Supporting Information

Pulse electrodeposited amorphous tunnel layer stabilises Cu_2O for efficient photoelectrochemical water splitting under visible-light irradiation

Hao Wu,[a,b] Zhaoke Zheng,[c] Cui Ying Toe,[b] Xiaoming Wen,[d] Judy N. Hart,[e] Rose Amal,[b] Yun Hau Ng*[a,b]

[a.] School of Energy and Environment, City University of Hong Kong, Kowloon, Hong Kong, SAR, P. R. China
Email: yunhau.ng@cityu.edu.hk

[b.] Particles and Catalysis Research Group, School of Chemical Engineering, UNSW Sydney, NSW 2052, Australia

[c.] State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China

[d.] Centre for Micro-Photonics, Faculty of Science, Swinburne University of Technology, John Street, Hawthorn, VIC 3122, Australia

[e.] School of Materials Science and Engineering, UNSW Sydney, NSW 2052, Australia

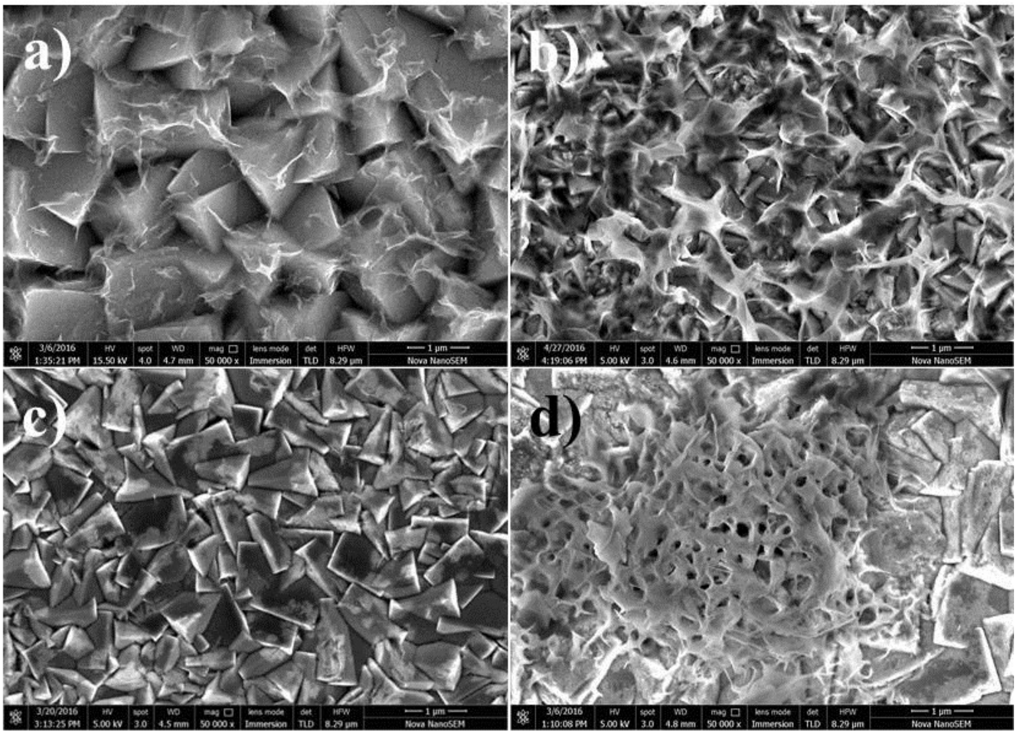

Figure S1. SEM images of pulse electrodeposited ZnO thin films on Cu_2O with a) 36 cycles and b) 60 cycles; SEM images of ZnO thin films electrodeposited on Cu_2O in a single-step process at constant potentials of c) -0.75 V and d) -1.1 V vs. Ag/AgCl (1 M KCl).

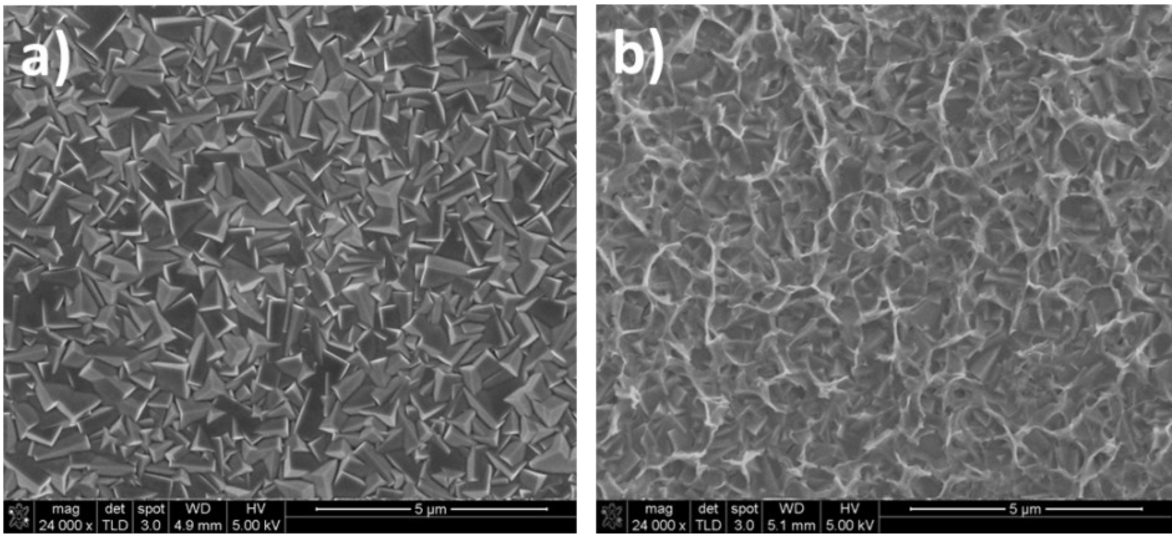

Figure S2. Low magnification SEM images showing top views of a) bare Cu_2O and b) TiO_2/ZnO/Cu_2O photoelectrodes.

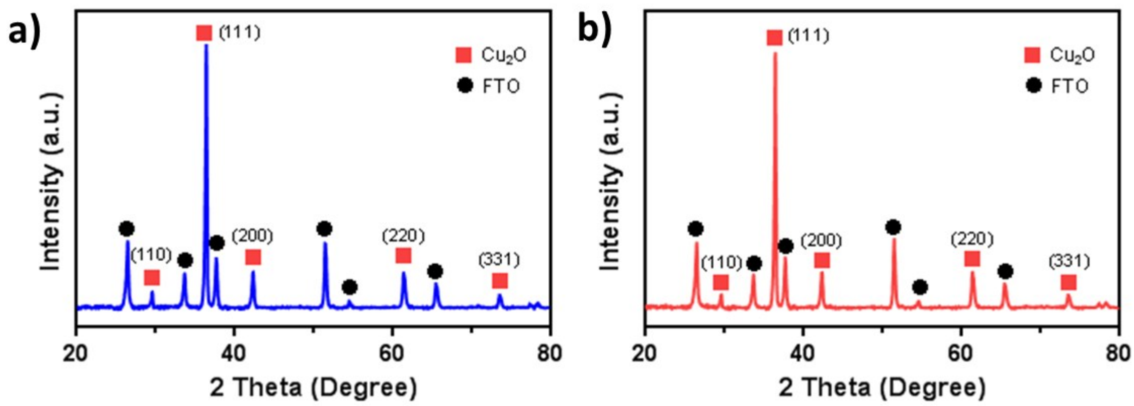

Figure S3. X-ray diffraction patterns of a) Cu_2O, and b) TiO_2/ZnO/Cu_2O photoelectrodes.

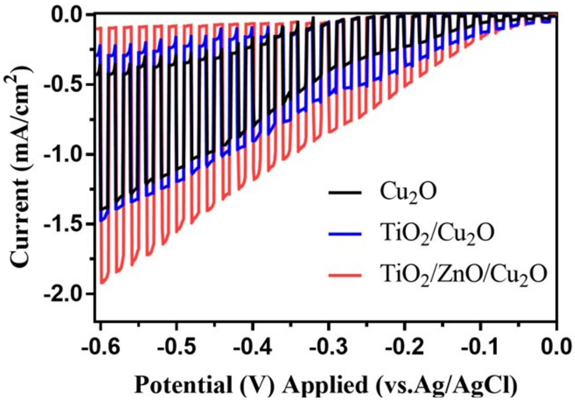

Figure S4. Linear sweep voltammetry (*I-V*) curves acquired at a scan rate of 2 mV s^{-1} for the Pt modified Cu_2O, TiO_2/Cu_2O and $TiO_2/ZnO/Cu_2O$ photoelectrodes.

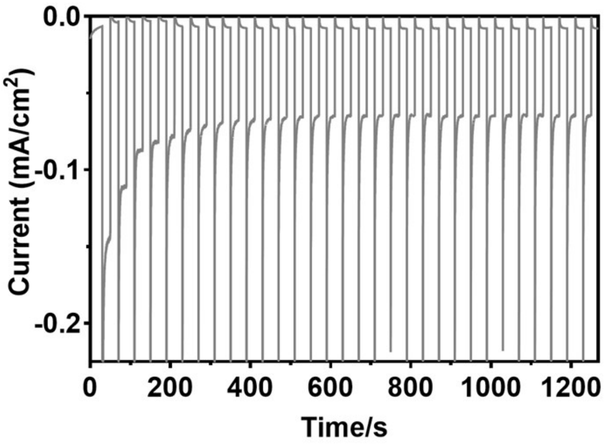

Figure S5. The *I-t* curve of ZnO/Cu_2O photoelectrode at -0.2 V vs. Ag/AgCl (1 M KCl) in 0.1 M Na_2SO_4 solution under visible-light irradiation (>420 nm)

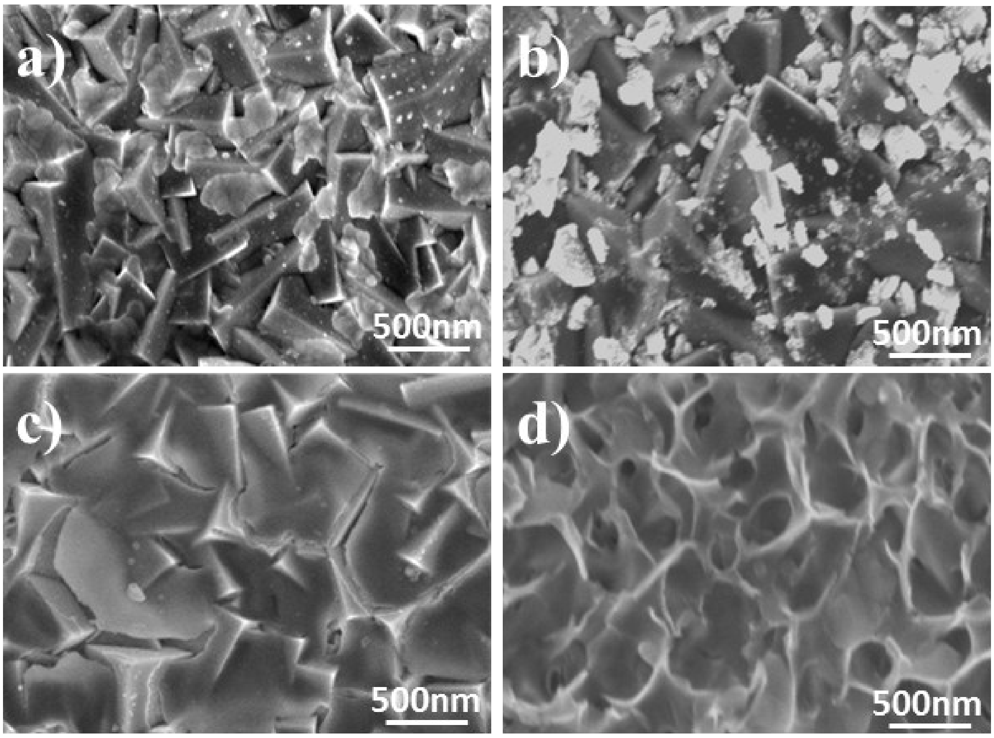

Figure S6. Post-reaction SEM images of a) bare Cu_2O, b) ZnO/Cu_2O, c) TiO_2/Cu_2O and d) $TiO_2/ZnO/Cu_2O$ photoelectrodes.

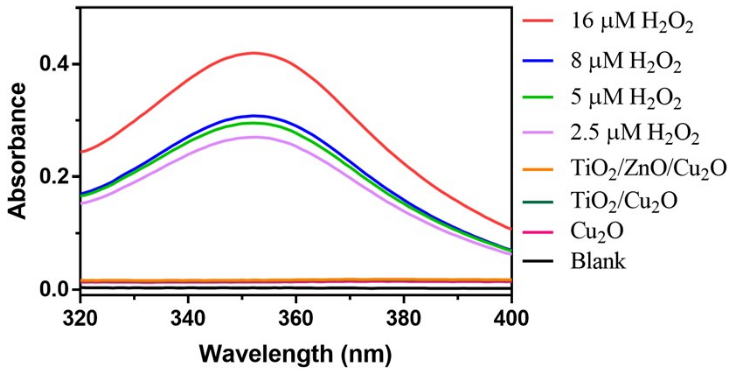

Figure S7. The absorption peaks at 350 nm from the standard H_2O_2 solutions, the blank solution and the electrolyte after PEC measurements of prepared photoelectrodes.

Ultra-pure N_2 with a flow rate of 50 ml/min was continuously purged through the electrolyte for 30 mins before the PEC measurements to remove the dissolved O_2. The electrolyte used in the PEC measurements is 0.1 M Na_2SO_4 with pH of 6.8 confirmed by an electrochemical pH meter, indicating a relatively acidic reaction condition. As shown in the equations below, Liming Dai et al. reported that H_2O_2 and H_2O are the products of O_2 reduction in acidic media.[1] In this process, the formation of H_2O_2 is an important intermediate which can be detected by UV-vis method. In theory, H_2O_2 molecules will react with iodide anions (I^-) under acidic condition ($H_2O_2 + 3I^- + 2H^+ \rightarrow I^{3-} + 2H_2O$) to produce triiodide anions (I^{3-}), which processes a strong absorption at 351 nm. Moreover, Figure S7 shows absorptions of several standard H_2O_2 solutions, revealing the high sensitivity of this method for H_2O_2 detection (2.5 μM).

$$Acid\ media: O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$

Subsequently, we operated a non-chopped *I-t* measurement on the $TiO_2/ZnO/Cu_2O$ sample for 20 mins. The theoretical value of H_2O_2 was calculated to be roughly 90 μM for the $TiO_2/ZnO/Cu_2O$ and 50 μM for the TiO_2/Cu_2O and Cu_2O photoelectrodes. However, the UV-vis result showed a negligible absorption at 350 nm for the electrolyte after *I-t* measurement, indicating the negligible amount of H_2O_2 generated. Even though we understand that the H_2O_2 is not the only product of O_2 reduction, the UV-vis results elucidate that less than 2.5 μM H_2O_2 (account for 2.7% of the theoretical value) was generated during the PEC measurement. Therefore, we can rule out the possibility of O_2 reduction under the current testing conditions.

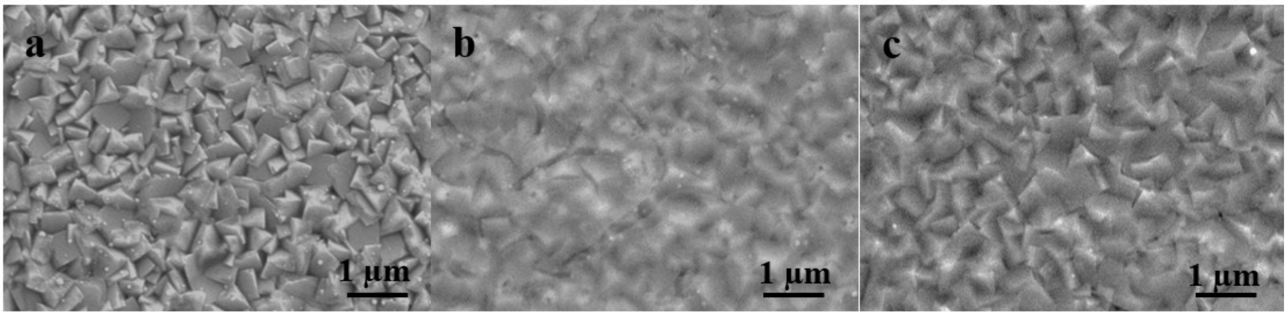

Figure S8. SEM images of the Pt modified a) Cu_2O photoelectrode, b) TiO_2/Cu_2O photoelectrode and c) $TiO_2/ZnO/Cu_2O$ photoelectrode.

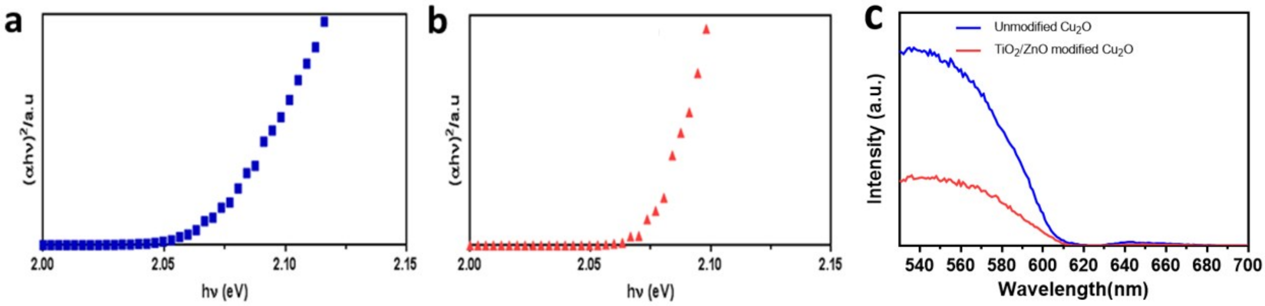

Figure S9. Tauc plots of a) bare Cu_2O and b) TiO_2/ZnO/Cu_2O; c) UV-vis absorbance spectra of Cu_2O and TiO_2/ZnO/Cu_2O.

Table S1. Photoelectrochemical H_2 Evolution Using Cu_2O-based Photocathodes[a]

Sample	Potential/V[b]	H_2/μmol	Faraday Efficiency
$TiO_2/ZnO/Cu_2O$	-0.6 V	21.79	95.7%
TiO_2/Cu_2O	-0.6 V	12.76	62.5%
ZnO/Cu_2O	-0.6 V	n.d.	n.d.
Cu_2O	-0.6 V	n.d.	n.d.

a. All faraday efficiencies measurements were performed with Pt cocatalyst and irradiated at λ > 420 nm for 1 h in 0.1 M Na_2SO_4 aqueous solution under an Ar atmosphere.

b. Versus Ag/AgCl (1 M KCl).

Reference

1 J. Zhang, Z. Xia and L. Dai, *Science Advances*, 2015, **1**, e1500564.