

Electronic Supplementary Information  
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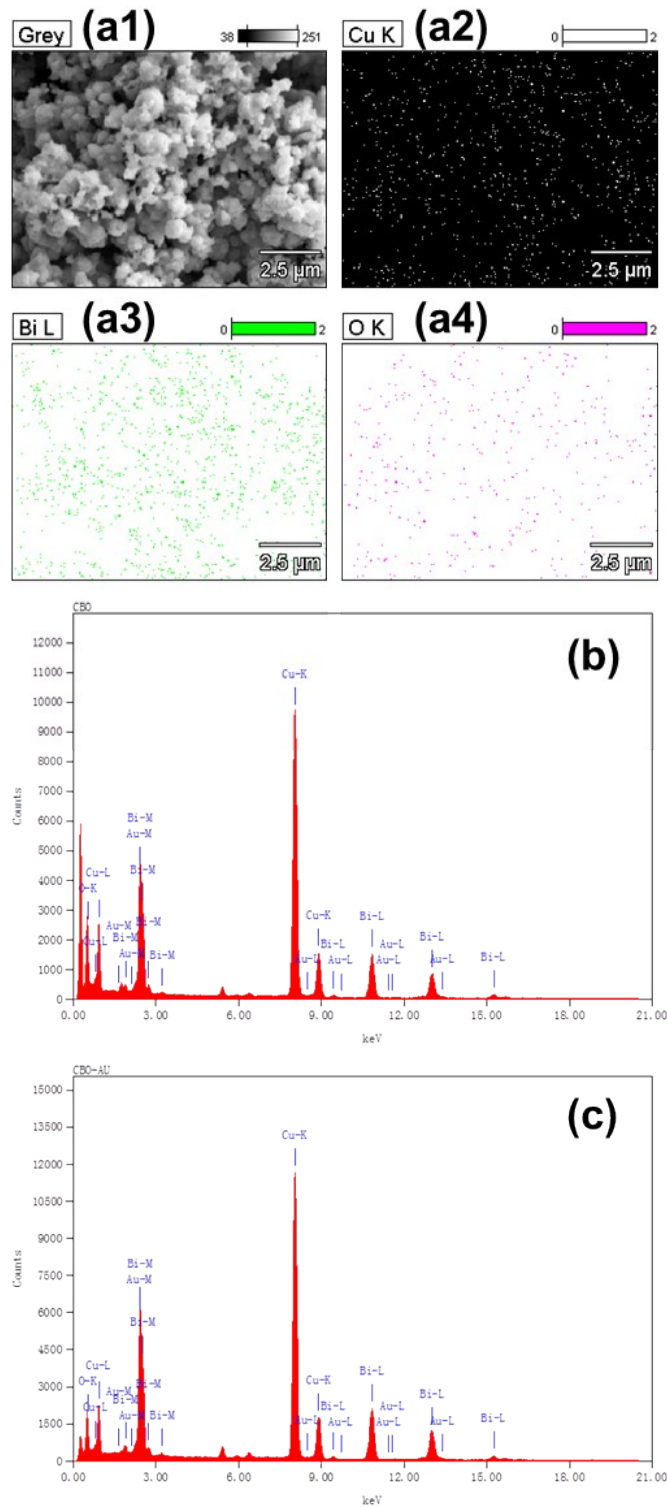
**P-type  $\text{CuBi}_2\text{O}_4$ : an Easily Accessible Photocathodic Material for High-efficient Water Splitting**

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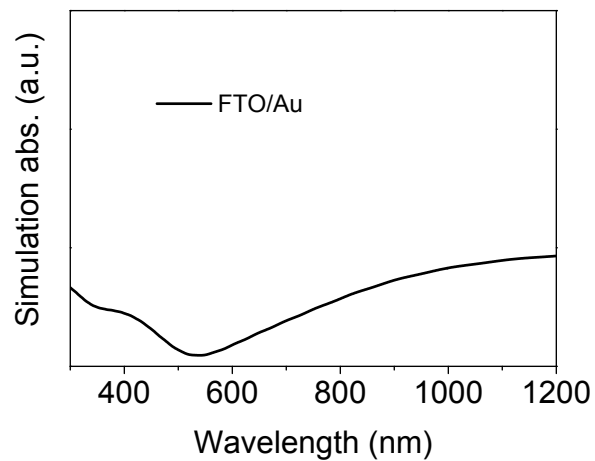
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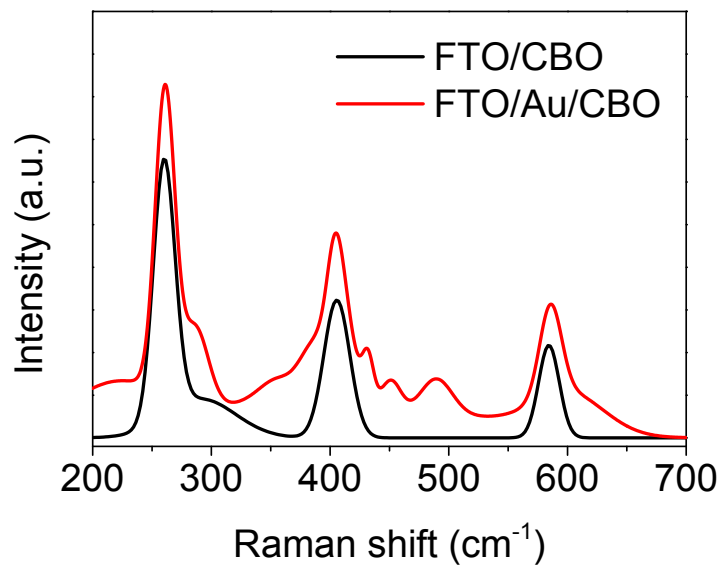
‡ These authors contribute equally to this work.



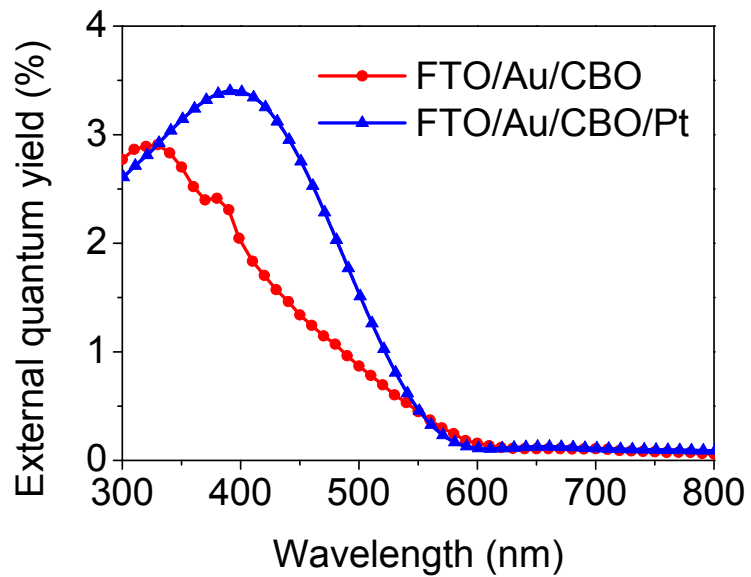
**Fig. S1** (a1) SEM image of CBO films on FTO, and corresponding EDX mapping image for (a2) Cu element, (a3) Bi element and (a4) O element. The representative EDX spectra of the CBO on FTO (b) and FTO/Au (c). In comparison with the spectrum from FTO/CBO, the spectrum of the particles from FTO/Au/CBO does not show the indication in containing Au in the crystals.



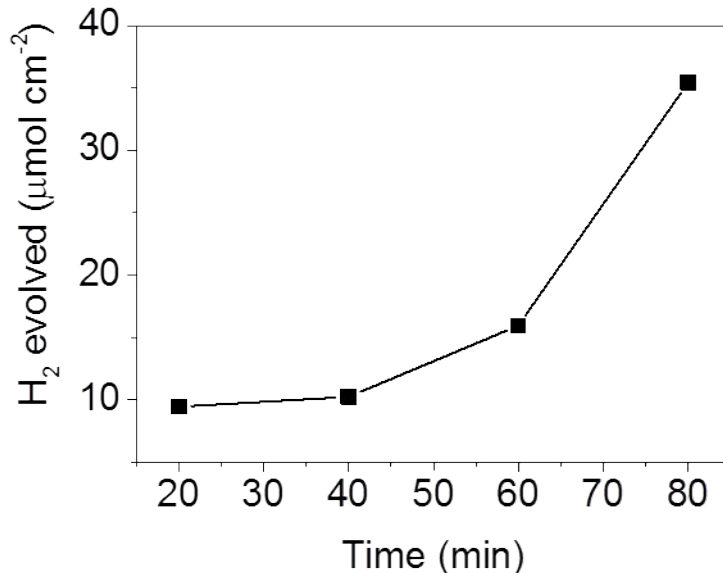
**Fig. S2** Simulated absorbance spectrum of the sample FTO/Au.



**Fig. S3** Raman spectra of CBO and Au/CBO on FTO glass. The distinct vibrational peaks at 262, 402 and 585 cm<sup>-1</sup> demonstrate the presence of CBO, which is consistent with the previous report.



**Fig. S4** Wavelength-dependent external quantum yield spectra of the photoelectrodes with or without Pt catalyst (the spectra were measured in a two-electrode configuration without any external bias).

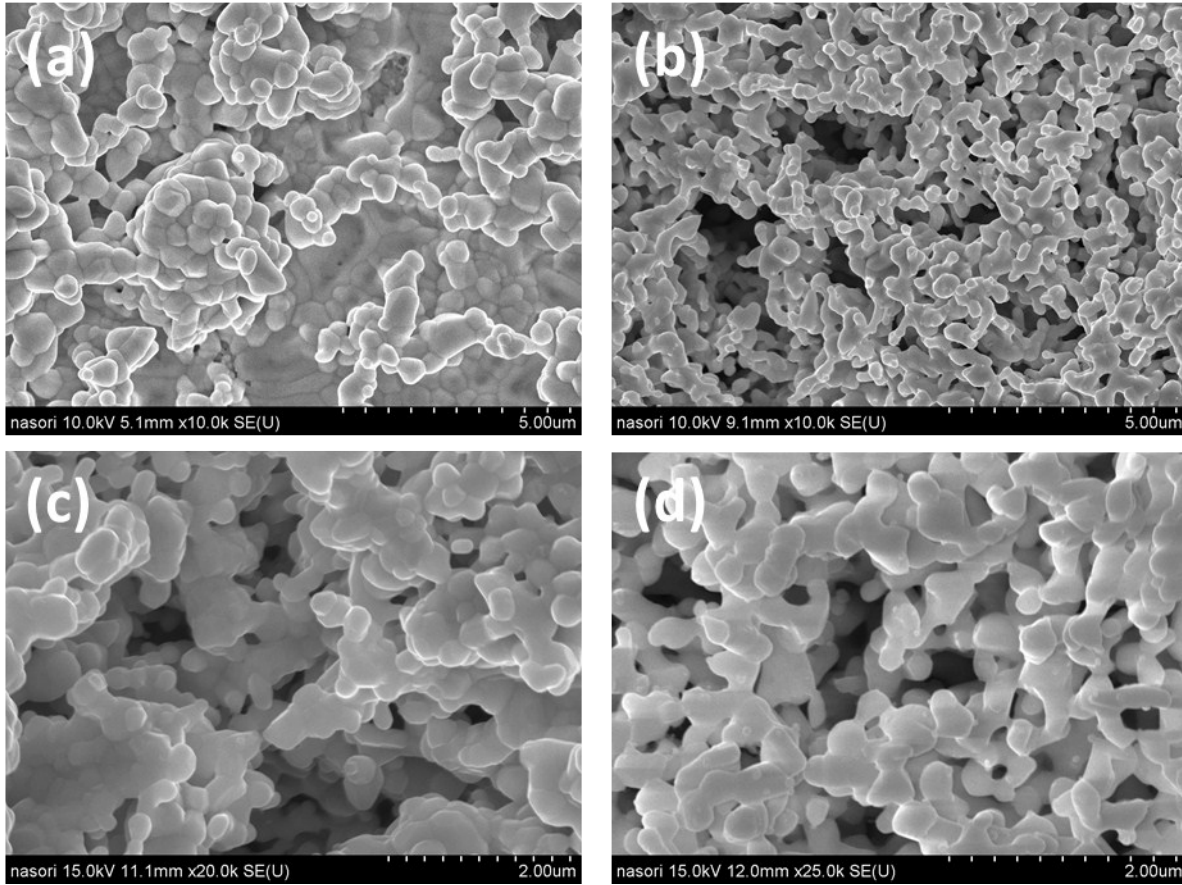


**Fig. S5** Hydrogen production on time measured under 0.2 V vs RHE with illumination of 100 mW cm<sup>-2</sup> Xe lamp for the FTO/Au/CBO photoelectrode with Pt nanoparticles. In our case, the water splitting reactor was small in volume and the amount of evolved hydrogen was about μmol scale. Such small amount of hydrogen was quite easy to dissolve in the electrolyte solution and cannot be easily detected by the gas chromatograph equipment. In spite of these limitations, the result clearly shows that the FTO/Au/CBO/Pt can actually work as photocathode for hydrogen production.

For H<sub>2</sub> generation measurement, the electrochemical cell with the electrodes was installed to the vacuum based system and then the remnant gas in the system was purged out completely, so that we could measure the generated H<sub>2</sub> and O<sub>2</sub> solely. As shown in Figure S5, The curve of H<sub>2</sub> generation shows somewhat variation from the typical linear feature. The amount of H<sub>2</sub> generation is in magnitude of several micro molar in the early time region. Such values are close to the minimum detecting limit of the used system and thus the variation from linear tendency of H<sub>2</sub> generation is unavoidable and understandable. To be more significant, in the process of H<sub>2</sub> generation, O<sub>2</sub> also evolves. The slightly dissolved O<sub>2</sub> in the electrolyte would also capture the electrons from the photocathodes and compete with the H<sub>2</sub> generation. Thus, we observed a slow H<sub>2</sub> generation process at the first stage. The Faradaic efficiency of the system was calculated as 84.49% for the water splitting reactor during 80 min, by the following equation: Faradaic efficiency = [ mols H<sub>2</sub> (GC) × N<sub>A</sub> × e × 2 ] / ( I × t ),<sup>[1]</sup> N<sub>A</sub> is 6.0221367×10<sup>23</sup> mol<sup>-1</sup>, e is 1.60 × 10<sup>-19</sup> C, I is the current during the GC measurement, t is the time.

**Before**

**After**



**Fig. S6** SEM images of FTO/Au/CBO before (a and c) and after (b and d) PEC measurement (3000 s).

## References

- [1] J. G. Kleingardner, B. Kandemir, K. L. Bren, *J. Am. Chem. Soc.* **2014**, *136*, 4–7.