Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Electronic supplementary information

Positive Onset Potential and Stability of Cu_2O-based Photocathodes in Water Splitting by Atomic Layer Deposition of a Ga_2O_3 Buffer Layer

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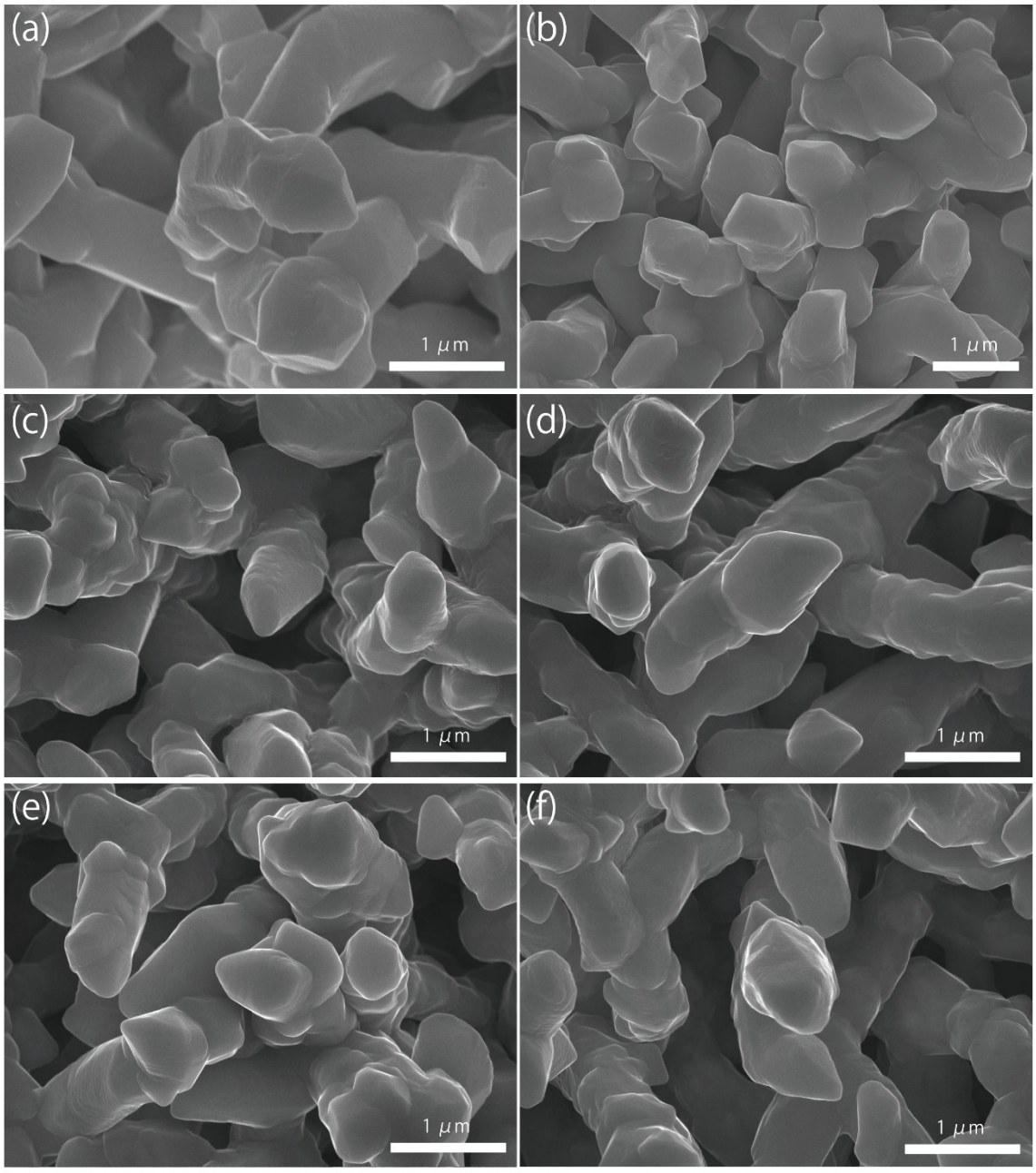

Figure S1. a) FE-SEM images of Cu_2O microcrystalline film prepared by annealing $Cu(OH)_2$ nanowires at 500ºC for 2 h. b-f) FE-SEM images of Cu_2O microcrystalline film coated with a 20 nm Ga_2O_3 buffer layer and a 15 nm TiO_2 protective layer by atomic layer deposition with a TiO_2 deposition temperature of 120, 150, 180, 220 and 260ºC, respectively. The deposition temperature of Ga_2O_3 thin layer was fixed at 150ºC.

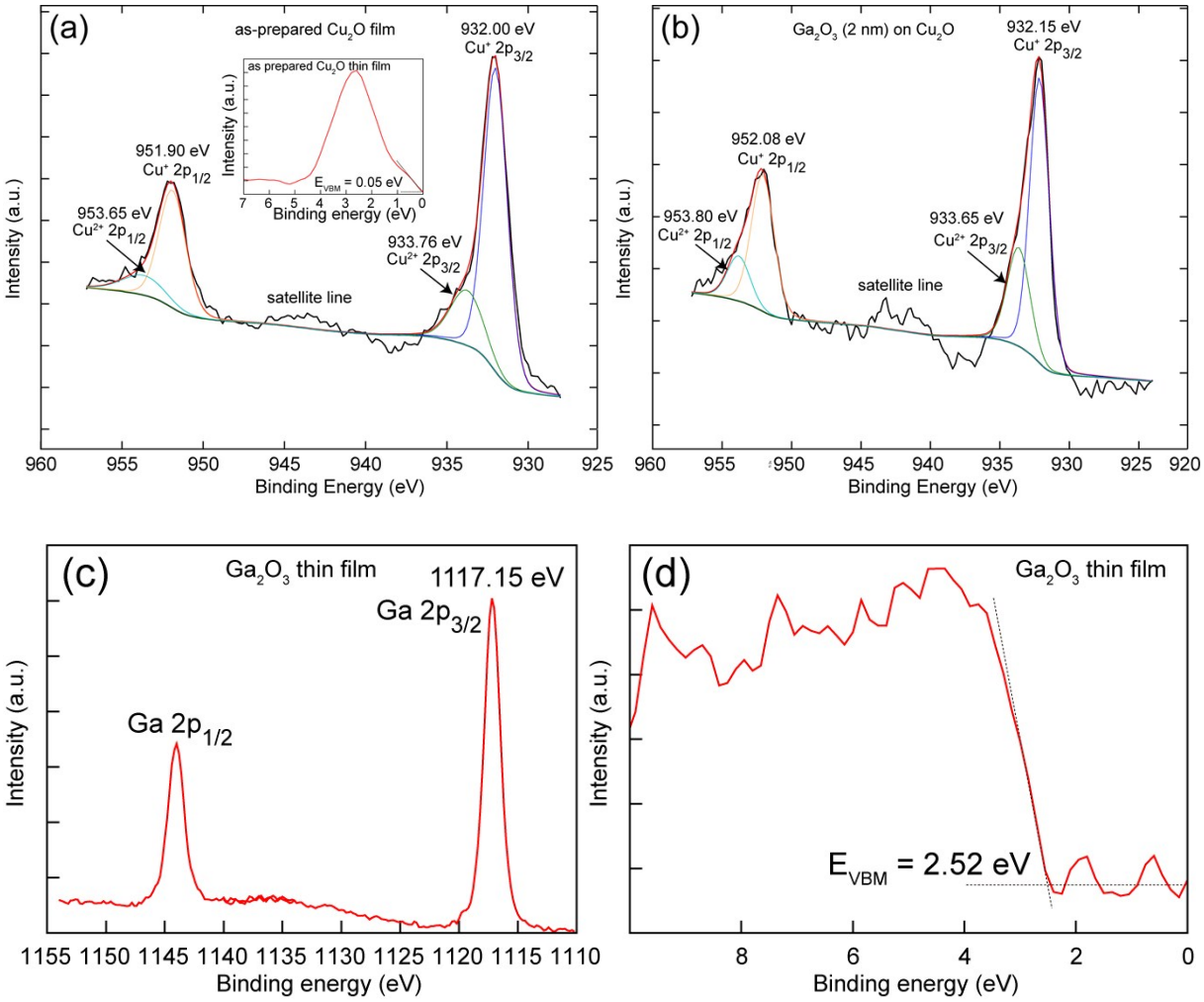

Figure S2. XPS spectra of Cu-2p core levels for as-prepared Cu_2O a) and Ga_2O_3 (2 nm)/Cu_2O multilayer sample b). The deposition temperature for Ga_2O_3 is 150ºC. b-d) XPS spectra of Ga_2O_3 thin film for Ga-2p core levels and valence band. The inset in a shows the XPS spectra of Cu_2O thin film for valence band.

X-ray photoemission spectrascopy (XPS) was applied to evalate the conduction band discontinuitiy ΔE_{CB} at Cu_2O/Ga_2O_3 heterojunction interface according to the equation:[1-2]

$$\Delta E_{CB} = \left(E^{Ga_2O_3-Cu_2O}_{Cu-2p} - E^{Ga_2O_3-Cu_2O}_{Ga-2p}\right) + \left(E^{Ga_2O_3}_{Ga-2p} - E^{Ga_2O_3}_{VBM}\right) - \left(E^{Cu_2O}_{Cu-2p} - E^{Cu_2O}_{VBM}\right) + \left(E^{Ga_2O_3}_{g} - E^{Cu_2O}_{g}\right).$$

The relative energy difference of Cu-2$p_{3/2}$ and Ga-2$p_{3/2}$ $\left(E^{Ga_2O_3-Cu_2O}_{Cu-2p} - E^{Ga_2O_3-Cu_2O}_{Ga-2p}\right)$, which was extracted from the Ga_2O_3(2 nm)/Cu_2O stack sample, is measured to be -185.85 eV. From the Cu_2O and Ga_2O_3 bulk film, the binding energies of Cu-2$p_{3/2}$ and Ga-2$p_{3/2}$ core levels ($E^{Cu_2O}_{Cu-2p}$ and $E^{Ga_2O_3}_{Ga-2p}$) with respect to valence band edge positions of Cu_2O and Ga_2O_3 are measured to be 931.95 eV and 1114.63 eV, respectively. The bandgap of the bulk Cu_2O ($E^{Cu_2O}_{g}$) and Ga_2O_3 ($E^{Ga_2O_3}_{g}$) were 2.0 eV [3] and 4.8-5.18 eV.[2, 4-6] Thus the ΔE_{CB} is determined to be between -0.37 and +0.01 eV.

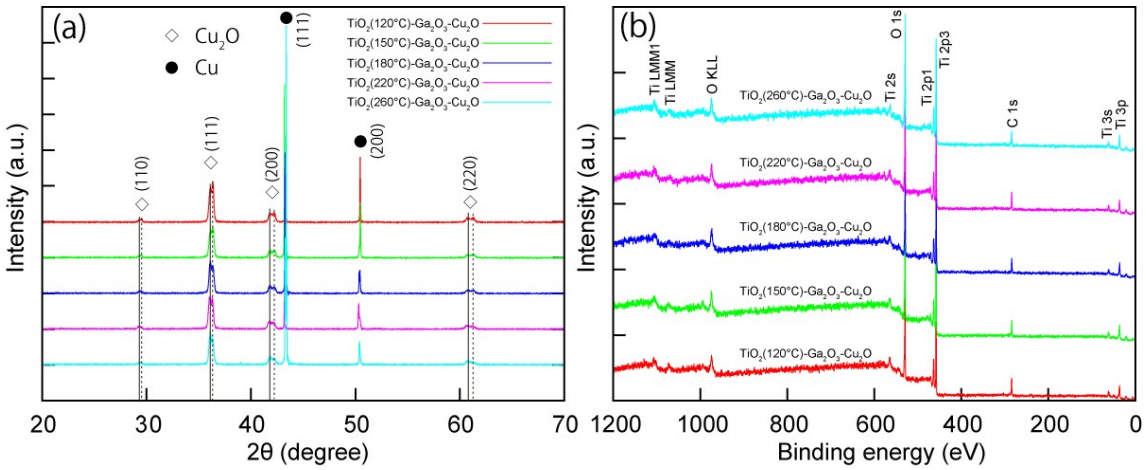

Figure S3. XRD a) and XPS spectra b) of the $TiO_2/Ga_2O_3/Cu_2O$ samples. The deposition temperature for Ga_2O_3 is 150ºC and the TiO_2 deposition temperature ranges from 120 to 220ºC. For the XRD data, two sets of diffraction peaks are clearly observed as the diffraction peaks are well indexed to the peaks of the cubic structure Cu_2O-I (indicated by a dashed line, space group Pn-3m, lattice constant 4.2600 Å, ICDD PDF card No. 1010941) and the Cu_2O-II (indicated by a solid line, space group Pn-3m, lattice constant 4.2685 Å, ICDD PDF card No. 9007497).

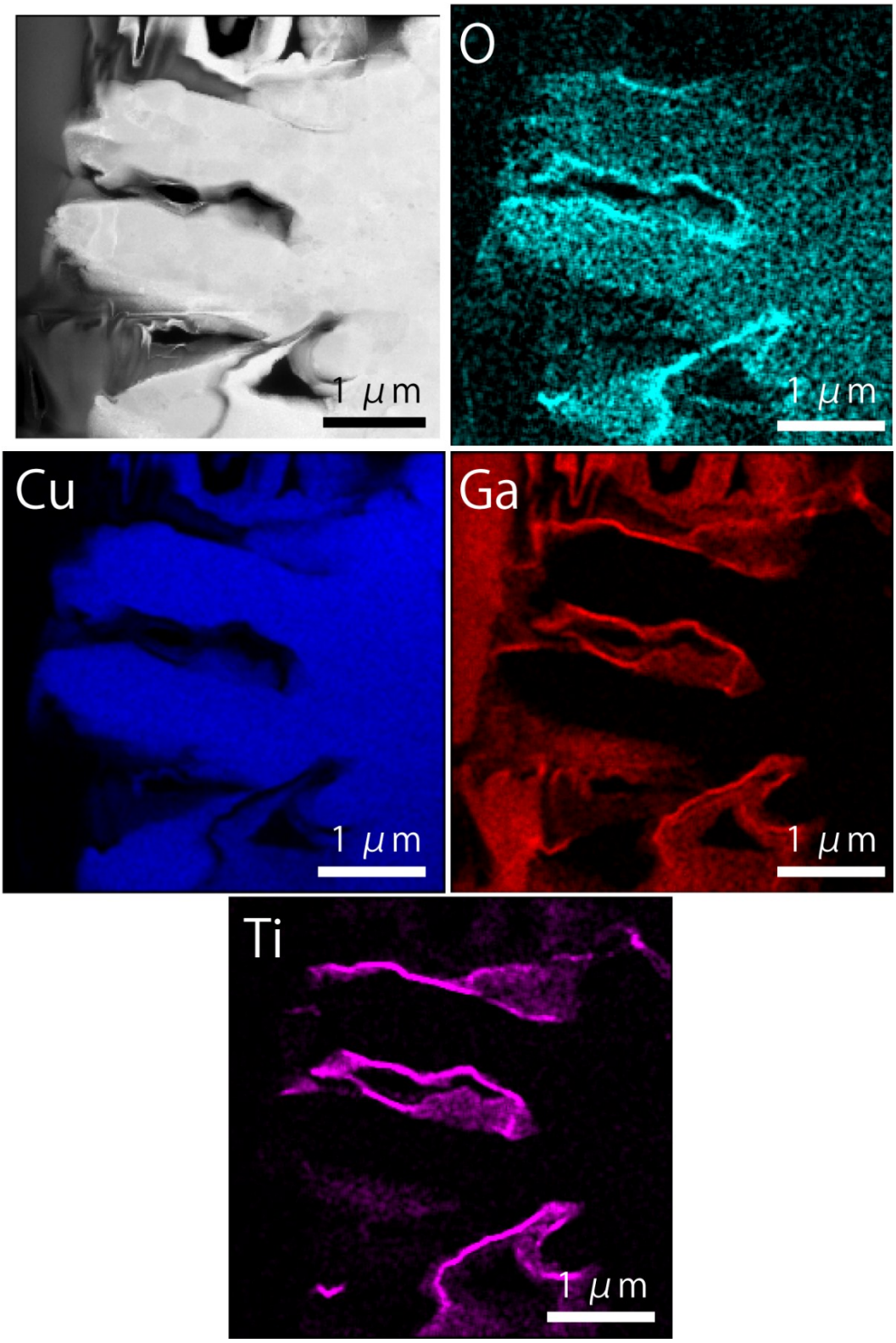

Figure S4. Large-area STEM-EDX element maps of a cross-section of the $TiO_2/Ga_2O_3/Cu_2O$ structure. The deposition temperature for Ga_2O_3 and TiO_2 are 150 and 220ºC, respectively.

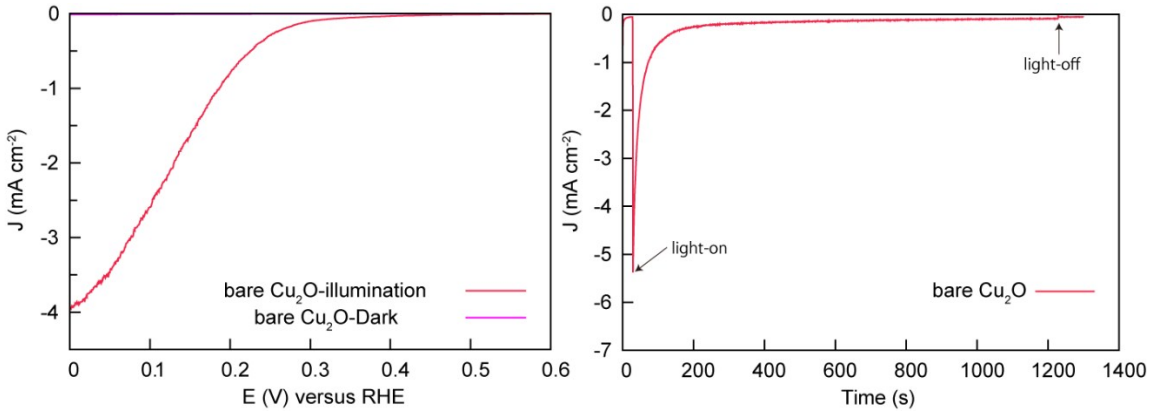

Figure S5. a) The linear sweep voltammetry scans of a the bare Cu_2O electrode. The scans were conducted in 0.5 M Na_2SO_4 electrolyte (pH = 6) under continuous illumination (Xe lamp) of visible light (cut-off filter > 420 nm, HOYA L42) at a scan rate 20 mV/s. b) Current-time curve of the Cu_2O electrode at 0 V vs. RHE under continuous visible light (> 420 nm) illumination.

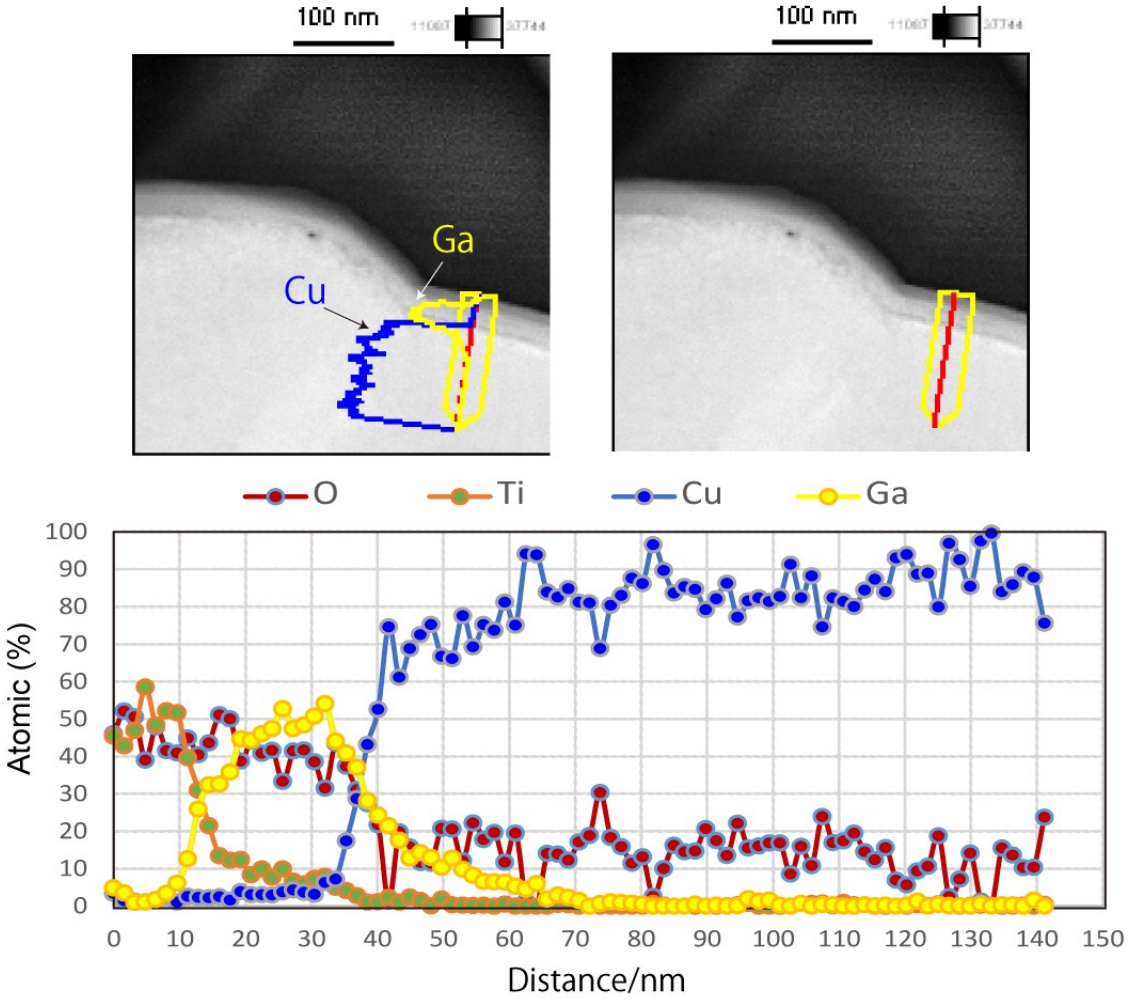

Figure S6. The line profiles for Ti, Ga and Cu elements across the TiO_2 and Ga_2O_3/Cu_2O interfaces.

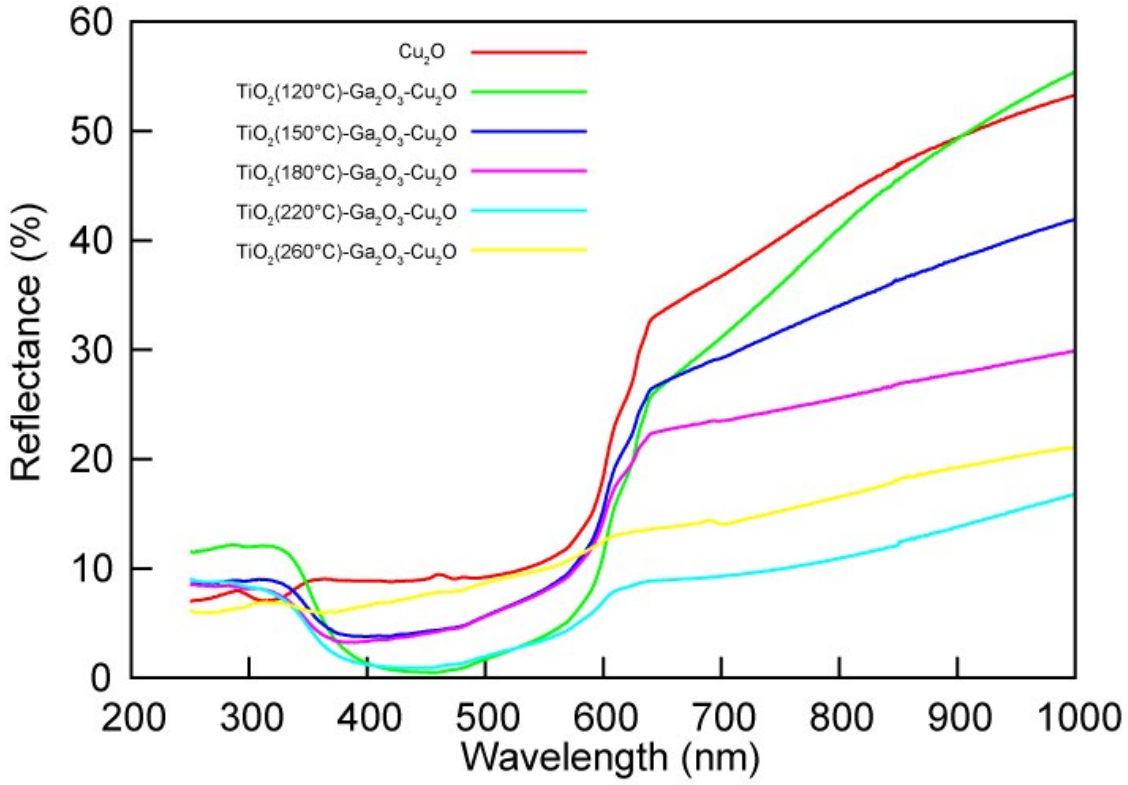

Figure S7. Diffuse reflectance spectra of the Cu_2O and $TiO_2/Ga_2O_3/Cu_2O$ samples for different TiO_2 deposition temperatures of 120, 150, 180, 220 and 260ºC.

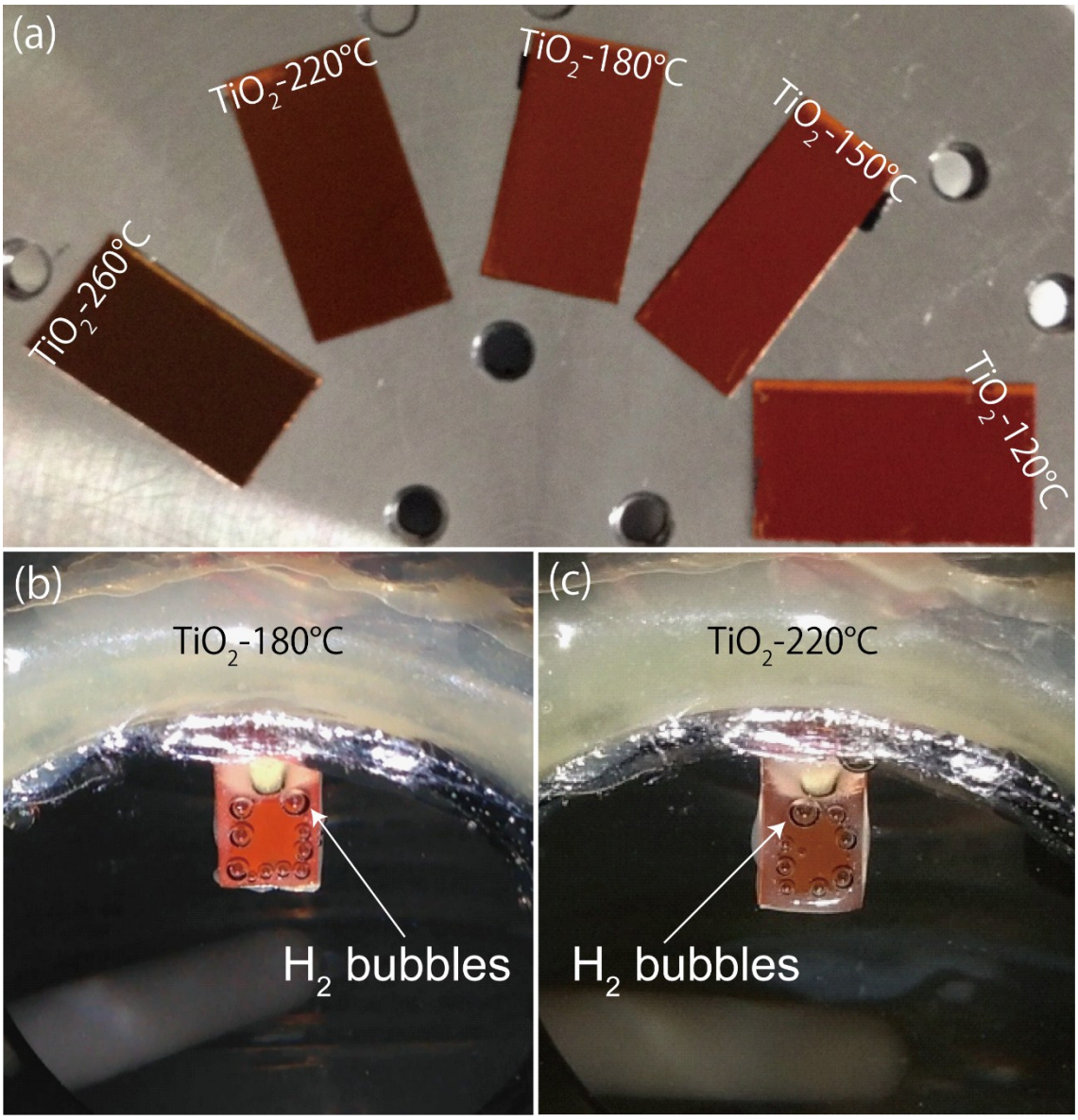

Figure S8. a) Photographs of the $TiO_2/Ga_2O_3/Cu_2O$ photocathodes prepared with different TiO_2 deposition temperatures, showing a changing color with the increase in temperature. b-c) H_2 bubbles evolving from the Pt/TiO_2(180ºC)/Ga_2O_3/Cu_2O and Pt/TiO_2(220ºC)/Ga_2O_3/Cu_2O samples under illumination of a Xe lamp at 0 V vs. RHE.

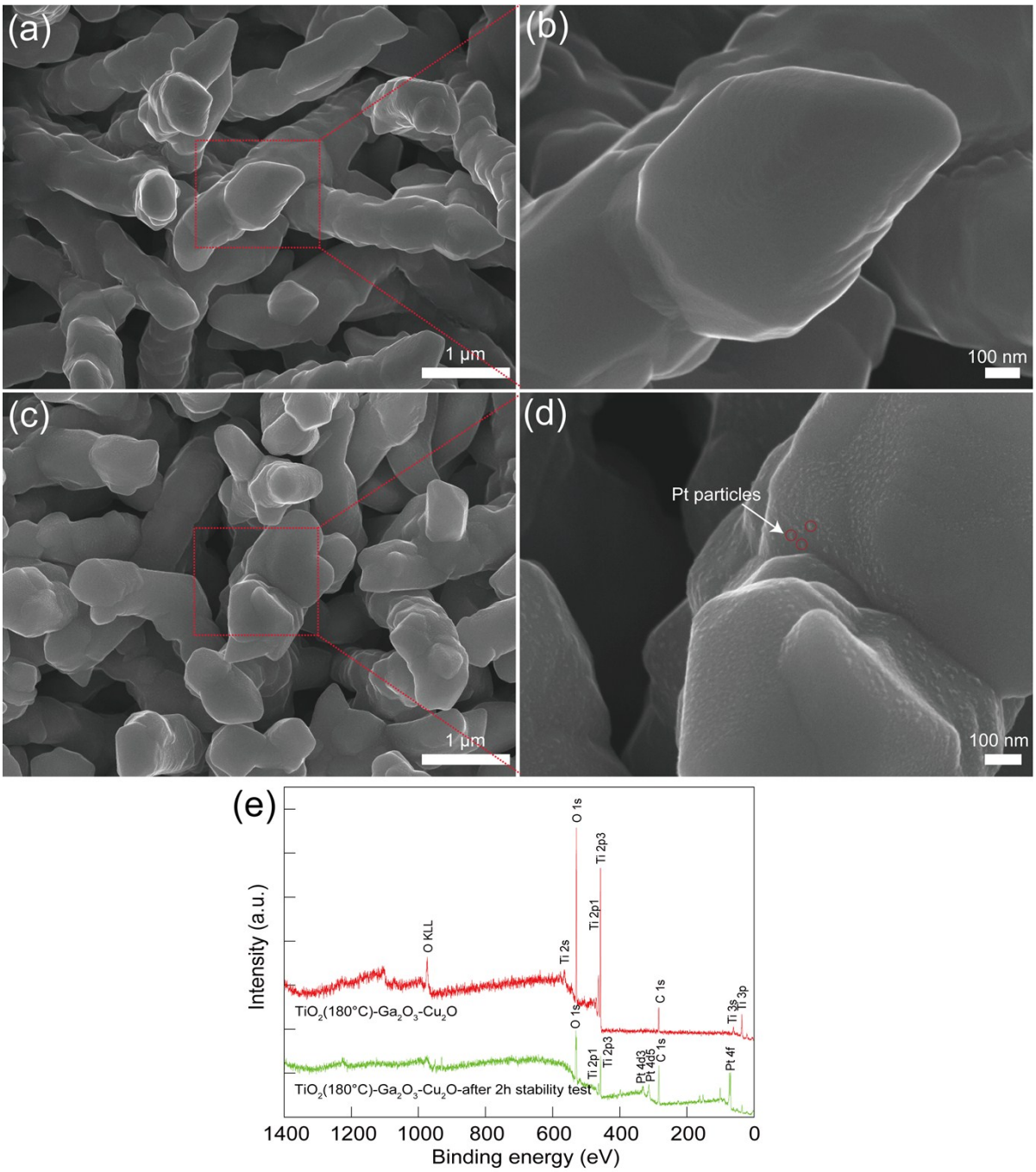

Figure S9. a-b) FE-SEM images of the TiO_2 (180ºC)/Ga_2O_3 (150ºC)/Cu_2O electrode before Pt coating and stability test. c-d) FE-SEM images of Pt/TiO_2 (180ºC)/Ga_2O_3 (150ºC)/Cu_2O electrode after 2 h stability test. e) XPS measurement results of the TiO_2 (180ºC)/Ga_2O_3 (150ºC)/Cu_2O electrode sample and Pt/TiO_2 (180ºC)/Ga_2O_3 (150ºC)/Cu_2O sample after 2 h stability test.

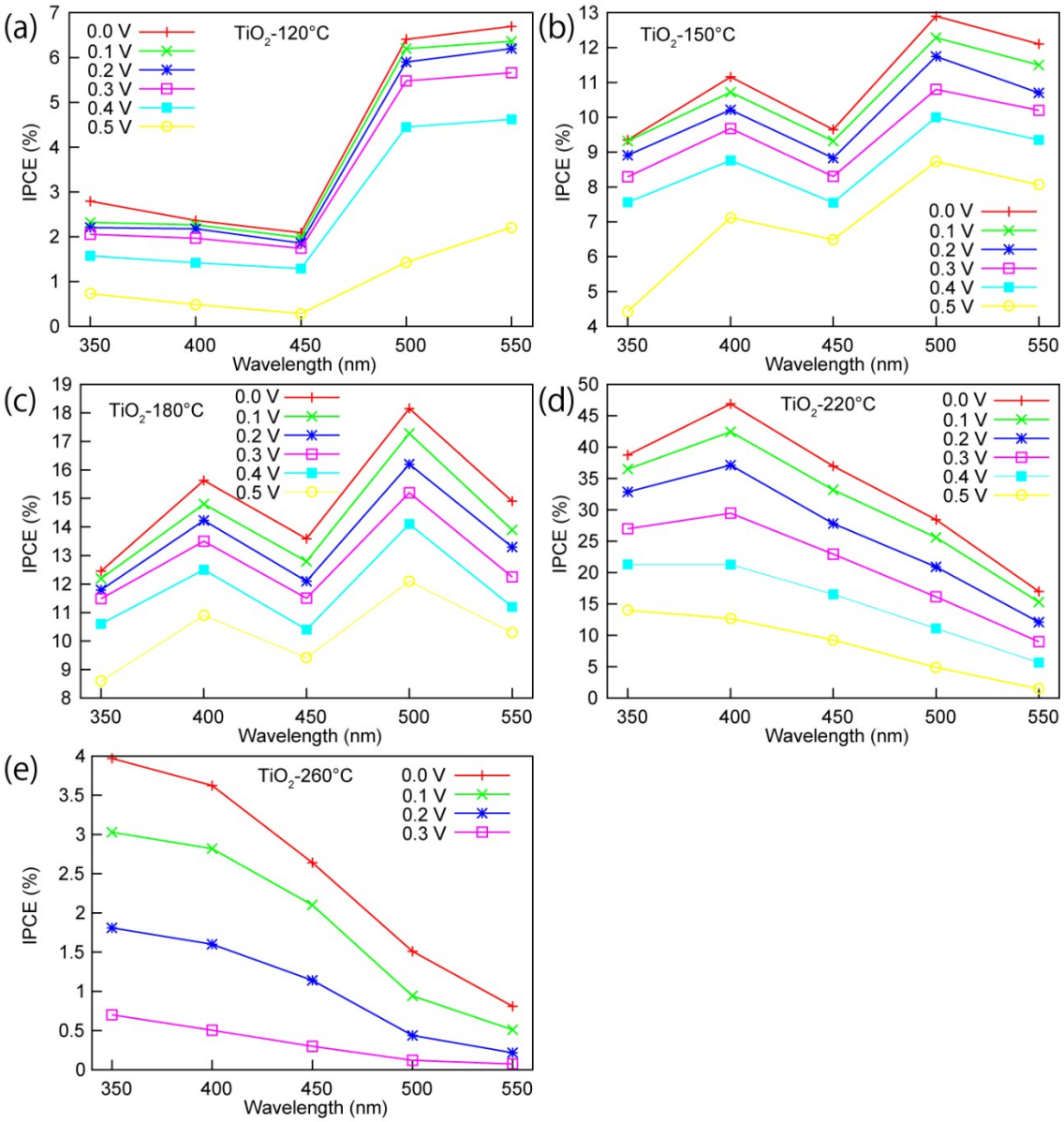

Figure S10. Wavelength dependence of IPCE for the Pt/TiO_2/Ga_2O_3/Cu_2O electrodes with a TiO_2 deposition temperature of 120 a), 150 b), 180 c), 220 d) and 260ºC e) at different applied potentials (vs. RHE).

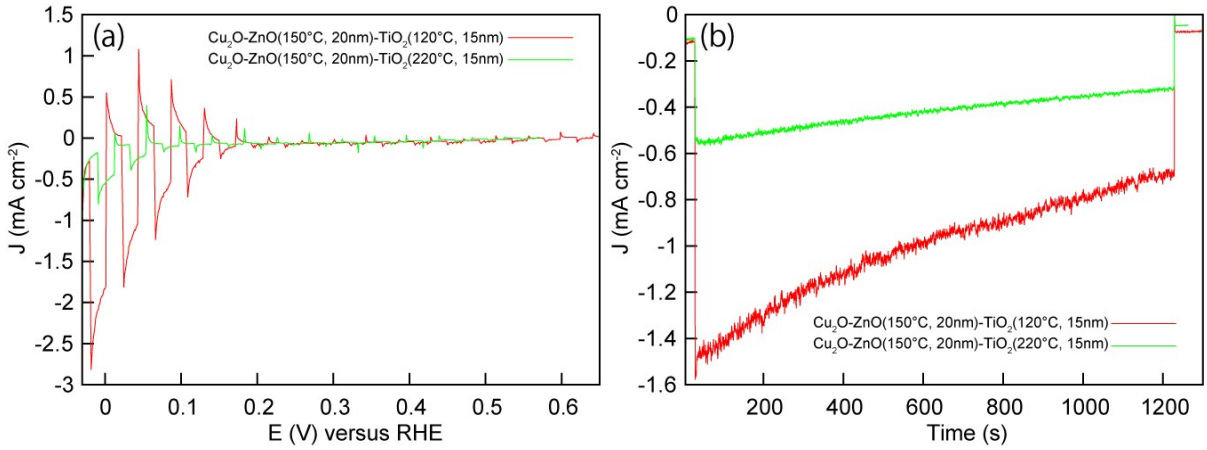

Figure S11. a) The current-potential curves for the Pt/TiO_2/ZnO/Cu_2O electrodes fabricated with TiO_2 deposition temperatures of 120 and 220ºC. The deposition temperature for ZnO was 150ºC. b) Current-time curve of the electrodes at 0 V vs. RHE under continuous light illumination. The measurements were conducted in 0.5 M Na_2SO_4-0.1 M KH_2PO_4 solution (pH = 4.26) under illumination of a 500 W Xe lamp at a scan rate 10 mV/s.

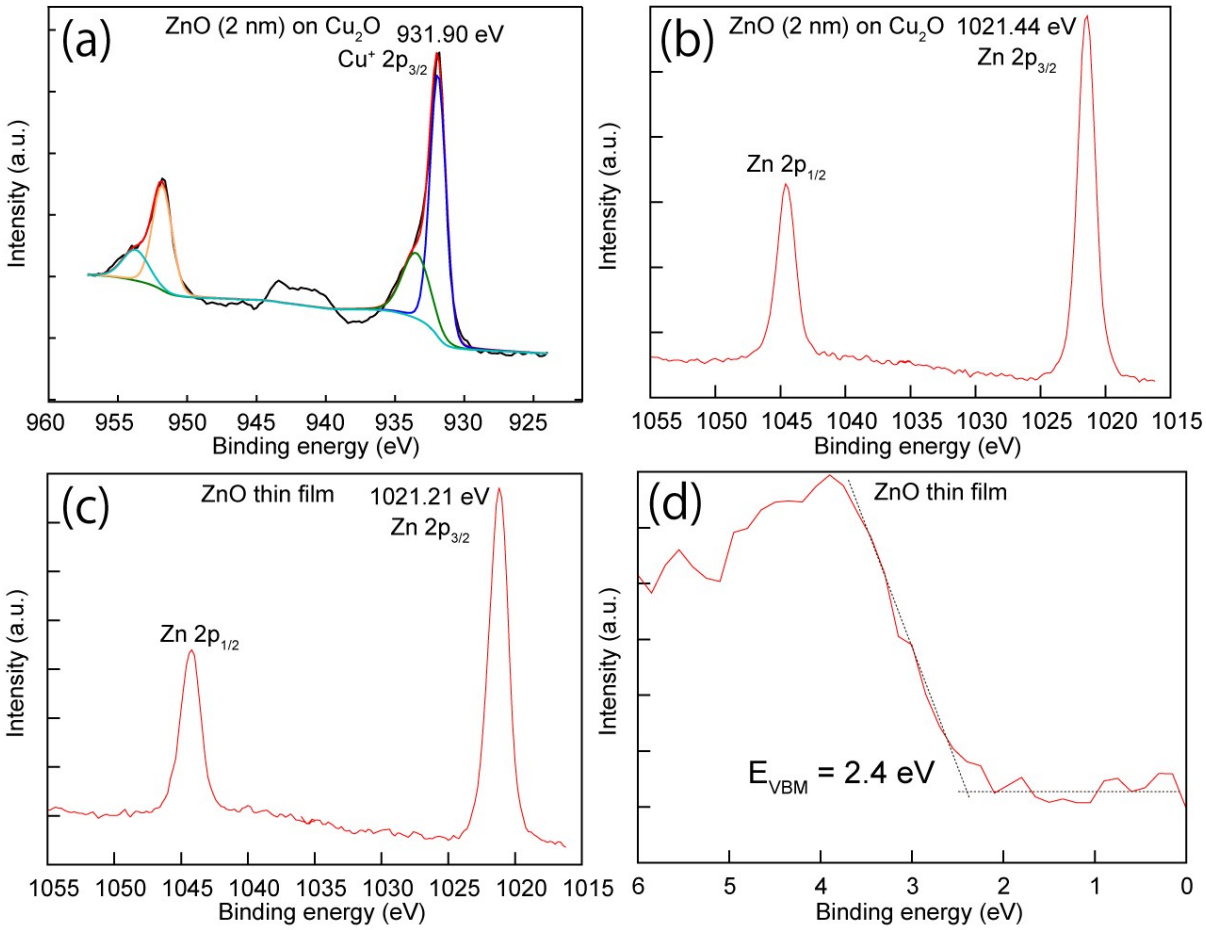

Figure S12. XPS spectra of the Cu-2p and Zn-2p core levels for the ZnO (2 nm)/Cu_2O multilayer sample a-b). The deposition temperature for ZnO is 150ºC. b-d) XPS spectra of ZnO thin film for Ga-2p core levels and valence band. By using the equation in Figure S2, the conduction band discontinuitiy ΔE_{CB} at Cu_2O/ZnO heterojunction interface is caculated to be in the range from -1.56 to -1.42 eV, in which a bandgap from 3.12 to 3.26 eV was used for ZnO.[7-9]

References

1 J. R. Waldrop, R. W. Grant, S. P. Kowalczyk and E. A. Kraut, *J. Vac. Sci. Technol. A* 1985, **3**, 835.

2 Y. S. Lee, D. Chua, R. E. Brandt, S. C. Siah, J. V. Li, J. P. Mailoa, S. W. Lee, R. G. Gordon and T. Buonassisi, *Adv. Mater.* 2014, **26**, 4704.

3 C. Li, Y. Li and J.-J. Delaunay, *ACS Appl. Mater Interfaces* 2014, **6**, 480.

4 D. J. Comstock and J. W. Elam, *Chem. Mater.* 2012, **24**, 4011.

5 T. Oshima, K. Kaminaga, H. Mashiko, A. Mukai, K. Sasaki, T. Masui, A. Kuramata, S. Yamakoshi and A. Ohtomo, *Jpn. J. Appl. Phys.* 2013, **52**, 111102

6 Y. B. Li, T. Tokizono, M. Liao, M. Zhong, Y. Koide, I. Yamada and J.-J. Delaunay, *Adv. Funct. Mater.* 2010, **20**, 3972.

7 Z. Q. Duan, A. Du Pasquier, Y. C. Lu, Y. Xu and E. Garfunkel, *Sol. Energy Mater. Sol. Cells* 2012, **96,** 292.