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The interfacial study on the $Cu_2O/Ga_2O_3/AZO/TiO_2$ photocathode for water splitting fabricated by pulsed laser deposition

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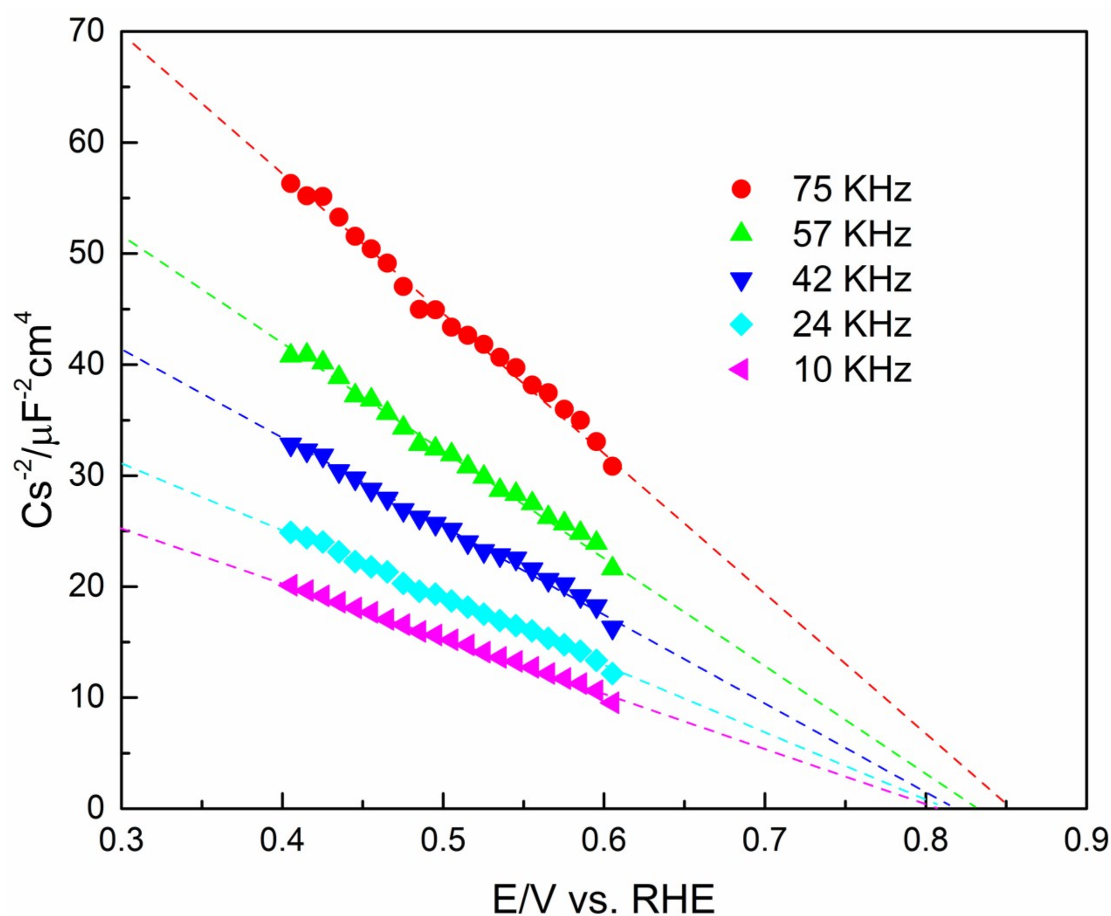

Figure S1. Mott−Schottky plot for the Cu_2O film from electrochemical impedance analysis in 0.1 M KOH solution (pH=13) in the dark.

The electrochemical impedance spectroscopy was carried out for the bare Cu_2O sample. For the bare Cu_2O, the electrolyte was 0.1M KOH in water (pH=13). The Cu_2O layer was scanned from 0.4V/RHE to 0.6V/RHE in dark and the frequencies were varied from 100KHz to 100mHz. Capacitance–voltage measurements and Mott–Schottky analysis were performed to get the flat band potential E_{fb} and the intrinsic accept density N_A in the near-surface region by the following equation:

$$\frac{1}{C^2} = \frac{2}{e\varepsilon\varepsilon_0 N_A}\left(E - E_{fb} - \frac{kT}{e}\right)$$

Where C is the space-charge capacitance of the semiconductor; e is the electron charge; ε_0 is the permittivity in vacuum; ε is the dielectric constant and E is the applied potential. The linear fit can extrapolate the flat band and the slope of the linear fit is an estimation of the charge carrier concentration. As show in Figure S1, the measured flat band potential was about +0.82 V/RHE. The carrier concentration calculated from the high frequencies was in the range from 1.7×10^{17} cm^{-3} to 4.2×10^{17} cm^{-3} using ε=6.6 of Cu_2O. We used the average value 2.95×10^{17} cm^{-3}. These values agreed with previous results.

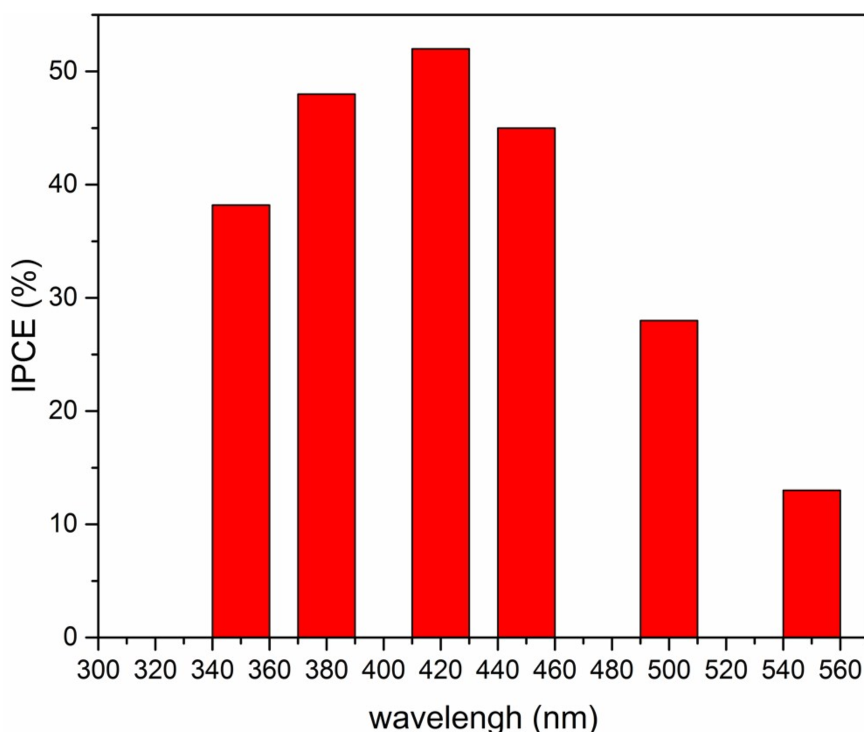

Figure S2. Wavelength dependence of IPCE measured at 0 V vs. RHE for the sample with Ga_2O_3 of 10Pa.

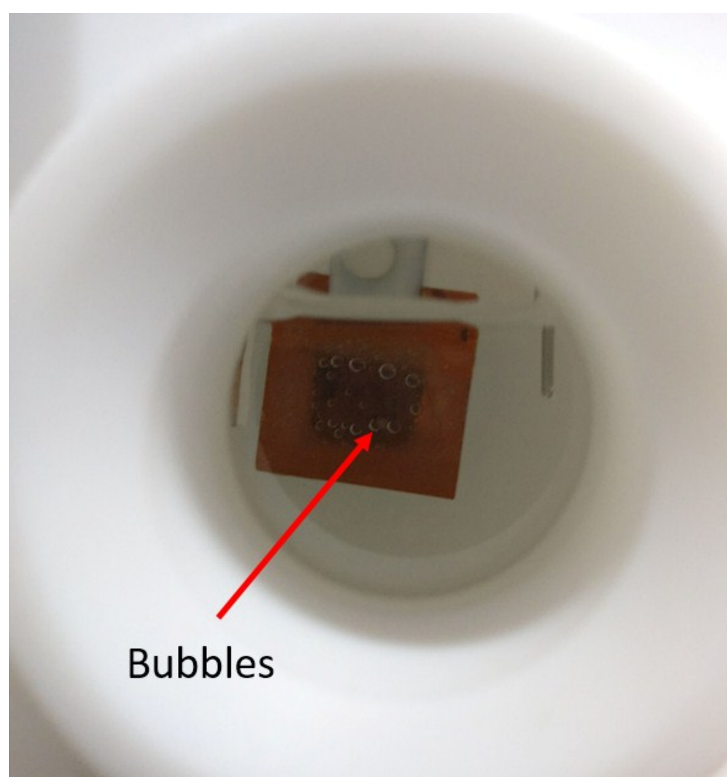

Figure S3. H_2 bubbles evolving from the illuminated photocathode biased at 0 V vs. RHE.

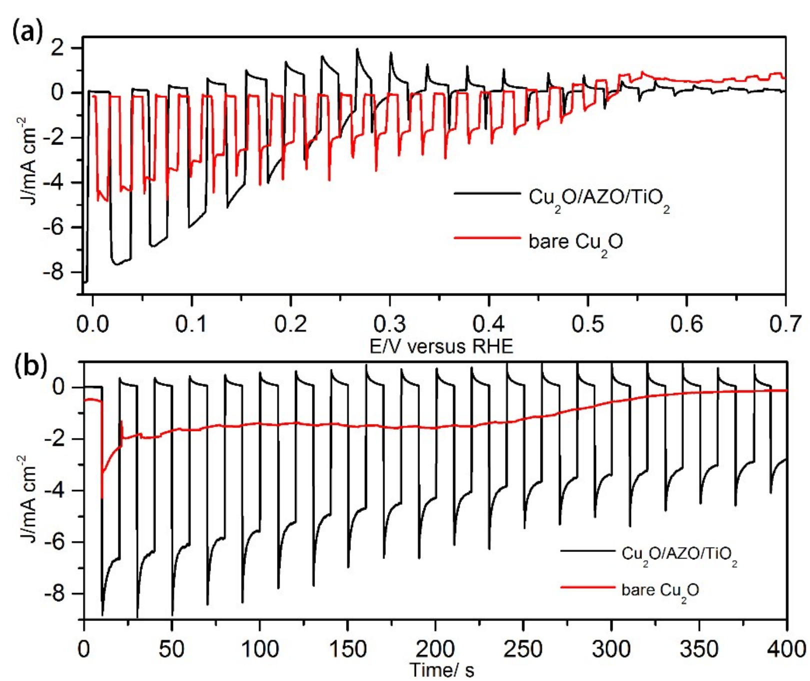

Figure S4. The photocurrent (a) and stability (b) of photocathode without the Ga_2O_3 and bare Cu_2O.

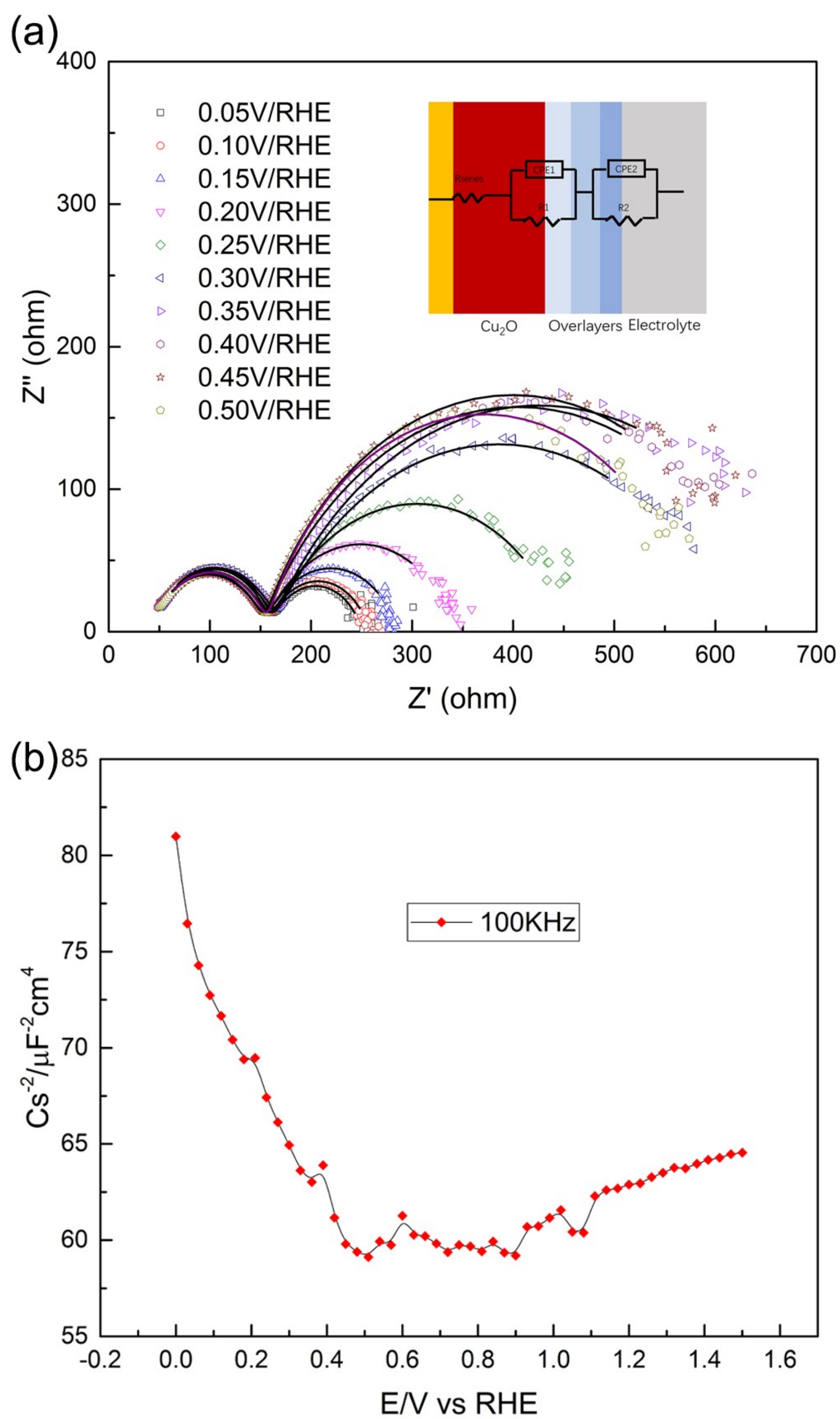

Figure S5. (a) Impedance spectra of Cu_2O/Ga2O3/AZO/TiO2 photocathode under 1 sun light. The inset shows the equivalent circuit used to fit the data. The black lines are fitted curve using this equivalent circuit. (b) Mott-Schottky (MS) plots of Cu_2O/Ga2O3/AZO/TiO2 photocathode measured at 100KHz with 10mV amplitude.

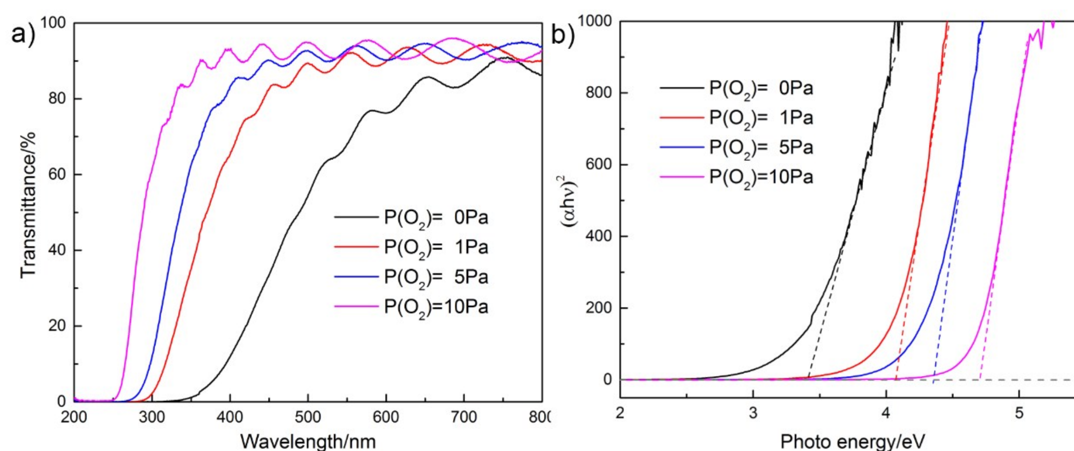

Figure S6. The transmittance (a) and the optical band gap (b) of Ga_2O_3 thin film deposited under different oxygen pressure.

Table S1 Binding energies and valence band maximum of Cu_2O layer, Ga_2O_3 layer (on Cu_2O layer). And binding energies (Ga, Cu) of the interface of Ga_2O_3/Cu_2O.

Sample	region	Binding energy (eV)
Cu_2O	Cu 2p3/2	932.49
	VBM	0.39
Ga_2O_3 ($P(O_2)$ =1 Pa)	Ga 2p3/2	1117.00
	VBM	2.54
Ga_2O_3($P(O_2)$ =1 Pa)/Cu_2O	Cu 2p3/2	932.80
	Ga 2p3/2	1117.80
Ga_2O_3 ($P(O_2)$ =10 Pa)	Ga 2p3/2	1118.22
	VBM	3.27
Ga_2O_3($P(O_2)$ =10 Pa)/Cu_2O	Cu 2p3/2	932.12
	Ga 2p3/2	1117.70

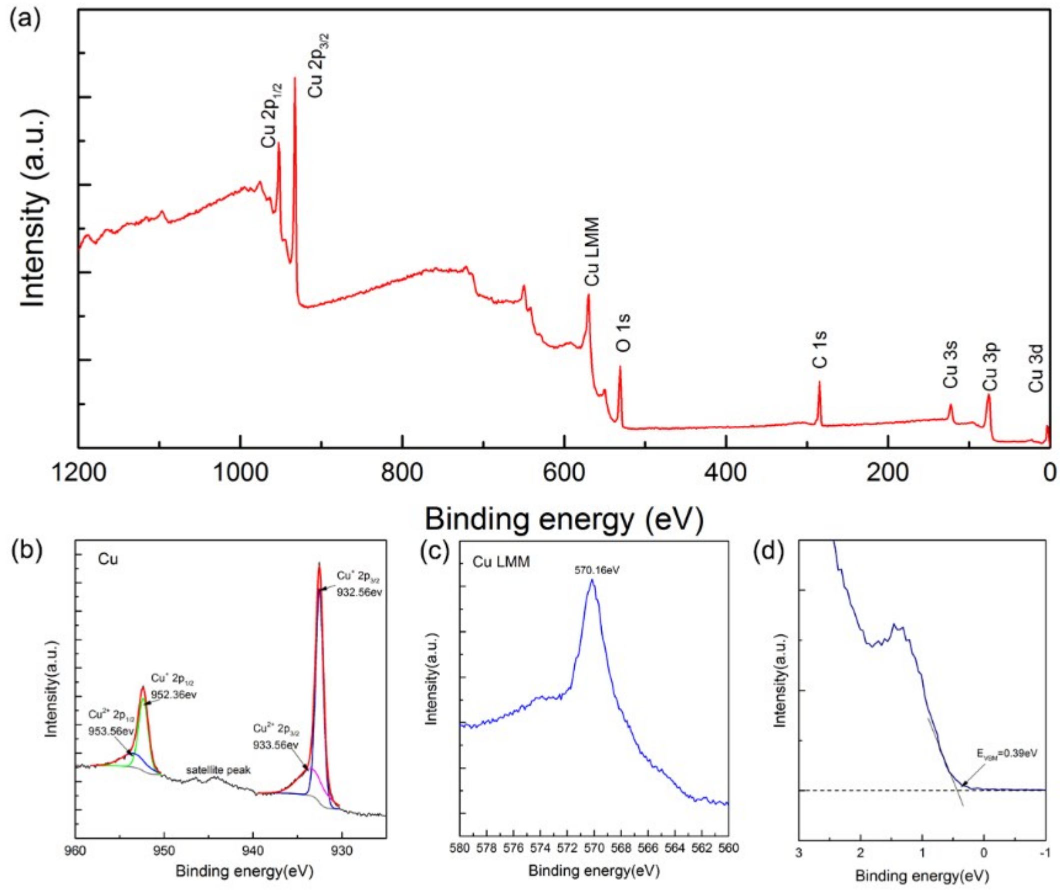

Figure S7. The XPS spectrum of the bare Cu_2O film. (a) The wide spectrum. (b) Cu 2p region. (c) Cu LMM peak. (d) The valence band maximum position.

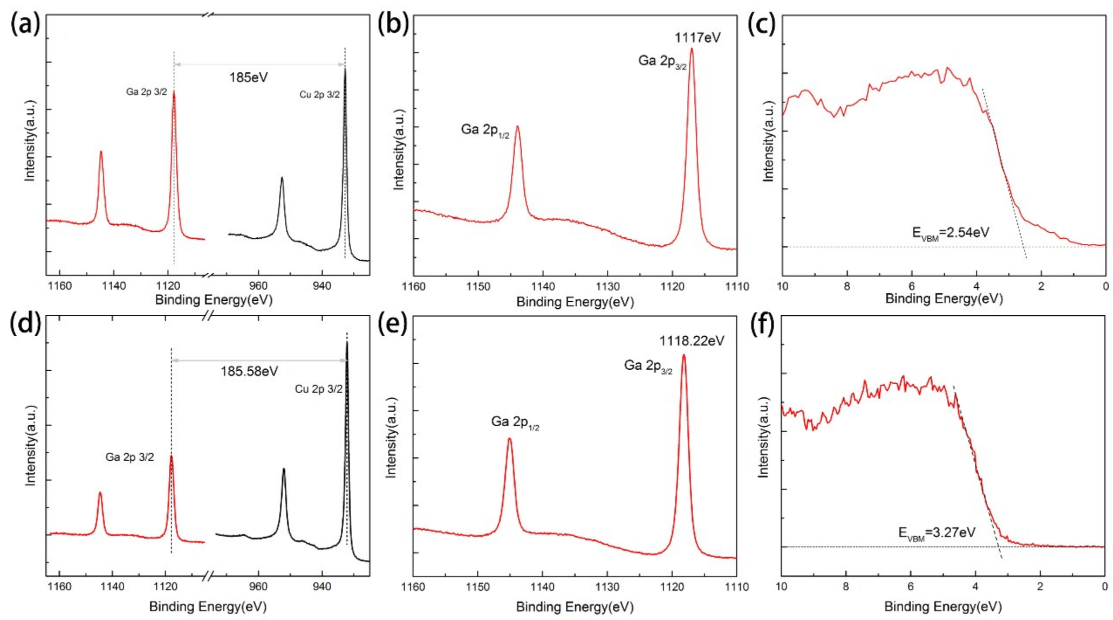

Figure S8. The Ga 2p and Cu 2p spectrum of sample with ultrathin Ga_2O_3 film on Cu_2O (a)(d), the Ga 2p spectrum (b)(e) and VBM spectrum (c)(f) of sample with thick Ga_2O_3 film on Cu_2O under the oxygen pressure for Ga_2O_3 deposition of 1Pa (a)(b)(c) and 10Pa (d)(e)(f).

The ΔE_{CB} at Cu_2O/Ga_2O_3 heterojunction was calculated according the following equation:

$$\Delta E_{CB} = \left(E_{Ga\text{-}2p}^{Ga_2O_3/Cu_2O} - E_{Cu\text{-}2p}^{Ga_2O_3/Cu_2O}\right) + \left(E_{Cu\text{-}2p}^{Cu_2O} - E_{VBM}^{Cu_2O}\right) - \left(E_{Ga\text{-}2p}^{Ga_2O_3} - E_{VBM}^{Ga_2O_3}\right) + \left(E_{Eg}^{Cu_2O} - E_{Eg}^{Ga_2O_3}\right).$$

The $\left(E_{Ga\text{-}2p}^{Ga_2O_3/Cu_2O} - E_{Cu\text{-}2p}^{Ga_2O_3/Cu_2O}\right)$ was obtained from the Cu_2O sample with an ultrathin Ga_2O_3 layer.

The bandgap of the bulk Cu_2O were 2.1eV, and that of Ga_2O_3 was 4.07 and 4.69eV for oxygen pressure of 1Pa and 10Pa respectively, which is extracted from Figure S3.

Band diagram

First, to form the p-n junction, all the Fermi levels of these layers will be equivalent. In the solution at 0V/RHE, all the Fermi level are equivalent at the hydrogen redox potential. We assume the pinning of band edge at the interface.

Even though Ga_2O_3 is a n-type semiconductor, the carrier concentration of amorphous Ga_2O_3 is very low, which can be indicated by the valence band edge in the XPS data. We tried to measure it by Hall system using van der Pauw method. But it also showed it is unmeasurable. Apparently, the electron concentration is not enough to form the p-n junction. Here, we can think nearly all the electrons are from the AZO layer, because the electron concentration of AZO is much higher than that of Ga_2O_3.We can estimate the thickness of the depletion layers by the equation:

$$N_D x_n = N_A x_p$$

Where N_D and N_A are the carrier concentration in AZO and Cu_2O, and x_n and x_p are the thickness of depletion layer in AZO and Cu_2O. The N_A of Cu_2O is calculated to be about 2.95×10^{17} cm^{-3} while the N_D of AZO is up to 10^{21} cm^{-3}. Most of the depletion layer of p-n junction is in the Cu_2O side. Further with the equation:

$$V_{bi}(p) = \frac{qN_A x_p^2}{2\varepsilon_{Cu_2O}}$$

For the expected build-in bias of 0.4V and 0.8V, which is estimated from Fig. 5(c), the depletion layer thickness in the Cu_2O (x_p) is approximately 140nm and 197nm.

For the Ga_2O_3 at the Cu_2O/Ga_2O_3 and Ga_2O_3/AZO, the bending offset was determined mainly by the energy offset between the Fermi level and the hydrogen redox potential while the thickness of the depletion layer was not easy to estimate. What can we know is, on one hand, the thickness of n-type Ga_2O_3 at the Cu_2O/Ga_2O_3 interface should be wide to form the p-n junction. On the other hand, there will be also a downward bending of Ga_2O_3 at the n-Ga_2O_3/n-AZO junction interface due to the different doping level.

As for the interface of AZO/TiO_2 and TiO_2 electrolyte, we assume the pinning of the band edge at the interface as the way from the literature. The electron concentration of these two layers is very high, So the thickness of depletion layers will be very thin

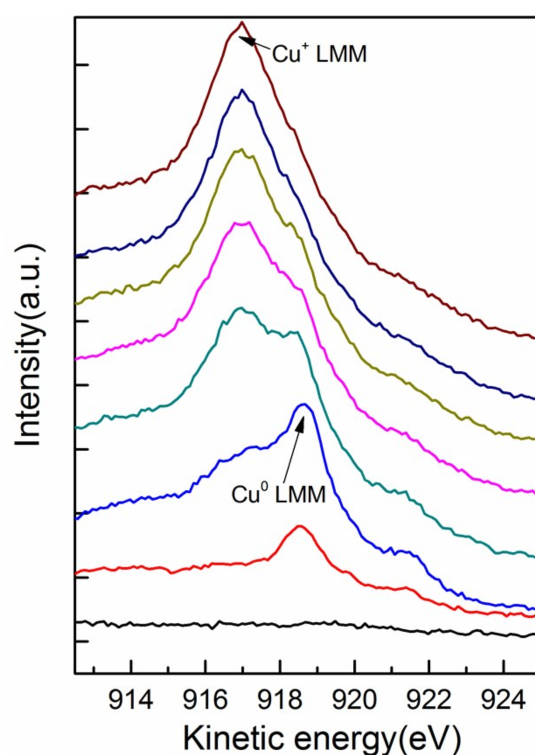

Figure S9. Cu LMM depth profiling as the etching time increase for the sample under oxygen pressure of 1Pa.