Supplementary Information

Spray pyrolysis of CuBi₂O₄ photocathodes: improved solution chemistry for

highly homogeneous thin films

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Figure S1. Photographs and SEM images of $CuBi_2O_4$ thin films prepared on FTO substrate by spraying total precursor solution concentrations and volumes of (a) 2 mM and 280 mL, (b) 10 mM and 56 mL, and (c) 20 mM and 28 mL with a substrate temperature of 450 °C.



Figure S2. XRD diffractograms for CuBi₂O₄ photocathodes synthesized by spray pyrolysis on FTO substrates (450 °C). Purple (|) and cyan (|) drop lines represent the reference patterns for CuBi₂O₄ (kusachite, PDF# 00-042-0334) and SnO₂ (cassiterite, PDF# 00-046-10884), respectively.



Figure S3. Photographs of different precursor solutions over time.



Figure S4. XRD diffractograms for the precipitate from the 20 mM precursor solution without additives (a) filtered and dried, before annealing and (b) after annealing at 500 °C for 2h in air. Blue vertical lines (|) represent the reference patterns for Bi_2O_3 (PDF# 01-071-0465).



Figure S5. ATR-IR reference spectra for various solvents and potential reaction products. The drop lines represent the peak location.



Figure S6. ATR-IR reference spectrum of the precipitate filtered from the 20 mM precursor solution without additives after 24h. The pink (|) drop lines represent the peak locations including that for the nitrate group in the bismuth oxynitrate species, [NO₃]⁻.



Figure S7. ATR-IR spectra of 20 mM $CuBi_2O_4$ precursor salts dissolved in 1 : 9 acetic acid : ethanol without additives. Purple (|) and pink (|) drop lines represent the peak locations from reference spectrums for ethyl acetate¹ and bismuth oxynitrate², respectively. Thin gray curves show the measurements carried out every 1 h between 4 h and 11 h.



Figure S8. ATR-IR spectra of 20 mM $CuBi_2O_4$ precursor salts dissolved in 1 : 9 acetic acid : ethanol with 5 % TEOF. Purple (|) and pink (|) drop lines represent the reference spectrums for ethyl acetate and bismuth oxynitrate, respectively. Thin gray curves show the measurements carried out every 1 h between 10 h and 23 h.



Figure S9. ATR-IR spectra of 20 mM CuBi₂O₄ precursor salts dissolved in 1 : 9 acetic acid : ethanol with 5 % TEOF and 1 % PEG. Purple (|) and pink (|) drop lines represent the reference spectrums for ethyl acetate and bismuth oxynitrate, respectively. Thin gray curves show the measurements carried out every 1 h between 13 h and 23 h.



Figure S10. ATR-IR spectra for 1:9 acetic acid: ethanol. Purple (|) drop lines represent the reference spectrums for ethyl acetate.



Figure S11. Direct reflectance of ~ 50 nm $CuBi_2O_4$ thin films deposited on FTO at 450 °C using 20 mM precursor solutions with 0 %, 1 %, 5 % and 10 % TEOF. Direct reflectance (Figure S 11 (d)) was derived by subtracting the diffuse reflectance (Figure S 11(c)) from the direct reflectance + diffuse reflectance (Figure S 11 (b)).



Figure S12. Photographs of the CuBi₂O₄ thin films deposited on FTO substrates at different temperatures using 20 mM precursor solution with 5 % TEOF.



Figure S13. Cross section SEM images of CuBi₂O₄ films on FTO deposited with 20 mM precursor solution with 5 % TEOF and 1 % PEG (a) ~ 110 nm (b) ~ 270 nm (c) ~ 420 nm.



Figure S14. Scherrer analysis of a CuBi₂O₄ film sprayed using 20 mM precursor solution with 5 % TEOF and 1 % PEG on FTO at 450 °C. The average crystallite size was calculated from the three peaks for CuBi₂O₄ at 2 Theta values of 20.82°, 27.95° and 30.66°. Instrumental broadening was corrected using a standard LaB₆ reference material.



Figure S15. Direct and indirect bandgap Tauc plots for CuBi₂O₄ films deposited with 20 mM precursor solution with 5 % TEOF and 1 % PEG on quartz substrates.



Figure S16. Electrochemical impedance spectroscopy (EIS) at 1.00 V vs. RHE for ~ 270 nm CuBi_2O_4 (sprayed using 20 mM precursor solution with 5 % TEOF and 1 % PEG on FTO at 450 °C) performed in 0.3 M K₂SO₄ and 0.2 M phosphate buffer (pH 6.65). Note that above 1 kHz, the real part of the impedance is constant, whereas the imaginary part has a slope of -1. This implies that the system behaves as a resistance in series with a pure capacitance, which is a prerequisite for Mott-Schottky analysis.



Figure S17. Mott–Schottky plot for ~ 270 nm $CuBi_2O_4$ (sprayed using 20 mM precursor solution with 5 % TEOF and 1 % PEG on FTO at 450 °C) performed in 0.3 M K_2SO_4 and 0.2 M phosphate buffer (pH 6.65) at 3 kHz, 5 kHz, and 7 kHz. Note that the system behaves as a simple RC series circuit for all three frequencies (Fig. S16); the Mott-Schottky conditions are thus fulfilled and the changes in capacitance can be assigned to changes in the width of the space charge layer as a function of the applied potential.



Figure S18. Linear sweep voltammetry scans in the dark for ~ 270 nm $CuBi_2O_4$ (sprayed using 20 mM precursor solution with 5 % TEOF and 1 % PEG on FTO at 450 °C) and ~ 100nm CuO (sprayed using 20 mM $Cu(NO_3) \cdot 3H_2O$ in ethanol on FTO at 450 °C) performed in 0.3 M K_2SO_4 and 0.2 M phosphate buffer (pH 6.65) with Ar bubbling in the dark.



Figure S19. Chopped (light/dark) linear sweep voltammetry scans for a \sim 270 nm CuBi₂O₄ photocathode (sprayed using 20 mM precursor solution with 5 % TEOF and 1 % PEG on FTO at 450 °C). The measurement was performed in 0.1 M KOH (pH 12.8) with Ar bubbling and with O₂ bubbling under back illumination.



Figure S20. Linear sweep voltammetry scan for a Pt wire performed in 0.1 M KOH with O₂ bubbling (pH 12.8).



Figure S21. Square wave voltammetry of a Pt wire measured with a potential step (2 s at 1.15 V_{RHE} and 2 s at 0.15 V_{RHE}) in 0.1 M KOH with O₂ bubbling (pH 12.8).



Figure S22. Constant potential measurement at 0.6 V vs RHE for a \sim 270 nm CuBi₂O₄ photocathode (sprayed using 20 mM precursor solution with 5 % TEOF and 1 % PEG on FTO at 450 °C) in the dark and light (AM1.5 irradiation). Measurements were done in 0.3 M K₂SO₄ and 0.2 M phosphate buffer (pH 6.65) with Ar bubbling and with H₂O₂.



Figure S23. Illustration of the experimental setup for diffuse reflectance (with the reflector off), and direct reflectance + diffuse reflectance (with the reflector on).



Figure S24. Dark and light current density for back illumination IPCE measurement of a ~ 270 nm $CuBi_2O_4$ film on deposited on FTO at 450 °C using 20 mM precursor solution with 5 % TEOF and 1 % PEG. The difference between light and dark current density was used to calculate the average photocurrent (J_{ph}) for each wavelength.



Figure S25. Power spectra for back illumination IPCE measurements measured with and without an FTO substrate.



Figure S 26. Atomic force microscopy (AFM) image of ~ 270 nm $CuBi_2O_4$ (sprayed using 20 mM precursor solution with 5 % TEOF and 1 % PEG on FTO at 450 °C). The ratio of real surface area to geometric surface area is estimated to be 29 / 25 = 1.2 based on the surface roughness.

References:

- 1. B. Nolin and R. N. Jones, Can. J. Chem., 1956, 34, 1382-1391.
- 2. H. Huang, Y. He, X. Li, M. Li, C. Zeng, F. Dong, X. Du, T. Zhang and Y. Zhang, *J. Mater. Chem. A*, 2015, **3**, 24547-24556.