# Supporting Information

# Photoelectrochemical overall water splitting with textured $CuBi_2O_4$ as photocathode

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# Experimental

## Fabrication of textured CuBi<sub>2</sub>O<sub>4</sub> photocathode

The fabrication of  $\text{CuBi}_2\text{O}_4$  film was carried out with a drop-casting protocol with some modifications. <sup>S1</sup> The precursor solution was prepared by dissolving 0.243g of Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and 0.058g of Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O in 10mL of ethanol and 2.5mL of acetic acid. *This precursor solution is stable for few hours and starts to decompose to produce white precipitations since Bi(NO<sub>3</sub>)<sub>3</sub> is very sensitive and easy to hydrolyze with water to form bismuth subnitrates. So the precursor solution was freshly prepared for each experiment. The resultant solution was dropped on precleaned FTO substrate (2cm × 2.5cm) with a dose of 20\mu\text{L/cm}^2. Then, the substrates were placed flat in a vacuum oven at 40°C to evaporate the solvent under vacuum. Finally, the as-prepared film was annealed in air at 550°C for 4 hours with a ramp rate of 10 °C /min to yield CuBi<sub>2</sub>O<sub>4</sub> film. For comparison, the plain CuBi<sub>2</sub>O<sub>4</sub> film was also prepared under ambient conditions while keeping all other parameters identical.* 

## Fabrication of photoanode TiO<sub>2</sub> nanorod array

 $TiO_2$  nanorod array photoanode was prepared following our previous paper.<sup>S2</sup> Typically, titanium butoxide was dissolved in 6M HCl aqueous solution to a very clear precursor solution. After that, the as-resultant solution was transferred into Teflon-lined autoclave, where pre-cleaned FTO substrates were vertically aligned on the bottom with a holder. The autoclave was sealed and kept at 150°C for 6 hours, and then cooled down to room temperature. The obtained TiO<sub>2</sub> nanorod array on FTO substrates was washed with DI water and annealed in air at 450°C for 2 hours.

### **Characterizations**

Scanning electronic microscopy (SEM, Zeiss Auriga 60 Field Emission Scanning Microscope) was used to observe the surface morphology and side cross-section of all  $CuBi_2O_4$  photocathode films. X-ray diffraction (XRD, Rigaku Flex600) was to identify the crystallinity and the microstructure of  $CuBi_2O_4$  photocathodes. The light absorption and transmission were recorded on an UV-VIS spectrometer (Beckman DU 800) through a transmission model.

### **Photoelectrochemical performances**

Photoelectrochemical performances were tested on a Gamry Potentiostat Reference 3000 in a onecomponent three-electrode cell, including CuBi<sub>2</sub>O<sub>4</sub> as the working electrode, Pt as the counter electrode and Ag/AgCl as the reference electrode. 0.1M Na<sub>2</sub>SO<sub>4</sub> aqueous solution (pH 6.8) was used as the electrolyte in the regular testing. O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> were used as the electron scavengers by purging highly pure O<sub>2</sub> for 30mins before testing or by adding appropriate amount of H<sub>2</sub>O<sub>2</sub> in 50mL of 0.1M Na<sub>2</sub>SO<sub>4</sub> aqueous electrolyte. Unless otherwise noted, the electrolyte used in photoelectrochemical testing is the 0.1M Na<sub>2</sub>SO<sub>4</sub> aqueous solution. The linear sweep voltammetry curve was recorded with scan starting from 0.3V to -0.6V vs Ag/AgCl in different electrolytes. The Mott-Schottky plots were acquired with the corresponding program at the frequency of 5k Hz within the potential range  $0 \sim 0.3 V vs$  RHE in 0.1M Na<sub>2</sub>SO<sub>4</sub> aqueous electrolyte. EIS impedance was recorded at -0.6V vs Ag/AgCl, and the Nyquist plots were fitted with Software Zview 2@Scribner. 300W Xe lamp with a AM 1.5G filter (NewPort 67005) was used as the light source for all the photoresponses. The transient photocurrent was recorded with the chopped light illumination controlled with a Shutter (Newport 71445), and the time constant  $\tau$  was defined with the following empirical protocol.<sup>S3</sup>

$$D = \frac{I_t - I_{Steady}}{I_{Initial} - I_{steady}}$$

Where the  $I_t$  is the photocurrent vs time,  $I_{\text{Steady}}$  is the photocurrent after reaching the steady state, and  $I_{\text{Initial}}$  is the initial spike photocurrent when the light is on. The time constant  $\tau$  was determined when  $\ln D = -1$ .

The measured potentials *vs* Ag/AgCl were converted to the reverse hydrogen electrode (*RHE*) according to the following equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.059pH + E_{Ag/AgCl}^{0}$$

Where  $E_{\text{RHE}}$  is the RHE potential,  $E_{Ag/AgCl}=0.1976$  V at 25°C,  $E_{Ag/AgCl}$  is the measured potentials against the Ag/AgCl reference electrode.

IPCE was measured by the same light source coupled with a monochromator (Oriel Cornerstone 130, 1/8cm). IPCE can be calculated as the equation,

$$IPCE = \frac{1240J}{\lambda I_{\lambda}}$$

Where *J* is the photocurrent density (mA/cm<sup>2</sup>),  $\lambda$  is the wavelength of the incident light (nm) and  $I_{\lambda}$  is the incident light power density (W/m<sup>2</sup>).

#### Construction of photoelectrochemical p/n tandem cell

The photoelectrochemical p/n tandem cell was constructed with the bare nanotextured  $CuBi_2O_4$  photocathode and the as-prepared  $TiO_2$  nanorod array photoanode. *Note: No co-catalysts were deposited on both photoelectrodes in the tandem cell testing*. As shown in **Fig. S13f**, these two photoelectrodes were easily contacted with copper wire that was fastened to FTO with silver paste and sealed outside with epoxy. This resultant tandem cell was immersed in electrolyte (1M NaOH) in the container with a quartz window. The light source is the same as that for photoelectrochemical testing.



**Figure S1**. SEM topview images for textured  $\text{CuBi}_2\text{O}_4$  (*a*, *b*) and plain  $\text{CuBi}_2\text{O}_4$  (*c*,*d*), respectively. The inset in *b* shows the schematic illustration of array-like textured  $\text{CuBi}_2\text{O}_4$  nanostructures on FTO substrate.

#### Preliminary mechanism for the formation of textured array structure

The formation of array-like architecture photocathode is highly sensitive to the environmental but under control. In our detailed study, both vacuum and moisture determine the geometry and morphology of the obtained CuBi<sub>2</sub>O<sub>4</sub> photocathodes. It is believed to be a hydrolysis process of Bi<sup>3+</sup> species with the following reactions: <sup>\$4,\$5</sup>

$$Bi(NO_3)_3(s) \rightarrow Bi^{3+} + 3NO_3^{-}$$
  
$$Bi^{3+} + NO_3^{-} + 2H_2O \leftrightarrow Bi(OH)_2NO_3(s) + 2H^{+}$$

With the proper control over the moisture (water standing by the substrates in the vacuum oven), the textured structure could be easily formed as a uniform and obscure film (*a in Fig. S2*). Without the presence of moisture (the vacuum pre-running for 2 hours to remove the moisture, then put the substrates and immediately run the vacuum program), the solvents could evaporate quickly before the hydrolysis of Bi(NO<sub>3</sub>)<sub>3</sub> started, which leads to the formation of a transparent gel film (*b in Fig. S2*), and finally very dense and transparent CuBi<sub>2</sub>O<sub>4</sub> film (SEM image *b3 in Fig. S2*) after annealing. Without vacuum and under ambient conditions, similarly dense film formed as shown in Figure S1. Analog cases were reported in literature for different materials under vacuum, but no mechanisms were proposed so far.<sup>S6</sup> It is supposed that the quick evaporation of the solvent under vacuum may help initiate the formation of textured film structures.



**Figure S2**. Digital pictures and SEM image for textured film (*a*) and dense non-textured film (*b*). *a1* and *b1* show the precursor films, and *a2* and *b2* CuBi<sub>2</sub>O<sub>4</sub> films after annealing and *b3* the SEM image for dense non-textured film.



**Figure S3**. The three-electrode photoelectrochemical cell using  $CuBi_2O_4$  as the photocathode for water splitting. The inset shows the band bending and charge transfer directions of *p*-type semicondcutor electrode in electrolyte, where the photogenerated electrons diffuse to the electrode/electrolyte interface whearas holes transfer to counter electrode through F-doped SnO<sub>2</sub> substrate and external circuit.



**Figure S4**. (*a*) Mott-Schottky plots for textured  $CuBi_2O_4$  photocathode at a frequency of 5K. And (*b*) shows the proposed band positions compared to the red-ox potentials of the water.



Figure S5. Transient photocurrent decay curves (light on/off) at (*a*) -0.4V vs Ag/AgCl when comparing the textured CuBi<sub>2</sub>O<sub>4</sub> and the plain CuBi<sub>2</sub>O<sub>4</sub>. (*b*) corresponds to the time constant curves (**In***D* vs Time). Here  $D = \frac{l - l_{steady}}{l_{standy}}$ 

the time constant  $\tau$  is determined as the time when  $\ln D = -1$ , where  $D = \frac{1}{I_{Initial} - I_{steady}}$ , *I* is the photocurrent *vs* time, *I*<sub>Initial</sub> is the spike photocurrent when light is on, and *I*<sub>steady</sub> is the steady photocurrent.



**Figure S6**. Investigations of electron scavengers' effects in the electrolyts on the photoelectrochemical performance of CuBi<sub>2</sub>O<sub>4</sub> photocathode. (*a*) Linear sweep voltammetry curves and (*b*) transient photocurrents by adding  $H_2O_2$  as scavenger with different doses from 0 to 2mL in 50mL of electrolyte (0.1M Na<sub>2</sub>SO<sub>4</sub>). (*c-f*) show the linear sweep voltammetry curves (*c*), transient photocurrents (*d*), normalized transient photocurrents (*e*) and the corresponding time constant parameter  $\ln D$  curves (*f*) when purging saturated O<sub>2</sub> in the electrolyte.



Figure S7. Impedance spectra comparing plain and textured  $\text{CuBi}_2\text{O}_4$  photocathodes at -0.6V vs Ag/AgCl (a). b represents the equivalent circuit in the photocathode system used for fitting the impedence spectra. Table S1 shows the fitting data using the equivalent circuit in b. The fitting was carried out with the software Zview 2@Scribner.



**Figure S8.** Cyclic voltammograms for plain and textured  $CuBi_2O_4$  photocathodes. Experiments were measured in 0.1M Na<sub>2</sub>SO<sub>4</sub> aqueous solution within a potential range (-0.15V ~ -0.05V vs Ag/AgCl) where no faradaic processes occur. The surface areas were estimated with integration to be 2.71×10<sup>-4</sup> for textured  $CuBi_2O_4$  and  $4.36\times10^{-5}$  for plain  $CuBi_2O_4$ , respectively. There is thus an around 6-time increase in the surface area for textured  $CuBi_2O_4$ , which is one contributor to the overall improvement.



Figure S9. XRD patterns for Plain and Textured CuBi<sub>2</sub>O<sub>4</sub> photocathodes.



**Figure S10.** IPCE spectra (*a*) and transmission spectra (*b*) for both textured and plain  $CuBi_2O_4$  photocathodes. Panel *c* shows the light scattering in textured  $CuBi_2O_4$  photocathode which increases the propagating length of the light and thus the light absorption capability.

CBO	Photocurrent @	Electrolyte	Light Source	Preparation	References	
Photocathode	Potential (mA/cm <sup>2</sup> )			Technique		
CBO/Pt	0.15@ 0V NHE	0.3M K <sub>2</sub> SO <sub>4</sub> pH 6.8	>420nm	Drop-casting	S7	
CuO/CBO/Pt	0.7 @ 0 V NHE	0.3M K <sub>2</sub> SO <sub>4</sub> pH 6.8	>420nm	Drop-casting	S7	
FTO/CBO	-0.23 @ 0.1V vs RHE	0.1 M Na <sub>2</sub> SO <sub>4</sub> pH 6.8	AM1.5G Simulator	Cathodically electrochemical deposition	S8	
FTO/Au/CBO	-0.5 @ 0.1V vs RHE	0.1 M Na <sub>2</sub> SO <sub>4</sub> pH 6.8	AM1.5G Simulator	Cathodically electrochemical deposition	S8	
FTO/Au/CBO/Pt	-1.24 @ 0.1V vs RHE	0.1 M Na <sub>2</sub> SO <sub>4</sub> pH 6.8	AM1.5G Simulator	Cathodically electrochemical deposition	S8	
CBO/Pt	0.8 @0.6 V RHE	0.1 M NaOH (pH 12.8) saturated with O <sub>2</sub>	AM1.5G Simulator	Electrodeposition	S9	
Ag-CBO/Pt	1.0@0.6 V RHE	0.1 M NaOH (pH 12.8) saturated with O <sub>2</sub>	AM1.5G Simulator	Electrodeposition	S9	
СВО	0.3@0.6 V RHE	0.3 M K <sub>2</sub> SO <sub>4</sub> and 0.2 M phosphate buffer	AM1.5G Simulator	Spray pyrolysis	S10	
СВО	2.0 @0.6 V RHE	$0.3 \text{ M K}_2\text{SO}_4$ and $0.2 \text{ M phosphate}$ buffer, with $\text{H}_2\text{O}_2$	AM1.5G Simulator	Spray pyrolysis	S10	
СВО	0.02 @ -0.25V vs Ag/AgCl	0.3 M Na <sub>2</sub> SO <sub>4</sub>	100 mW/cm <sup>2</sup>	Hydrothermal	S11	
CBO/Pt	0.5 @ 0.4 V RHE	0.3 M K <sub>2</sub> SO <sub>4</sub> and 0.2 M phosphate buffer	AM1.5G Simulator	Drop-casting	S12	
СВО	0.07@ 0.6V vs RHE	0.1 M Na <sub>2</sub> SO <sub>4</sub> adjusted pH 10.8	Xe lamp, >420nm	Electrochemical Synthesis	S13	
СВО	0.05 @ -0.4V vs Ag/AgCl	0.1 M Na <sub>2</sub> SO <sub>4</sub> pH 6.8	Xe lamp, 400 W	Spray-coating	S14	
CBO/CuO	0.28 @ -0.4V vs Ag/AgCl	0.1 M Na <sub>2</sub> SO <sub>4</sub> pH 6.8	Xe lamp, 400 W	Spray-coating	S14	
СВО	0.03 @ -0.4V vs Ag/AgCl	0.1 M Na <sub>2</sub> SO <sub>4</sub> pH 6.8	500W Xe lamp,>420nm filter	Electrodeposition	S15	
СВО	0.12@ -0.3V vs Ag/AgCl	0.5 M Na <sub>2</sub> SO <sub>4</sub>	AM 1.5, 100 mWcm <sup>-2</sup>	Flux-mediated one- pot solution process	S16	
Gradient CBO	1.0 @ 0V vs RHE   2.5 @ 0.6V vs   RHE (With H <sub>2</sub> O <sub>2</sub> )	0.3 M $K_2SO_4$ and 0.2 M phosphate buffer ( $H_2O_2$ )	AM1.5G Simulator	Spray pyrolysis	S17	
Textured CBO	0.72 @ -0.6V vs Ag/AgCl	0.1 M Na <sub>2</sub> SO <sub>4</sub> pH 6.8	AM1.5G Simulator	Vacuum Drop- casting	This work	
Textured CBO	1.77 @ 0.4V vs RHE	1 M NaOH pH 13.6	AM1.5G Simulator	Vacuum Drop- casting	This work	
Note. Some photocurrent values were roughly read from LSV curves in the corresponding literature.						

Table S2. Summar	y for the recently	published C	CuBi <sub>2</sub> O <sub>4</sub> photo	ocathodes for s	solar fuel generation.
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**Figure S11**. Linear sweep voltammetry curve for bare nanotextured  $\text{CuBi}_2\text{O}_4$  photocathode in 1M NaOH aqueous solution as electrolyte. The inset shows the enlarged potential area 0.7-1.0V vs RHE, indicating that photoresponse could be detected up to at least 1.0V vs RHE. Such  $\text{CuBi}_2\text{O}_4$  photocathode demosntrates strong activity even in this basic electrolyte, and significant photocurrent of 1.77 mA/cm<sup>2</sup> at 0.4V vs RHE, 1.55 mA/cm<sup>2</sup> at 0.5V vs RHE, and 0.75 mA/cm<sup>2</sup> at 0.6V vs RHE, respectively. These large photocurrents at positive potentials enable this kind of photocathodes to couple with most of the regular n-type semicondcutor photoanodes for assembling p/n photoelectrochemical tandem cell.



**Figure S12**. Two-electrode photoelectrochemical testing. (*a*) Linear sweep voltammetry curves for  $TiO_2$  nanorod photoanode or  $CuBi_2O_4$  photocathode, respectively. (*b*,*c*) The chronoamperometry spectra for  $CuBi_2O_4$  photocathode with periodic chopped light for 5mins and 20mins. The insert in c shows the picture for  $CuBi_2O_4$  photocathode after 20mins testing. (*d*) The chronoamperometry spectrum for  $TiO_2$  photoanode with periodic chopped light for 5mins and 20mins.

Two-electrode configuration was performed with the photoelectrode (TiO<sub>2</sub> nanorod photoanode or CuBi<sub>2</sub>O<sub>4</sub> photocathode) as the working electrode and Pt wire as the reference electrode. Twoelectrode PEC measurement enables more accurate probe on the internal photovoltage generated in photoelectrode.<sup>S12</sup> As regularly, small photocurrents display compared to the three-electrode configuration (Fig. S12a). Apparently, the linear sweep voltammetry curves overlapped for CuBi<sub>2</sub>O<sub>4</sub> photocathode and TiO<sub>2</sub> photoanode with joint point at a voltage of around 0.5V and a photocurrent of 0.5mA/cm<sup>2</sup>. This phenomenon is consistent with three-electrode configuration and means the photoelectrochemical tandem cell containing CuBi<sub>2</sub>O<sub>4</sub> photocathode and TiO<sub>2</sub> photoanode is able to split water without any external bias. The chronoamperometry was performed thus at the joint potential 0.5V. Through the illumination by the chopped light, photocurrents for both photoanode and photocathode degrade from a transient spike to a steady value around  $0.2\text{mA/cm}^2$  (Fig. S12c &d). This transient photocurrent degrading is reversible with the light on/off, which means this kind of photocathode is relatively stable in two-electrode PEC measurements. Even after 20min running (Fig. S12c), no color change occurs for CuBi<sub>2</sub>O<sub>4</sub> photocathode as shown as the inset in Fig. S12c. This explains why the PEC tandem cell shows high joint photocurrents in both three- and two-electrode configurations but demonstrates slow bubble generation rate in the video. One of the reason is the sluggish OER and HER reactions without co-catalysts on the surfaces. This study demonstrates the feasibility for the unbiased water splitting using CuBi<sub>2</sub>O<sub>4</sub> based photoelectrochemical tandem cell, however, further investigations with surface engineering and co-catalysts optimization are in high demand.



**Figure S13**. Construction of the photoelectrochemical p/n tandem cell. (*a*) Schematic illustration of the photoelectrochemical tandem cell. (*b*) Schematic photocurrent curves generated for photoanode and photocathode, separatedly. (*c*) The schematic configuration we used in this paper for p/n tandem cell. (*d* & *e*) SEM images for CuBi<sub>2</sub>O<sub>4</sub> photocathode and TiO<sub>2</sub> photoabode. (*f*) the real photoelectrochemical tandem cell starts to generate hydrogen and oxygen bubbles on both electrode upon the light illumination. *Note: No hydrogen evolution and oxygen evolution co-catalysts were used on either photocathode or photoanode.* 

#### **References**

S1. S. Berglund, F. Abdi, P. Bogdanoff, A. Chemseddine, D. Friedrich, R. van de Krol. Comprehensive Evaluation of  $CuBi_2O_4$  as a Photocathode Material for Photoelectrochemical Water Splitting. *Chem. Mater.*, **2016**, *28*, 4231-4242.

S2. J. Li, S. K. Cushing, P. Zheng, T. Senty, F. Meng, A. D. Bristow, A. Manivannan, N. Wu. Solar Hydrogen Generation by a CdS-Au-TiO<sub>2</sub> Sandwich Nanorod Array Enhanced with Au Nanoparticle as Electron Relay and Plasmonic Photosensitizer. *J. Am. Chem. Soc.*, **2014**, *136*, 8438-8449.

S3. J. Li, S. Cushing, P. Zheng, F. Meng, D. Chu, N. Wu. Plasmon-induced photonic and energy transfer enhancement of solar water splitting by a hematite nanorod array. *Nature Communications*, **2013**, *4*, doi:10.1038/ncomms3651.

S4. L. Miersch, T. Rueffer, M. Schlesinger, H. Lang, M. Mehring. Hydrolysis studies on Bismuth Nitrate: synthesis and crystallization of four novel polynuclear basic bismuth nitrates. *Inorganic Chemistry*, **2012**, 51, 9376-9384.

S5. L. Miersch, M. Schlesinger, R. W. Troff, C. A. Schalley, T. Rueffer, H. Lang, M. Mehring. Hydrolysis of basic Bismuth Nitrate-formation and stability of novel bismuth oxido clusters. *Chem.-Eur. J.*, **2011**, 17, 6985-6990.

S6. R. Hofmockel, U. Zschieschang, U. Kraft, R. Roedel, N. H. Hansen, M. Stolte, F. Wurthner, K. Takimiya, K. Kern, J. Pflaum, H. Klauk. High-mobility organic thin-film transistors based on a small-molecule semicondcutor deposited in vacuum and by solution shearing. *Organic Electronics*, **2013**, 14, 3213-3221.

S7. H. S. Park, C.-Y. Lee and E. Reisner. Photoelectrochemical reduction of aqueous protons with a  $CuO|CuBi_2O_4$  heterojunction under visible light irradiation. *Phys. Chem. Chem. Phys.*, **2014**, 16, 22462-22465.

S8. D. Cao, N. Nasori, Z. Wang, Y. Mi, L. Wen, Y. Yang, S. Qu, Z. Wang and Y. Lei. *p*-type CuBi<sub>2</sub>O<sub>4</sub>: an Easily Accessible Photocathodic Material for High-efficient Water Splitting. *J. Mater. Chem. A.*, **2016**, 4, 8995-9001.

S9. D. Kang, J. C. Hill, Y. Park, and K.-S. Choi. Photoelectrochemical Properties and Photostabilities of High Surface Area CuBi<sub>2</sub>O<sub>4</sub> and Ag-Doped CuBi<sub>2</sub>O<sub>4</sub> Photocathodes. *Chem. Mater.*, **2016**, 28, 4331-4340.

S10. F. Wang, A. Chemseddine, F. F. Abdi, R. van de Krol, S. P. Berglund. Spray pyrolysis of CuBi<sub>2</sub>O<sub>4</sub> photocathodes: improved solution chemistry for highly homogeneous thin films. *J. Mater. Chem. A.*, **2017**, 5, 12838-12847.

S11. L. Zhu, P. Basnet, S. R. Larson, L. P. Jones, J. Y. Howe, R. A. Tripp, and Y. Zhao. Visible Light-Induced Photoeletrochemical and Antimicrobial Properties of Hierarchical  $CuBi_2O_4$  by Facile Hydrothermal Synthesis. *ChemistrySelect* **2016**, *1*, 1518-1524.

S12. S. P. Berglund, F. F. Abdi, P. Bogdanoff, A. Chemseddine, D. Friedrich, and R. van de Krol. Comprehensive Evaluation of  $CuBi_2O_4$  as a Photocathode Material for Photoelectrochemical Water Splitting. *Chem. Mater.* **2016**, 28, 4231-4242.

S13. N. T. Hahn, V. C. Holmberg, B. A. Korgel, and C. Buddie Mullins. Electrochemical Synthesis and Characterization of *p*-CuBi<sub>2</sub>O<sub>4</sub> Thin Film Photocathodes. *J. Phys. Chem. C* **2012**, 116, 6459-6466.

S14. M. K. Hossain, G. F. Samu, K. Gandha, S. Santhanagopalan, J. Ping Liu, C. Janáky, and K. Rajeshwar. Solution Combustion Synthesis, Characterization, and Photocatalytic Activity of  $CuBi_2O_4$  and Its Nanocomposites with CuO and  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub>. *J. Phys. Chem. C* **2017**, 121, 8252-8261.

S15. Y. Nakabayashi, M. Nishikawa, Y. Nosaka. Fabrication of CuBi<sub>2</sub>O<sub>4</sub> photocathode through novel anodic electrodeposition for solar hydrogen production. *Electrochimica Acta*, **2014**, 125, 191-198.

S16. Y.-H. Choi, K. D. Yang, D.-H. Kim, K. T. Nam, S.-H. Hong. *p*-Type CuBi<sub>2</sub>O<sub>4</sub> thin films prepared by flux-mediated one-pot solution process with improved structural and photoelectrochemical characteristics. *Materials Letters*, **2017**, 188, 192-196.

S17. F. Wang, W. Septina, A. Chemseddine, F. F. Abdi, D. Friedrich, P. Bogdanoff, R. van de Krol, S. D. Tilley, and S. P. Berglund. Gradient self-doped  $CuBi_2O_4$  with highly improved charge separation efficiency. *J. Am. Chem. Soc.*, **2017**, 139, 15094-15103.