Electronic Supplementary Information

Fabricating Highly Efficient Heterostructured CuBi₂O₄ Photocathode for Unbiased Water Splitting

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Chemicals

Bismuth (III) nitrate pentahydrate (Bi(NO₃)₃.5H₂O), potassium iodide (KI), pbenzoquinone, copper (II) acetate hydrate (Cu(CH₃COO)₂. H₂O), nitric acid were purchased from Sigma Aldrich. All reagents used in this experiment were analytical grade without further purification. Conductive fluorine doped tin oxide (FTO, 10×40 \times 2.3 mm, 15 Ω sq⁻¹, Nippon Glass) glass substrates were used for all working electrodes. Milli-Q water (18.2 M Ω) was used throughout the experiment. Acetone, ethanol, and milli-Q water were used to ultrasonically wash the FTO glass substrates and then dried with nitrogen gas.

Synthesis of CuO photocathode

To understand the contribution of CuO layer on the CuBi₂O₄/CuO heterojunction photocathode, pure CuO photocathode was synthesized using electrodeposition in a three-electrode configuration system with FTO as working electrode, a Pt wire as counter electrode, and KCl saturated Ag/AgCl electrode as reference electrode. The FTO substrates were immersed in 50 ml of aqueous 0.2 M Cu(CH₃COO)₂• H₂O and the electrodeposition reaction was carried out for 300 s at a constant potential of -0.3 V vs Ag/AgCl at room temperature. The films were then annealed at 450 °C (ramping rate 2 °C min⁻¹) in air for 3 h to form CuO photocathode.

Synthesis of BiVO₄ and CoPi/BiVO₄

To prepare BiVO₄ photoanode, the as prepared BiOI electrodes were placed in 100 °C oven and a solution of dimethyl sulfoxide (DMSO) containing 0.2 M vanadyl acetylacetonate (VO(acac)₂) was placed on BiOI electrode. When the solution dried, the electrodes were moved to muffle furnace and calcined at 450 °C (ramping rate 2 °C min⁻¹) in air for 3 h to form BiVO₄. Afterwards, the electrodes were soaked in 1 M NaOH to

remove excess V_2O_5 and washed with milli-Q water.¹ Cobalt phosphate (CoPi) cocatalyst was deposited by photo-assisted electrodeposition method following the previously reported method.²

Calculation for molar ratio of CuO in heterojunction CuBi₂O₄/CuO photocathodes

From ICP-OES measurement, mass concentration of Bi is 84.6 mg L^{-1}

Molar concentration of $Bi = \frac{84.6 \text{ mg } L^{-1}}{208.98 \text{ g mol}^{-1}} = 0.405 \text{ mmol } L^{-1}$

Molar concentration of $CuBi_2O_4 = 0.5 * 0.405 \text{ mmol } L^{-1} = 0.203 \text{ mmol } L^{-1}$

From ICP-OES measurement, mass concentration of Cu is 24.4 mg L^{-1}

Molar concentration of $Cu = \frac{24.4 \text{ mg } L^{-1}}{63.546 \text{ g mol}^{-1}} = 0.384 \text{ mmol } L^{-1}$

Molar concentration of CuO = (0.384 - 0.203)*mmol* $L^{-1} = 0.182$ *mmol* L^{-1}

Molar ratio of CuO (%) =
$$\frac{0.182 \text{ mmol } L^{-1}}{(0.182 + 0.203) \text{ mmol } L^{-1}} * 100\% = 47.2\%$$

Tauc Plot

Tauc plot has been utilized to derive the direct bandgap of the photocathodes. For the tauc plot, the y-axis is $(\alpha hv)^2$ where hv can be attained simply by using $hv = 1240/\lambda$ (nm). The absorption coefficient (α) can be obtained from the UV-Vis spectrometer while measuring the absorbance of the films. The spectrometer use following equation to originate the value of α .³

For absorbance, $\alpha = 2.303 A/t$

where A is the absorbance and t is the thickness of the film.

IPCE measurement

It was obtained using an Oriel Cornerstone 260 1/4 m monochromators with a 300 W Oriel Xenon lamp as the simulated light source. The power density at a specific wavelength was measured by a Newport 1918-c power meter. The IPCE can be calculated according to following equation.

$$IPCE (\%) = \frac{j (mA cm^{-2}) * 1239.8 (V.nm)}{\lambda (nm) * I (mW cm^{-2})} * 100_{\%}$$

j is the photocurrent density (mA cm⁻²) measured from the electrochemical workstation, λ refers to the incident light wavelength (nm), and I is the light density measured at a specific wavelength (mW cm⁻²).

Computational details

The density functional theory (DFT) calculations were performed by Vienna Ab Initio Simulation Package (VASP).⁴⁻⁶ The interactions between electrons and ions was described by the projector augmented-wave (PAW) method.⁷ The Perdew–Burke–Ernzerhof (PBE) functional of the generalized gradient approximation (GGA)^{8, 9} was applied to treat the exchange-correlation interactions of valence electrons. The GGA+U correction by Dudarev's approach on Cu atom (U-J= 6.5eV) was adopted to give a more accurate description of the strongly localized d-orbitals.^{10, 11} The plane wave cut-off energy was set to 400 eV and a Gamma centered $3\times4\times1$ k-points grid was applied. The structures were fully relaxed until the max residual forces and the energy of the whole systems were converged to 0.005 eV/Å and 1×10^{-6} eV respectively. The vacuum layer of 20 angstroms was applied to avoid interaction between the adjacent layers. The

workfunction (Φ) is calculated by $\Phi=E_{vac}-E_{f}$ where E_{vac} and E_{f} represent the vacuum level and fermi level respectively.



Figure S1. XRD patterns of BiOI template and BiOI template with loaded Cu precursor.



Figure S2. Loading varying amount of Cu precursor on BiOI through electrodeposition.



Figure S3. The photograph images of (a) the front, (b) the backside of as-prepared $CuBi_2O_4/Bi_2O_3$ electrode and (c) the image of peeled electrode. (d) The XRD patterns of $CuBi_2O_4/Bi_2O_3$ (orange) and the peeled electrode (black).



Figure S4. The cross-sectional view SEM images of (a) BiOI, (b) BiOI with Cu precursor, (c,e) pure $CuBi_2O_4$ and (d,f) $CuBi_2O_4/CuO$ electrode.



Figure S5. The original SEM images of (a) pure CuBi₂O₄ and (b) CuBi₂O₄/CuO electrode.



Figure S6. The light absorption spectra of pure $CuBi_2O_4$ (black) and $CuBi_2O_4$ /CuO (red) electrode.



Figure S7. UPS spectrum of pure (a) $CuBi_2O_4$ and (b) CuO photocathodes. The light source is He I (21.2 eV). And the spectrum is calibrated with the UPS of Au.



Figure S8. The magnified LSV curves of pure $CuBi_2O_4$ (black) and $CuBi_2O_4/CuO$ (red) photocathodes at potential ranging from 1.0 to 1.3 V_{SHE} .



Figure S9. The photocurrent of CuO photocathodes (Cu precursor electrodeposited for 300 s).



Figure S10. *i-t* curve of anodization treatment.



Figure S11. Stability of $CuBi_2O_4/CuO$ photocathode under AM 1.5 G, 100 mW cm⁻² illumination in 0.1 M NaOH electrolyte with 1 % H₂O₂.



Figure S12. IPCE of pure $CuBi_2O_4$ (black), pure CuO (green) and $CuBi_2O_4/CuO$ (red) photocathodes at the potential of 0.56 V_{SHE} .

Table S1. Summary on the performance of $CuBi_2O_4$ photocathodes for HER.

NO. (SHOWN IN FIGURE 3B)	ELECTROLYTE (PH)	ELECTRODE	PHOTOCURRENT [MA CM ⁻²] (POTENTIAL [V VS RHE])	ONSET POTENTIAL [V VS RHE]	REF.
THIS WORK	0.1 M NaOH (pH 13)	CuBi ₂ O ₄ CuBi ₂ O ₄ /CuO	1.1 (0.5) 2.6 (0.5)	1.16 1.12	
1	$0.3 \text{ M K}_2\text{SO}_4$ with 0.2M phosphate buffer (pH 6.65)	CuBi ₂ O ₄ /CdS/TiO ₂ /Pt CuBi ₂ O ₄	1.0 (0.0) 2.5 (0.6) with H ₂ O ₂	~0.6	12
2	0.3 M K ₂ SO ₄ with 0.2M phosphate buffer (pH 6.65) 0.1 M KOH	$\begin{array}{c} CuBi_2O_4\\ CuBi_2O_4\\ CuBi_2O_4\end{array}$	0.3 (0.6) 2.0 (0.6) with H ₂ O ₂ 1.6 (0.6) with O ₂ electron scavenger	0.8 ~1.0	13
3	$0.3 \text{ M K}_2\text{SO}_4$ with 0.2M phosphate buffer (pH 6.65)	FTO/Cu:NiO/ CuBi ₂ O ₄	0.5 (0.6) 2.83 (0.6) with H ₂ O ₂	~0.9 ~1.1	14
4	0.1 M Na ₂ SO ₄ (pH=6.8)	FTO/ CuBi ₂ O ₄ FTO/Au/ CuBi ₂ O ₄ FTO/Au/ CuBi ₂ O ₄ /Pt	0.23 (0.1) 0.50 (0.1 1.2 (0.1)	~1.1 ~ 1.1 1.0	15
5	0.1 M Na ₂ SO ₄ (pH 6.8) 1 M NaOH (13.6)	Plain CuBi ₂ O ₄ Textured CuBi ₂ O ₄ Textured CuBi ₂ O ₄ Nanotextured CuBi ₂ O ₄	0.1 (0.0) above 0.7 (0.0) 2.0 (0.0) with H ₂ O ₂ 1.77 (0.4)	~ 0.7 1.0	16
6	0.132 M KOH and 0.05M KCl (pH 13)	CuBi ₂ O ₄ -O CuBi ₂ O ₄ -S CuBi ₂ O ₄ -S/TiO ₂	0.45 (0.25) 0.67 (0.25) 0.82 (0.25)	1.1	17
7	0.1 M Na ₂ SO ₄ (pH 10.8)	$CuBi_2O_4$ front $CuBi_2O_4$ Back	0.044 (0.64) 0.055 (0.64)	~ 1.1 ~ 1.1	18

8	0.2 M K ₂ HPO ₄ with 0.3 M K ₂ SO ₄ (pH =6.65)	$\begin{array}{c} CuBi_2O_4/Pt\\ CuBi_2O_4 \end{array}$	Up to 0.5 (0.4) 1.26 (0.5) with H ₂ O ₂	~ 1.0	19
9	0.1 M NaOH (pH 12.8)	CuBi ₂ O ₄ /Ag- CuBi ₂ O ₄ CuBi ₂ O ₄ /Ag- CuBi ₂ O ₄ /Pt	0.46 (0.6) 0.6 (0.6)	1.1	20

Photocathodes	$R_s(\Omega)$	$R_{bulk}(\Omega)$	$R_{ct}(\Omega)$
CuBi ₂ O ₄	74.61	6124	1331
CuBi ₂ O ₄ /CuO	64.72	1710	795.4
Anodized	63.27	1830	227.1
CuBi ₂ O ₄ /CuO			

Table S2: Resistances of $CuBi_2O_4$ and $CuBi_2O_4/CuO$ photocathodes measured by EIS shown in Figure 4b.

References

- 1. T. W. Kim, K. S. Choi, Science 2014, 343, 990.
- Z. Wang, Y. Qi, C. Ding, D. Fan, G. Liu, Y. Zhao and C. Li, *Chem. Sci.*, 2016, 7, 4391-4399.
- 3. S. M. Sze and K. K. Ng, Physics of semiconductor devices, John wiley & sons, 2006.
- 4. G. Kresse and J. Furthmüller, Comput. Mater. Sci., 1996, 6, 15-50.
- 5. G. Kresse and J. Furthmüller, Phys. Rev. B, 1996, 54, 11169.
- 6. G. Kresse and J. Hafner, Phys. Rev. B, 1994, 49, 14251.
- 7. G. Kresse and D. Joubert, Phys. Rev. B, 1999, 59, 1758.
- 8. J. P. Perdew, M. Ernzerhof and K. Burke, J. Chem. Phys., 1996, 105, 9982-9985.
- 9. J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865.
- 10. M. Cococcioni and S. De Gironcoli, Phys. Rev. B, 2005, 71, 035105.
- S. Dudarev, G. Botton, S. Savrasov, C. Humphreys and A. Sutton, *Phys. Rev. B*, 1998, 57, 1505.
- F. Wang, W. Septina, A. Chemseddine, F. F. Abdi, D. Friedrich, P. Bogdanoff, R. van de Krol, S. D. Tilley and S. P. Berglund, *J. Am. Chem. Soc.*, 2017, 139, 15094-15103.
- F. Wang, A. Chemseddine, F. F. Abdi, R. van de Krol and S. P. Berglund, *J. Mater. Chem. A*, 2017, 5, 12838-12847.
- 14. A. Song, P. Plate, A. Chemseddine, F. Wang, F. F. Abdi, M. Wollgarten, R. van de Krol and S. P. Berglund, J. Mater. Chem. A, 2019, 7, 9183-9194.
- 15. D. Cao, N. Nasori, Z. Wang, Y. Mi, L. Wen, Y. Yang, S. Qu, Z. Wang and Y. Lei, J. Mater. Chem. A, 2016, 4, 8995-9001.
- 16. J. Li, M. H. Griep, Y. Choi and D. Chu, Chem. Commun., 2018.
- J. Yang, C. Du, Y. Wen, Z. Zhang, K. Cho, R. Chen and B. Shan, *Int. J. Hydrog. Energy*, 2018, 43, 9549-9557.
- N. T. Hahn, V. C. Holmberg, B. A. Korgel and C. B. Mullins, *J. Phys. Chem. C*, 2012, **116**, 6459-6466.
- S. P. Berglund, F. F. Abdi, P. Bogdanoff, A. Chemseddine, D. Friedrich and R. van de Krol, *Chem. Mater.*, 2016, 28, 4231-4242.
- 20. D. Kang, J. C. Hill, Y. Park and K.-S. Choi, Chem. Mater., 2016, 28, 4331-4340.