# Supporting information

## Photoelectrochemical Performance of $CuBi_2O_4$ Photocathode with $H_2O_2$ as Scavenger

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**Materials**

FTO glass substrate (TEC 7), 100mm*100mm*2.2mm, R=6-8ohm/sq, Bismuth(III) nitrate pentahydrate ($Bi(NO_3)_3$. 5H2O, ACS reagent, ≥98.0%), Copper(II) nitrate trihydrate ($Cu(NO_3)_2.3H_2O$, ) acetic acid ($CH_3CO_2H$, ACS reagent, ≥99.7%), and ethanol ($CH_3CH_2OH$, anhydrous, ≥99.5%) was procured from Sigma Aldrich. Deionized water was used to prepare all aqueous solutions. All the reagents were used without any purification process.

**Characterization Equipment**

To analyze the crystallinity of samples X-ray diffraction (XRD) were carried out (Bruker D8Advance). The morphological properties were studied by transmission electron microscopy (TM, JEOL, JEM-2100F) and scanning electron microscope (Quanta 250 FEG) utilized to study the thin film of photocatalysts on the surface of FTO glass. A 785 nm laser was used for Raman characterization by a labRam HR micro-Raman spectrophotometer (Bruker, model: Senteraa 2009, Germany). A Thermo Thermo Scientific Sigma Probe spectrometer detector was utilized to record the X-ray photoelectron spectroscopy data. The bandgap and adsorption of photocatalysts were evaluated by the UV-DRS method (Perkin Elmer UV-Vis-NIR model Lambda 950).

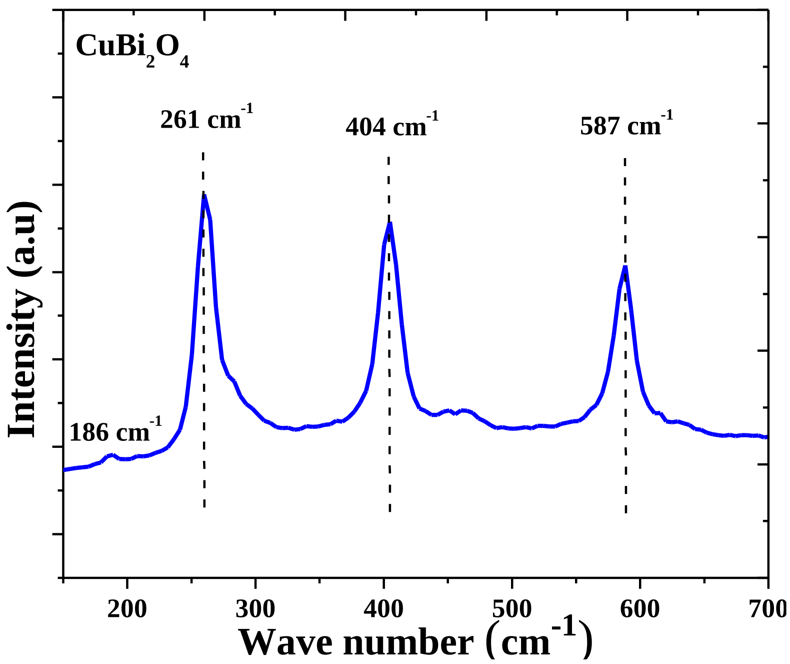


**Figure *S1.*** Raman spectra of $CuBi_2O_4$ photocathode.

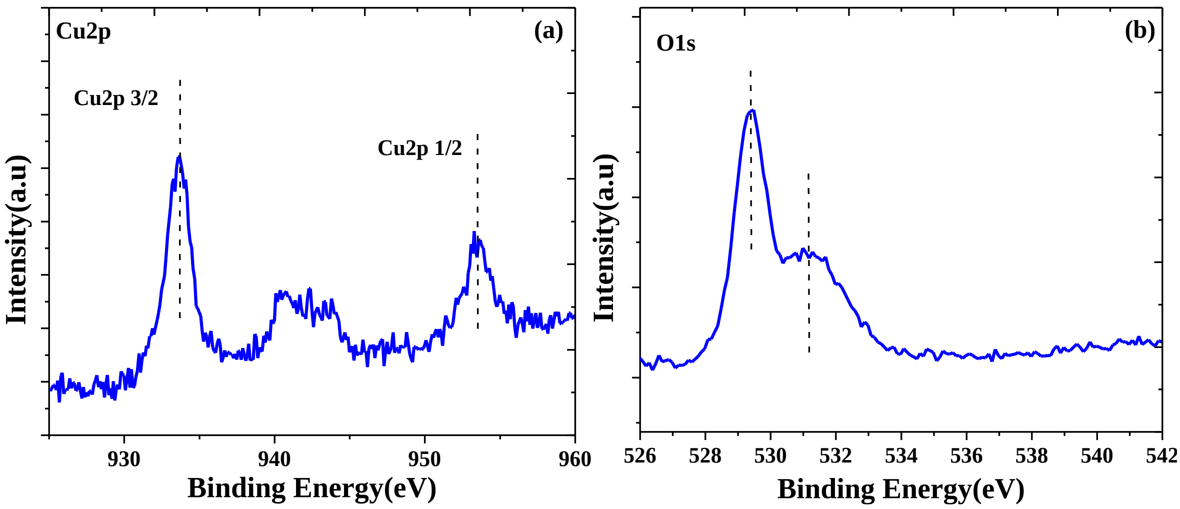


**Figure *S2***. XPS High-resolution of (a) Cu2p and (b) O1s for $CuBi_2O_4$ photocathode.

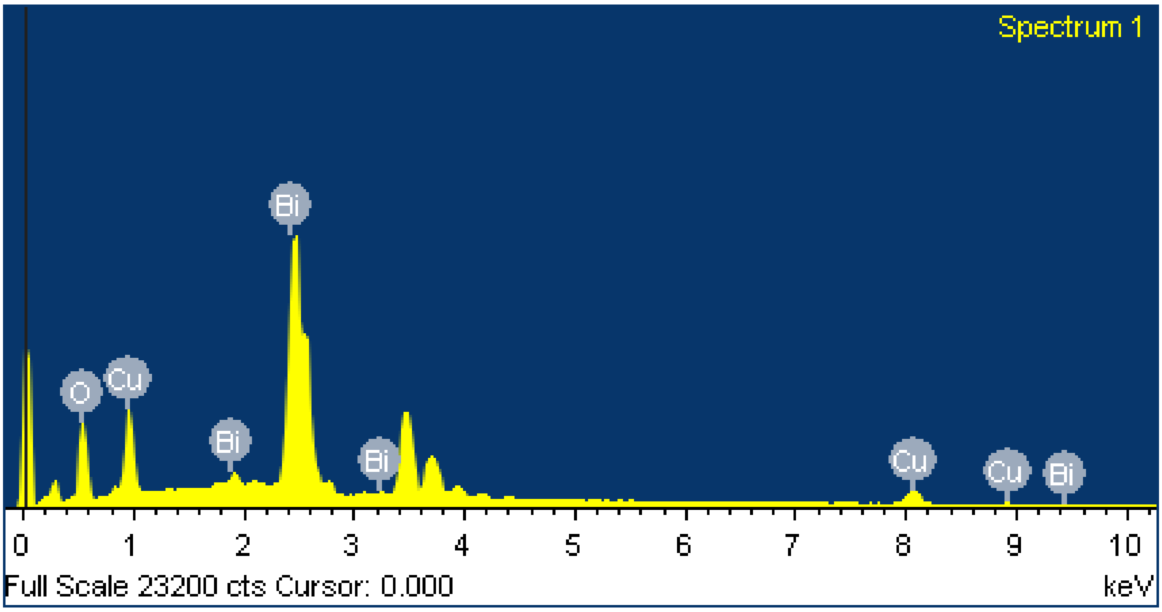


**Figure *S3***. EDX spectra of the $CuBi_2O_4$ photocathode.

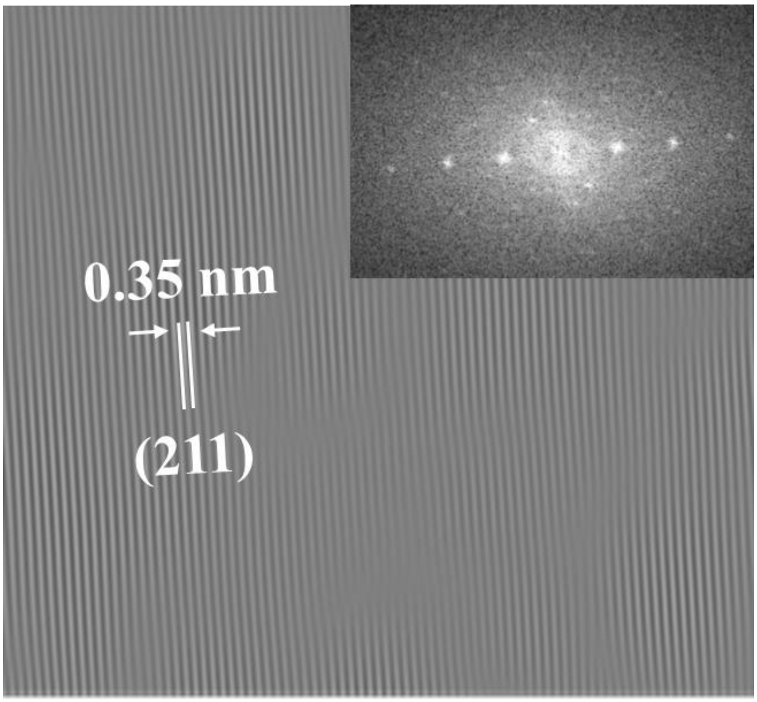


**Figure *S4***. Inverse fast Fourier transformed (IFFT) image showing interplanar spacing of 0.35 nm corresponding to (211) lattice plane of $CuBi_2O_4$ [1].

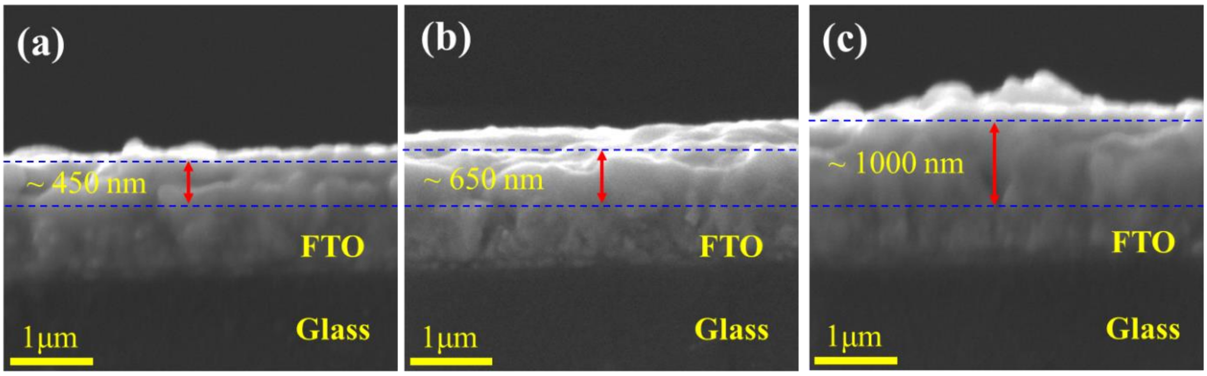


**Figure *S5***. SEM cross-section of the #1-$CuBi_2O_4$, #2-$CuBi_2O_4$, and #4-$CuBi_2O_4$ photocathodes.

**Mott-Schottky equation and constant volume:**

The charge carrier density of the photocathodes was obtained from the following formula [2-4].

$$\frac{1}{C^2} = \frac{2}{\varepsilon\varepsilon_0 A^2 e N_A}(V_{fb} - V - \frac{K_B T}{e})$$
$$Slope = \frac{-2}{\varepsilon\varepsilon_0 A^2 e N_A} \rightarrow N_A = \frac{-2}{\varepsilon\varepsilon_0 A^2 e(Slope)}$$
$$int\,e\,rcept = V_{fb} - \frac{K_B T}{e} \rightarrow V_{fb} = int\,e\,rcept + \frac{K_B T}{e}$$

$$\varepsilon = 98\ for\ CuBi2O4$$
$$\varepsilon_0 = 8.854 * 10^{-12} F.m^{-1}$$
$$e = 1.6 * 10^{-19} C$$
$$K_B = 1.381 * 10^{-23} j.K^{-1}$$
$$T = 298K$$

Where C, e, ε, $\varepsilon_0$, $N_A$, A, $V_{fb}$, and $k_B$ are the space charge region capacitance, unit charge, relative permittivity (98 for $CuBi_2O_4$), permittivity of free space, acceptor density, electrode area, flat band potential, and Boltzmann's constant, respectively.

**Table S1**. PEC parameters of the $CuBi_2O_4$ photocathodes.

| Photocathode | $R_s$(Ω/cm$^2$) | $R_{ct}$(Ω/cm$^2$) | Slope | Intercept | $N_A$(1/cm$^3$) | $V_{fb}$ ($V_{RHE}$) |
|---|---|---|---|---|---|---|
| #1-$CuBi_2O_4$ | 12.42 | 1823.45 | $-1.27 \times 10^{10}$ | 1.32 | $2.82 \times 10^{19}$ | 1.34 |
| #2-$CuBi_2O_4$ | 14.61 | 850.37 | $-3.09 \times 10^9$ | 1.25 | $1.20 \times 10^{20}$ | 1.27 |
| #4-$CuBi_2O_4$ | 13.86 | 1467.29 | $-4.81 \times 10^9$ | 1.27 | $7.48 \times 10^{19}$ | 1.29 |
| #2-$CuBi_2O_4$ $H_2O_2$ | 15.89 | 433.12 | $-2.12 \times 10^9$ | 1.2 | $1.69 \times 10^{20}$ | 1.22 |

## Reference:

[1] D. Cao, N. Nasori, Z. Wang, Y. Mi, L. Wen, Y. Yang, S. Qu, Z. Wang, Y. Lei, p-Type CuBi2O4: an easily accessible photocathodic material for high-efficiency water splitting, Journal of Materials Chemistry A, 4 (2016) 8995-9001.

[2] J. Jiaqi, Reaction Kinetics of Photoelectrochemical $CO_2$ Reduction on a $CuBi_2O_4$-Based Photocathode, ACS applied materials & interfaces, v. 14 (2022) pp. 17509-17519-12022 v.17514 no.17515.

[3] S.P. Berglund, F.F. Abdi, P. Bogdanoff, A. Chemseddine, D. Friedrich, R. van de Krol, Comprehensive Evaluation of CuBi2O4 as a Photocathode Material for Photoelectrochemical Water Splitting, Chemistry of Materials, 28 (2016) 4231-4242.

[4] F. Wang, W. Septina, A. Chemseddine, F.F. Abdi, D. Friedrich, P. Bogdanoff, R. van de Krol, S.D. Tilley, S.P. Berglund, Gradient Self-Doped CuBi2O4 with Highly Improved Charge Separation Efficiency, Journal of the American Chemical Society, 139 (2017) 15094-15103.