# Supplementary Information

## Complete Surface Coverage of ZnO Nanorod Arrays by Pulsed electrodeposited $CuInS_2$ for Visible Light Energy Conversion

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### Experimental details

Preparation of a ZnO nanorod film on a FTO substrate

A ZnO nanorod film was prepared by a chemical bath deposition (CBD) method. A seeding technique was used prior to CBD process, involving the formation of ZnO seed particles on the cleaned FTO substrate by the thermal decomposition of zinc acetate. [1] The FTO substrates were pre-cleaned with Milli-Q water, ethanol (99.5%, Sigma-Aldrich) and acetone (99.8%, Chem-Supply) under mild sonication followed by drying in vacuum before use. Several drops of a solution containing 0.005 mol/L of zinc acetate (Ajax Finechem) dissolved in ethanol were applied on the transparent FTO substrates. After 10 seconds, the substrate was rinsed with ethanol and dried with nitrogen gas. The dropwise process with zinc acetate was repeated for five times before calcined for 20 min at 350 °C to form ZnO seeds from thermal decomposition of zinc acetate. The whole seeding procedure was repeated for two times to obtain an evenly distributed ZnO seed layer on the FTO substrate.

After that, the seeded substrate was sealed in a scotch bottle with 100 mL aqueous solution consisted of half 0.05 mol/L of zinc nitrate (98%, Sigma-Aldrich) and half 0.05 mol/L of hexamethylenetetramine (99%, Sigma-Aldrich), commonly used as a structure-directing agent.[2] Each solution was preheated to 90°C for 5 min before mixing together to speed up the reaction in the CBD process. The bottle was then kept in the oven at 90°C for 3 h for the first growth cycle. The second cycle was done by simply topping up fresh solutions and repeating the first cycle. The obtained ZnO nanorod thin films were rinsed thoroughly in Milli-Q water and dried in air. At last, the transparent ZnO nanorod film was calcined for 30 min at 450 °C to completely remove the remaining organic components.

Preparation of $CuInS_2$ nanoparticles on the ZnO nanorod film

$CuInS_2$ nanoparticles on the ZnO nanorod film were deposited by a pulsed electrodeposition method, the resultant ZnO/FTO film as the working electrode and a Pt foil as the counter electrode. The $CuInS_2$ nanoparticles was deposited electrochemically by applying a repetitive on-

off time square pulse generated by a functional generator (TG4001, Thurlby Thandar Instruments), applying a cathodic pulse (-1.25 V, 100 ms) and short-circuit pulse (0 V, 100 ms) alternatively. Depending on the electrolyte chosen, two pulsed electrodeposition methods, namely simultaneously pulsed electrodeposition and sequential pulsed-electrodeposition, were chosen to deposit $CuInS_2$ on ZnO nanorods. The details of the precursors as well as the sample names chosen for the pulsed electrodeposition are presented in the table below. For a simultaneously pulsed electrodeposition, i.e. "simultaneous Cu and In deposition" sample, 60 mL of an aqueous solution containing 10 mmol/L of $CuCl_2$ (99.9%, Ajax Finechem), 10 mmol/L of $InCl_3$ (98%, Sigma-Aldrich) and 100 mmol/L of $Na_2S_2O_3$ (98%, Sigma-Aldrich) was chosen for the electrolyte in the two-electrode cell. Similarly, for a sequential pulsed-electrodeposition, the same concentrations of Cu/In/S precursors were deposited in two steps, namely (1) "Cu deposition followed by In" and (2) "In deposition followed by Cu" samples.

**Table S1**: Experimental sequences for $CuInS_2$-ZnO obtained from simultaneous and sequential pulsed-electrodeposition.

| Method Name | Sample Name | Precursors for Pulsed Electrodeposition | |
|---|---|---|---|
| **Simultaneously PED** | "simultaneous Cu and In deposition" | Step 1: $CuCl_2$, $InCl_3$, $Na_2S_2O_3$ | |
| **Sequential I PED** | "Cu deposition followed by In" | Step 1: $CuCl_2$, $Na_2S_2O_3$ | Step 2: $InCl_3$ |
| **Sequential II PED** | "In deposition followed by Cu" | Step 1: $InCl_3$, $Na_2S_2O_3$ | Step 2: $CuCl_2$ |

The-obtained $CuInS_2$/ZnO film was dried and annealed at 500 °C for 1 h in a gas mixture of 92% $N_2$ and 8% $H_2$ to facilitate crystallization. Before the heating, $N_2$ was purged through the tube furnace for 2 h to completely remove the air. Subsequently, the heating was performed with the ramping rate of 5 °C/min from room temperature to 500°C. The gas flow rate was maintained at 50 mL/min throughout the process.

Characterization of the obtained $CuInS_2$-ZnO films

The crystallographic phase structures of the deposited films were characterized using an X-ray diffractometer (X'pert Pro MRD, Philips) with Cu $K_\alpha$ radiation at 45 kV and 40 mA, a step size of 0.013° and a scan step time at 97.92 s in the 2θ range of 25° to 60°. The morphological features were determined using a scanning electron microscope (SEM, S900 Hitachi). The UV-Vis diffuse reflectance spectra were obtained using a UV/Vis/NIR spectrophotometer (Perkin Elmer LAMBDA 1050) with GaP (1200-900nm) and Si (900-250nm) detectors. A high-resolution transmission electron microscopy (HRTEM, CM200 Philips) was employed to examine the lattice fringes of electrodeposited $CuInS_2$ and ZnO crystals, as well as the interface between the $CuInS_2$ nanoparticles and the ZnO nanorod film. The $CuInS_2$ film thickness can be estimated from the TEM image of an individual ZnO nanorod after coating (Figure S4). Elemental mapping of the resultant $CuInS_2$-ZnO was performed using SEM-EDAX. See Figure S5 for the results.

Photoelectrochemical (PEC) characterization

The photoelectrochemical properties of the $CuInS_2$-ZnO films were examined under potentiostatic conditions in a three-electrode system using $CuInS_2$-ZnO films as the working electrode, Ag/AgCl as the reference electrode and a platinum wire as the counter electrode in an aqueous solution containing 0.25 mol/L of $Na_2S$ and 0.35 mol/L of $Na_2SO_3$ at pH 12. An electrolytic cell made out of Teflon with a flat quartz window was used. The photocurrent responses were measured under visible light illumination using a 300 W Xenon lamp with a cut off filter ($\lambda \geq 435$ nm). The illuminated area of the working electrode was fixed at 0.196 $cm^2$.

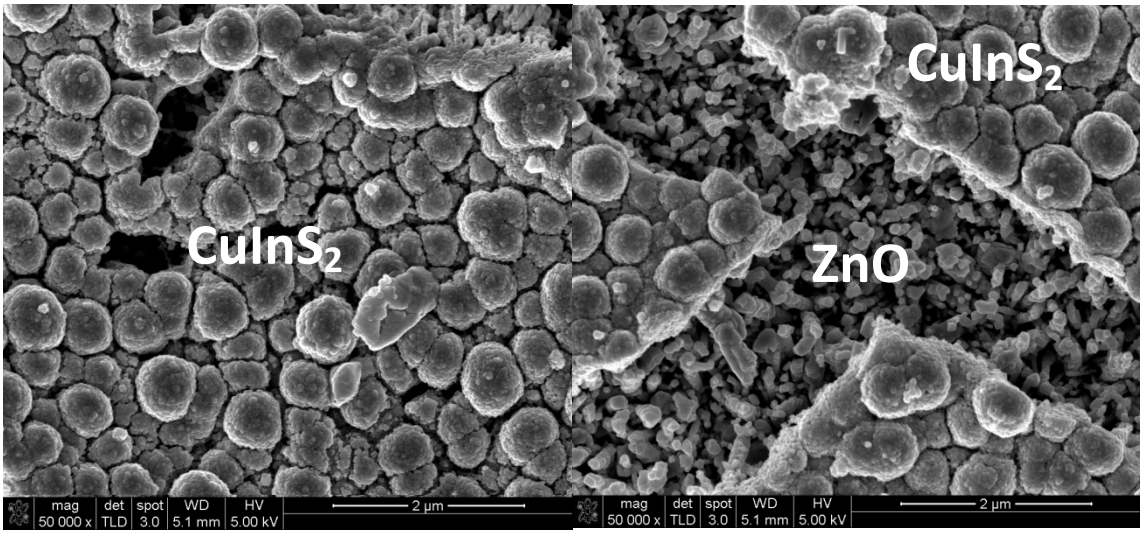


**Figure S1** Surface morphology of $CuInS_2$-ZnO from non-pulsed electrodeposition for 10 min using Cu/In/S precursors in the electrolyte

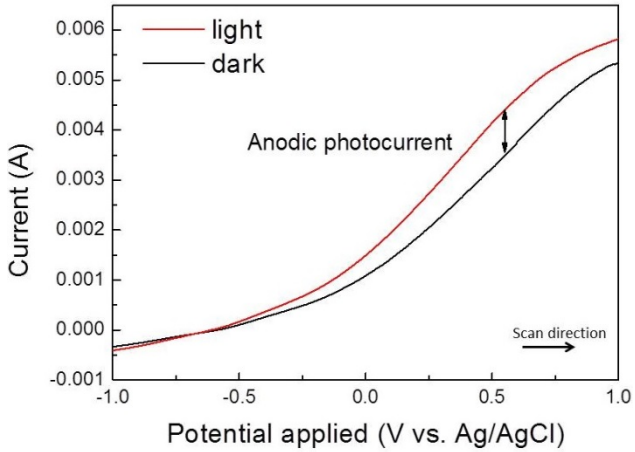


**Figure S2** Current-voltage curve of $CuInS_2$ (reference electrode: Ag/AgCl)

The $CuInS_2$ prepared in this work is an n-type semiconductor. The n-type behavior of $CuInS_2$ is indicated by the current-voltage measurement in Figure S2. The anodic photocurrent generated upon visible light (> 435 nm) verified its n-type nature.

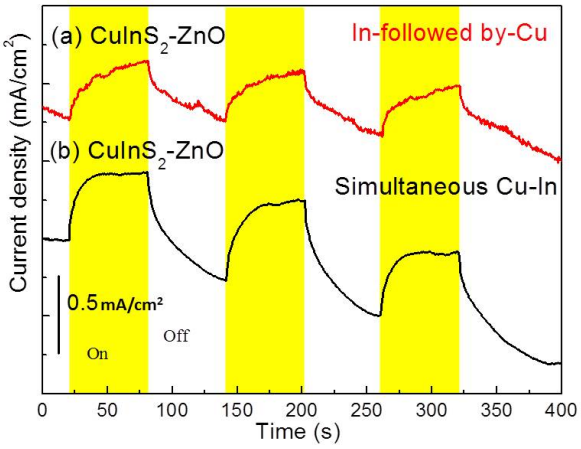


**Figure S3** Photocurrent response of pulsed electrodeposited $CuInS_2$-ZnO under different conditions at 0.75 V vs. Ag/AgCl in electrolyte containing 0.25 mol/L $Na_2S$ and 0.35 mol/L $Na_2SO_3$ (pH = 12) under visible light irradiation ($\lambda \geq 435$ nm)

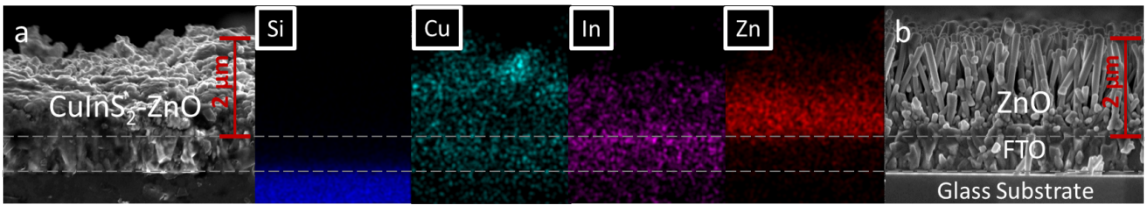


**Figure S4** (a) Cross-sectional SEM image and SEM-EDX mapping of $CuInS_2$-ZnO using "Cu deposition followed by In" method (b) Cross-sectional SEM image of bare ZnO

Film thicknesses of ZnO and $CuInS_2$-ZnO films were estimated from the cross-sectional SEM images as shown below. The bare ZnO nanorods film has the thickness of ~2 μm while the $CuInS_2$-ZnO composite is thinner at ~1.3 μm on average. The complementary EDAX elemental mapping of $CuInS_2$-ZnO film supports the identification of the individual component in the composite film. The thinner $CuInS_2$-ZnO layer was also evident by the lower XRD peak intensity for ZnO (Figure 1, manuscript) as compared with the bare ZnO film. The shortened ZnO is attributed to its chemical dissolution promoted by the $H^+$ released from the metallic precursors. This is confirmed by the detection of dissolved Zn in the electrolyte after the electrodeposition using ICP analysis.

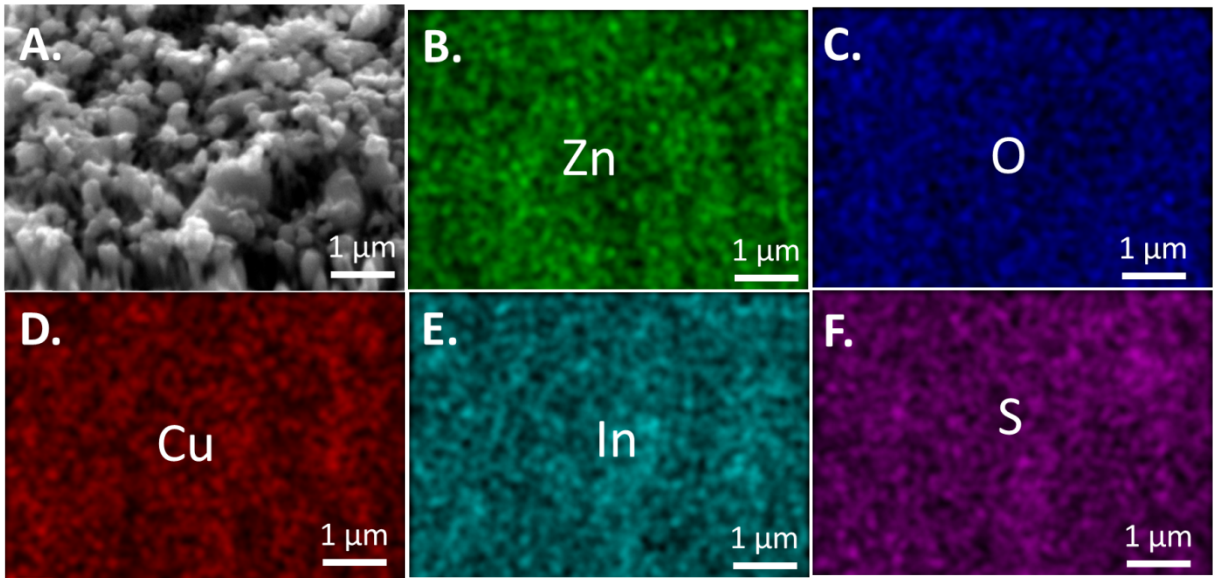


**Figure S5** SEM-EDAX mapping of $CuInS_2$-ZnO film

The elemental mapping of the tilted top view over a considerable area of $CuInS_2$-ZnO confirms the presence of elemental Cu, In, S, Zn and O. Good homogeneity of the electrodeposition is achieved. Combined with the HRTEM image analyzing the interface, ZnO nanorods have been successfully deposited with $CuInS_2$.

References

[1] L. Vayssieres, *Adv. mater.,* 2003, **15**, 464.
[2] L. Vayssieres, K. Keis, S.-E. Lindquist and A. Hagfeldt, *J. Phys. Chem. B*, 2001, **105**, 3350 .