grow ZnO nanwire arrays at 100°C for 8 h. Then, the autoclave was cooled down to room temperature. The obtained ZnO nanwire arrays were washed with deionized water and ethanol to remove any ionic residual several times, then dried in an oven at 60°C for 30 min.

3. Preparation of Bi_2MoO_6/ZnO hierarchical heterostructure

In a typical case[3], 2 mM $Bi(NO_3)_3 \cdot 5H_2O$ and 1 mM $Na_2MoO_4 \cdot 2H_2O$ were dissolved in 25mL of ethylene glycol under magnetic stirring respectively. Mixing the two solutions above， then 150 mL ethanol was added into the mixed solution slowly and kept on stirring for 15 min. The resulting clear solution was transferred into a 100 mL Teflon-lined stainless steel autoclave. Then the as-prepared ZnO nanwire arrays with the coating side facedown were immersed in the solution which was heated to 160°C and maintained for 8 h. Then, the autoclave was cooled down to room temperature. The obtained Bi_2MoO_6/ZnO hierarchical heterostructure were washed with deionized water and ethanol to remove any ionic residual several times, then dried in an oven at 80°C for 30 min in air. The as-synthesised sample was denoted as ZBM-3. By changing the precursor concentration for synthesizing Bi_2MoO_6 can get four other samples of Bi2MoO6/ZnO, which were denoted as ZBM-1, ZBM-2, ZBM-4 and ZBM-5 in proper sequence. And pure Bi_2MoO_6 was synthesized in the absence of ZnO nanwire arrays at the same other reaction conditions. The detail experimental conditions for the preparation of ZBM-1, ZBM-2, ZBM-4 and ZBM-5 are given in Table S1.

4. Photoelectrochemical Characterization

All photoelectron chemical properties of pure ZnO nanwire arrays and the Bi_2MoO_6/ZnO hierarchical heterostructures were performed in a 3-electrode system with a piece of Pt foil (3×2 cm2) as counter electrode, a saturated calomel electrode (SCE) as reference electrode, and the as-prepared ZnO nanwire arrays and Bi_2MoO_6/ZnO hetero-structures were employed to be the working electrodes with a surface area of 2 cm^2, respectively. 0.2 M Na_2SO_4 aqueous solution (with pH buffered to 7.0) as the electrolyte. The electrochemical measurements were tested on an electrochemical workstation (CHI660D). All photoelectrodes were illuminated from the front side by a 300 W Xe lamp (HSX-F/UV 300) equipped with a visible light cutoff filter (HSX-F300, Beijing NBeT Technology Co., Ltd) calibrated to 100 mW/cm^2.

Linear sweep voltammograms were measured under a bias voltage between 0 V and 1.0 V (vs.SCE) with a scan rate of 0.1 V/s. Amperometric I–t curves were tested at a bias voltage of +0.2 V (vs.SCE). The optoelectrical properties of the as-prepared pure ZnO nanowire arrays and the Bi_2MoO_6/ZnO hetero-structures under the illumination of various monochromatic light were also achieved via an automatic monochromator (7ISWS, purchased from Beijing 7-Star Optical Instruments Co., Ltd, China) and the above relevant electrochemical instruments. The electrochemical impedance spectroscopy (EIS) measurements were performed via the CHI-660D workstation in a three-electrode cell by applying an AC voltage with 5 mV amplitude in a frequency range from 1 Hz to 100 kHz under open circuit potential conditions.

5. In-situ X-ray photoelectron spectroscopy measurements

Our in-situ XPS is modified by normal XPS attached to a controllable light source. The sample is placed into the vacuum chamber of the XPS instrument with an optical fiber which connected with the outside light source. Firstly, a normal XPS scanning is performed in the dark for one circle and then the optical fiber is turned on for the next circle, repeated the cycle testing process several times. The wavelength of the light can be fixed to visible or UV light by put in or out the 420 nm cut-off filter.

Reference

[1] T. Wang, B. J. Jin, Z. B. Jiao, G. X. Lu, J. H.Ye and Y. P. Bi, *J. Mater. Chem. A*, 2014, **2**, 15553-15559.

[2] T. Wang, B. J. Jin, Z. B. Jiao, G. X. Lu, J. H.Ye and Y. P. Bi, *Chem. Commun.*, 2015, **51**, 2103-2106.

[3] M. Y. Zhang, C. L. Shao, J. B. Mu, Z. Y. Zhang, Z. C. Guo, P. Zhang and Y. C. Liu, *CrystEngComm*, 2012, **14**, 605-612.

Additional Figures and Discussions

Table S1 Experimental conditions of Bi_2MoO_6/ZnO hetero-structures (ZBM is short for Bi_2MoO_6/ZnO hetero-structure).

	Precursors (mM)		
	ZnO NWA	Bi_2MoO_6	
		$Bi(NO_3)_3 \cdot 5H_2O$	$Na_2MoO_4 \cdot 2H_2O$
Bi_2MoO_6	0	2	1
ZBM-1	2×5 cm^2 ITO	2	1
ZBM-2	2×5 cm^2 ITO	4	2
ZBM-3	2×5 cm^2 ITO	6	3
ZBM-4	2×5 cm^2 ITO	8	4
ZBM-5	2×5 cm^2 ITO	10	5

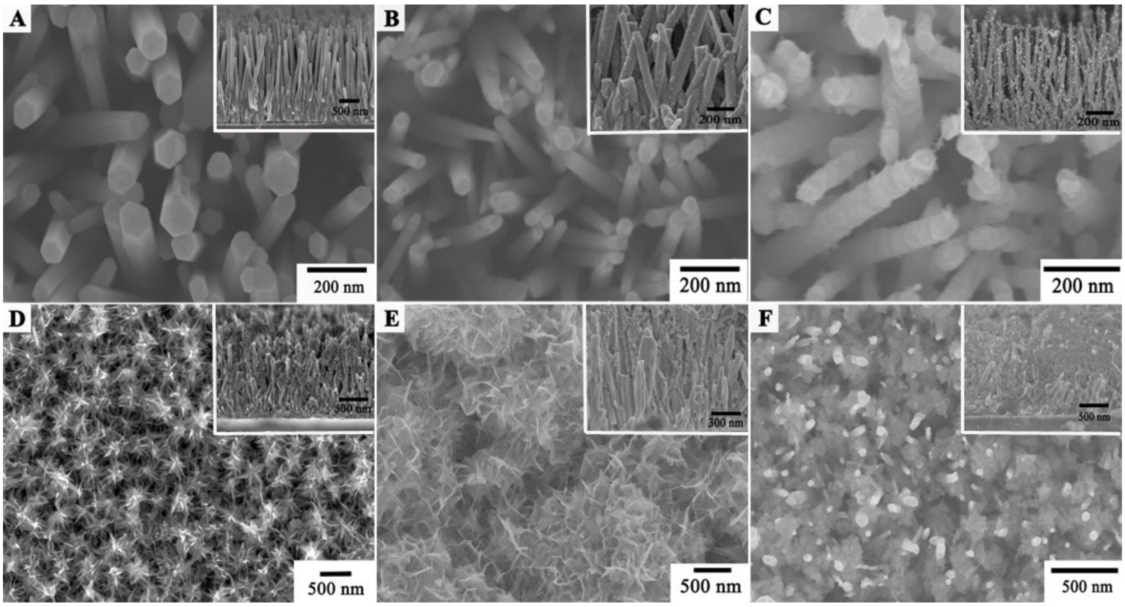

Fig. S1 SEM images of (A) ZnO nanowire arrays, (B, C, D, E, F) Bi_2MoO_6/ZnO hetero-structures noted as ZBM-1, ZBM-2, ZBM-3, ZBM-4, ZBM-5,respectively (the inset SEM is the corresponding cross-sectional images).

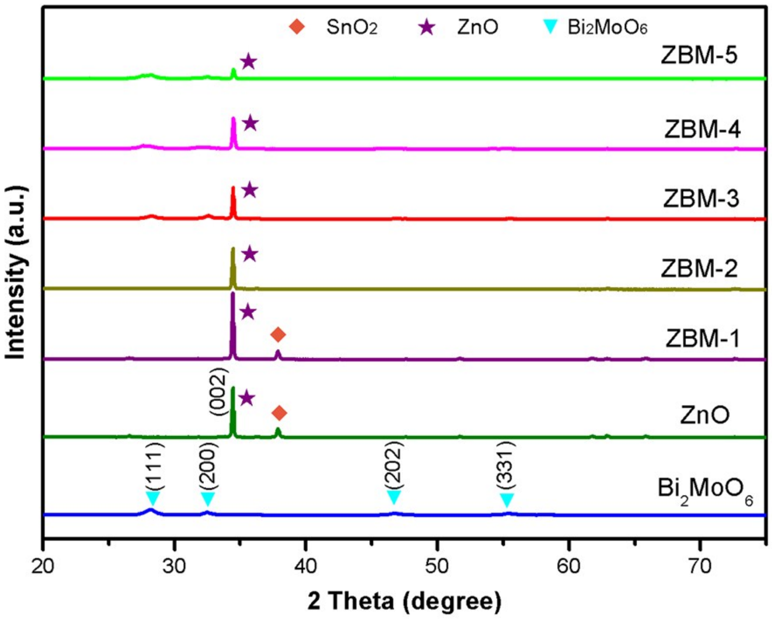

Fig. S2 XRD patterns of ZnO nanowire arrays, Bi_2MoO_6 and Bi_2MoO_6/ZnO hetero-structures.

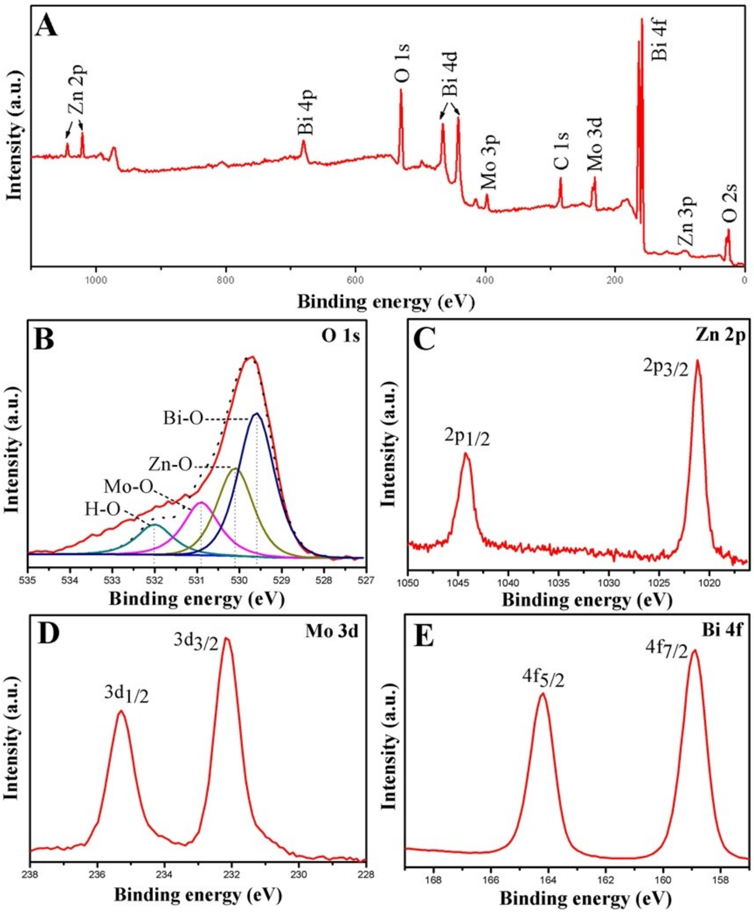

Fig. S3 (A) XPS fully scanned spectra and high-resolution XPS spectra of (B) O 1s, (C) Zn 2p, (D) Mo 3d, (E) Bi 4f of the Bi_2MoO_6/ZnO hetero-structure (ZBM-3).

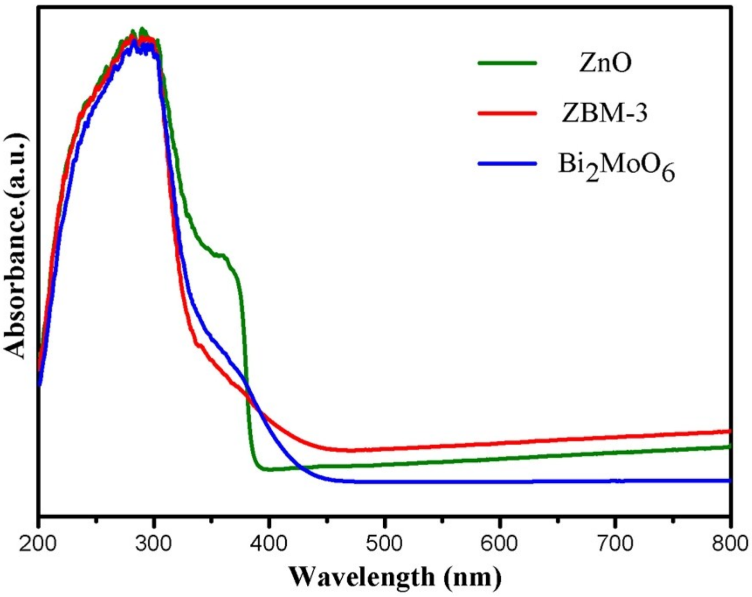

Fig. S4 Ultraviolet-visible diffusive absorption spectra of ZnO NWA, pure Bi_2MoO_6 and Bi_2MoO_6/ZnO hetero-structure (ZBM-3).

Results and discussion

In order to further study the optical properties of the as-prepared Bi_2MoO_6/ZnO hierarchical hetero-structures, ultraviolet-visible light absorption spectra of ZnO nanowire arrays, pure Bi_2MoO_6 and Bi_2MoO_6/ZnO hetero-structure were clarified. As a wide-band-gap oxide semiconductor, ZnO has an intense absorption wavelength with a steep edge of about 390 nm but almost no absorbance in the visible light range. Whereas Bi_2MoO_6 has absorbance in the visible light range with an absorbance edge around 450 nm. When Bi_2MoO_6 and ZnO nanowires arrays compound together, the absorption edges showed significant red-shift and extend into the visible light region obviously. This indicates that the sensitization of Bi_2MoO_6 for ZnO nanowires arrays can extend the photo-absorption range of the ZnO nanowires arrays. [1]

Reference

[1]. G. Tian, Y. Chen, R. Zhai, J. Zhou, W. Zhou, R. Wang, K. Pan, C. Tian and H. Fu, *J. Mater. Chem. A*, 2013, **1**, 6961–6968.

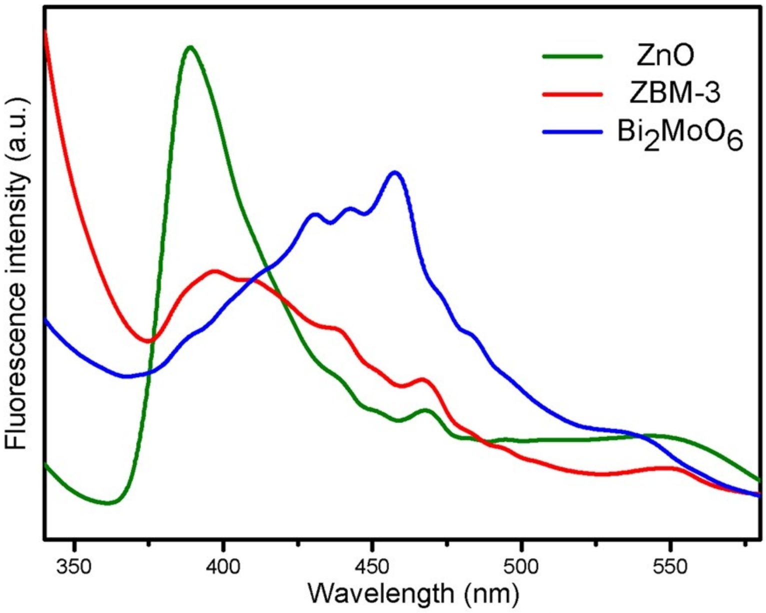

Fig. S5 Photoluminescence (PL) spectra of ZnO NWA, pure Bi_2MoO_6 and Bi_2MoO_6/ZnO hetero-structure (ZBM-3).

Results and discussion

To evaluate the extent of electron–hole recombination of the as-prepared samples, ultraviolet and visible photoluminescence(PL) measurements was studied. As showed in Fig. S5, for the Bi_2MoO_6/ZnO hetero-structures, a strong emission centered at 400 nm as well as a weak emission at 550 nm are observed. These two peaks are all correspond to the electron−hole recombination of ZnO nanowires. PL intensity of Bi_2MoO_6/ZnO hetero-structures at 400nm and 550nm is much lower compared to ZnO nanowires while between 420~550 the intensity is lower than Bi_2MoO_6. According to the PL emission results from recombination of photogenerated electron–hole pairs and the relation between PL intensity and photoelectric activity, the above result indicates suppression of recombination of the electron–hole pairs and promotion of the photoelectric activity of ZnO nanowire arrays after loaded Bi_2MoO_6.

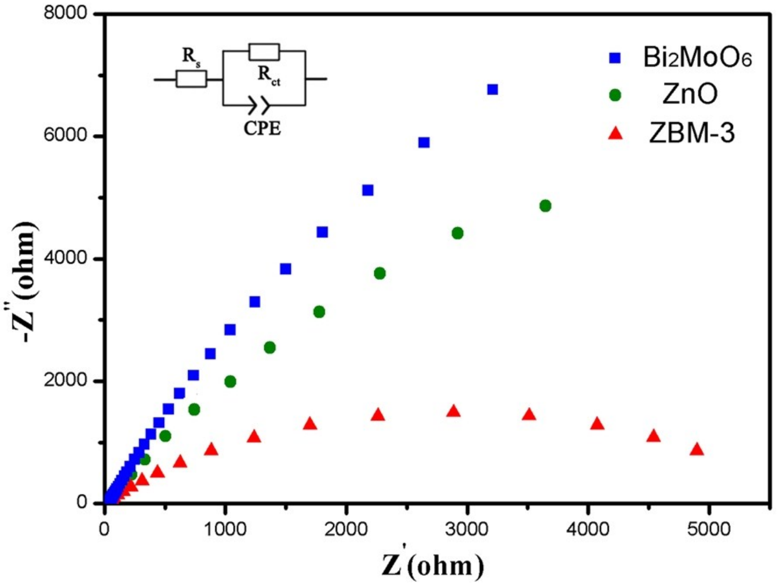

Fig. S6 Electrochemical impedance spectroscopy (EIS) Nyquist plots of ZnO nanowire arrays, pure Bi_2MoO_6 and ZBM-3 (Bi_2MoO_6/ZnO hetero-structure).

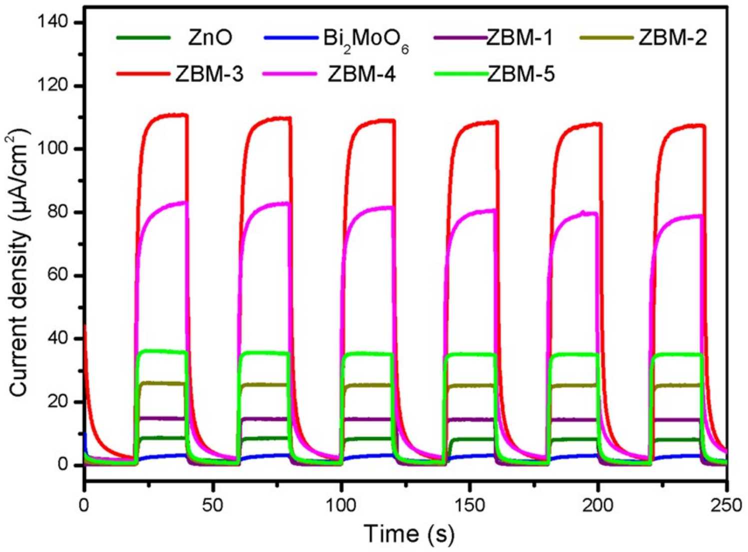

Fig. S7. Amperometric I–t curves of ZnO nanowire arrays, pure Bi_2MoO_6 and Bi_2MoO_6/ZnO hetero-structures at an applied voltage of +0.2 V with 20 s light on/off cycles.

Results and discussion

Generally, when the energy from light irradiation is equal to or greater than the band gap of the semiconductor, electrons in the conduction band and holes in the valence band will be generated. Then these photo-generated charge carriers can trigger a redox reaction on the semiconductor surface. Because ZnO is chemically less stable under light illumination, so we conducted all the PEC studies in a 0.2 M Na_2SO_4 aqueous solution with the pH of 7.0.

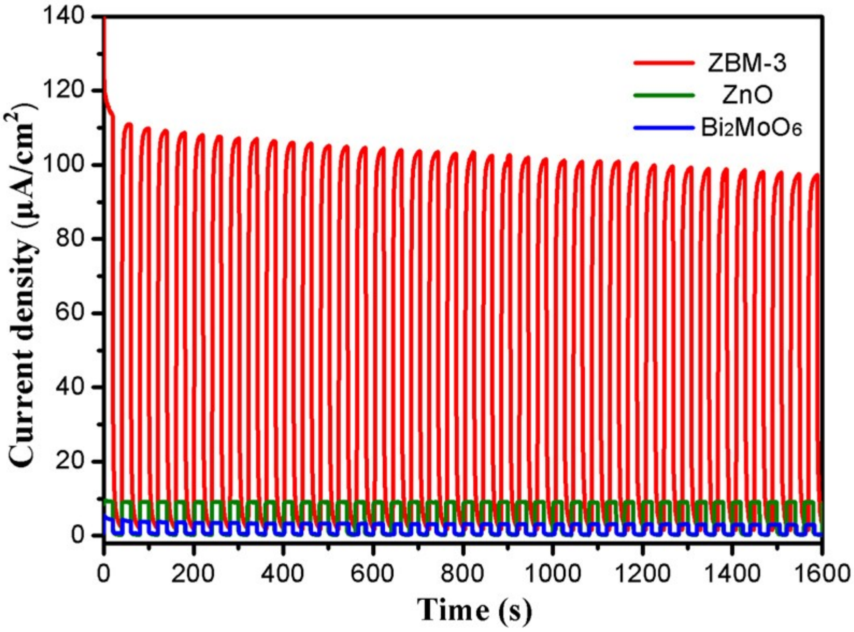

Fig. S8 Working lifetime of ZnO nanowire arrays, pure Bi_2MoO_6 and ZBM-3 (Bi_2MoO_6/ZnO hetero-structure) under chopped visible light illumination.

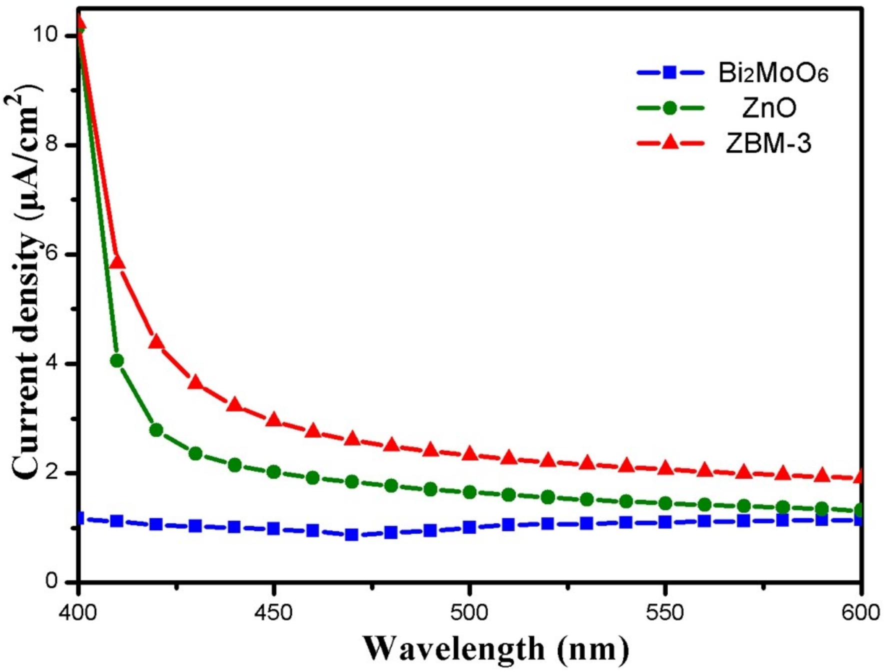

Fig. S9. Photoelectric conversion performances of ZnO nanowire arrays, pure Bi_2MoO_6 and Bi_2MoO_6/ZnO hetero-structure (ZBM-3) under a certain monochromatic light.

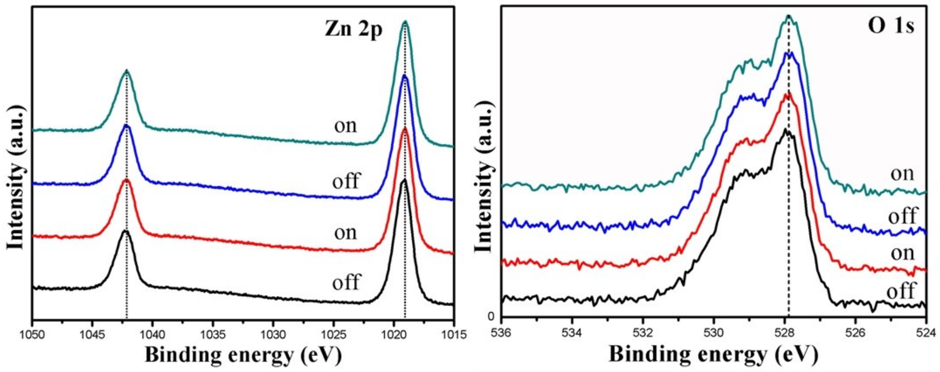

Fig. S10 In-situ Zn 2p and O 1s XPS spectra of ZnO nanowire arrays under visible light with on/off cycles.

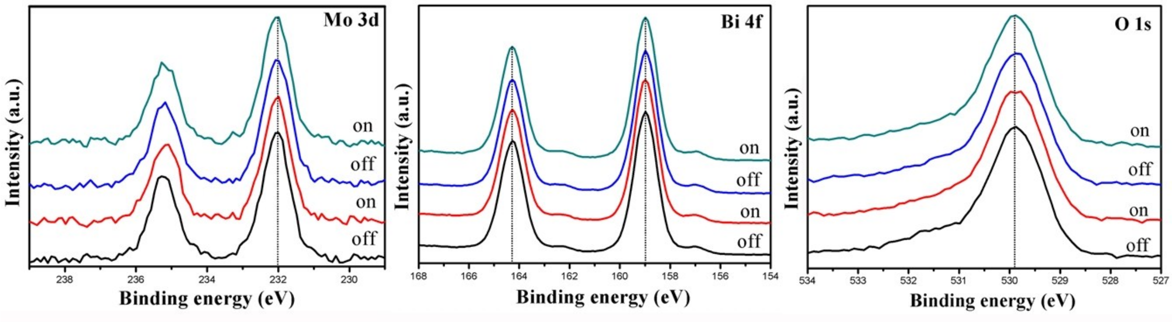

Fig. S11 In-situ Mo 3d, Bi 4f and O 1s XPS spectra of pure Bi_2MoO_6 under visible light with on/off cycles.

The possible mechanism for *in-situ* XPS

The XPS characterization is generally utilized to analyze the chemical binding states, which related with electron density changes of each element in the compound. However, in the case of semiconductor samples, except for routine XPS measurements for the chemical binding states is the same as other material systems, the light irradiation could further induce the peak shifts of binding energy of various elements due to the electron transfer from the valence band (VB) to the conduction band (CB) and holes leave behind on the valence band. More specifically, the valence band and conduction band of semiconductors were composed of spin-orbits of various elements. Thereby, the charge transfer and electron density changes among various elements could be well and truly detected by XPS spectra. In contrast, when light irradiation was turned off, the excited electron on the conduction band will come back to the valence band and recombined with holes, and all the binding energy peaks of various elements will shift to their original positions. Therefore, this in-situ XPS technique could truly reflect the charge transfer and electron density changes of various elements in the semiconductors under light irradiation.