

Electronic Supplementary Information

Wrapping the walls of n-TiO₂ nanotubes with p-CuInS₂ nanoparticles using pulsed-electrodeposition for improved heterojunction photoelectrodes

Jung-Ho Yun^a, Yun Hau Ng^a, Shujuan Huang^b, Gavin Conibeer^b and Rose Amal^{a*}

^aARC Centre of Excellence for Functional Nanomaterials, School of Chemical Engineering,

^bARC Photovoltaics Centre of Excellence, the University of New South Wales, Sydney NSW
2052 Australia.

Fax: +612-9385-5966; Tel: +612-9385-4361; Email: r.amal@unsw.edu.au

Experimental details

Anodization of TiO₂ nanotube (TNT) array: The TNT array was prepared by anodizing Ti foil (99.7 %, Aldrich) with 20 x 20 x 0.127 mm dimension in ethylene glycol based fluoride electrolyte. The Ti foils were first cleaned with acetone in mild sonication and Milli-Q water followed by vacuum drying before anodization. The electrolytes were prepared by mixing ethylene glycol (> 99 %, Aldrich) and 0.5 wt. % of NaF (99 %, Ajax Chemicals) with water of 5 wt. %. A two-electrode system was used for anodization, with Ti foil as the anode, and platinum plate and wire as the cathode. An in-house designed sealed anodic cell was used as the reactor. A constant distance was maintained between electrodes, and the area of anode exposed to the electrolyte was controlled. A programmable DC power supply (PST-3201, GW Instek) interfaced with a computer was used to monitor the anodization current density. An applied potential of 60 V and an anodization time of 1 h were employed. After anodization, the TNT array samples were rinsed with Milli-Q water in a sonication bath to remove debris of broken tubes, and dried at 110 °C for 1 h, followed by calcination at 450 °C for 3 h with a ramping rate of 5 °C min⁻¹ in air.^[1]

Fabrication of CuInS₂-TiO₂ nanotube (CIS-TNT) heterojunction photoelectrode: To fabricate CIS-TNT p-n heterojunction photoelectrode, prior to deposition of CIS onto the TNT, the calcined TNT array was placed in the sealed anodic cell, in which the CIS was deposited electrochemically by applying a square pulse with a switch to a cathodic pulse (-2 V, 200 ms) and short circuit pulse (0 V, 200 ms) ; the pulse was employed by a function generator (TG4001, Thurlby Thandar Instruments). The CIS precursor solution was prepared with CuCl₂, InCl₃, and Na₂S₂O₃ in molar ratio of 1 : 0.8 ~ 1.65 : 4 ~ 10. After CIS deposition, the

CIS-TNT array samples were annealed at 500 °C for 1 h with ramping rate of 5 °C min⁻¹ in a tube furnace under Ar gas stream.

Photoelectrochemical measurement: Cathodic or anodic current analyses of pure CIS samples prepared by using different precursor molar ratio were taken in 0.1 M LiCl at room temperature at short-circuit condition using Autolab potentiostat (model PGSTAT302N). Photocurrent density analyses of TNT and CIS-TNT samples were performed in 0.1 M Na₂S and 0.02 M Na₂SO₃ under 1 V at room temperature. Prior to measurement, all electrolytes were purged with Ar gas for 10 mins. In all measurements, Pt and Ag/AgCl were employed as counter and reference electrode, respectively. Xe lamp with cut-off filter (420 or 435 nm) was used as the light source.

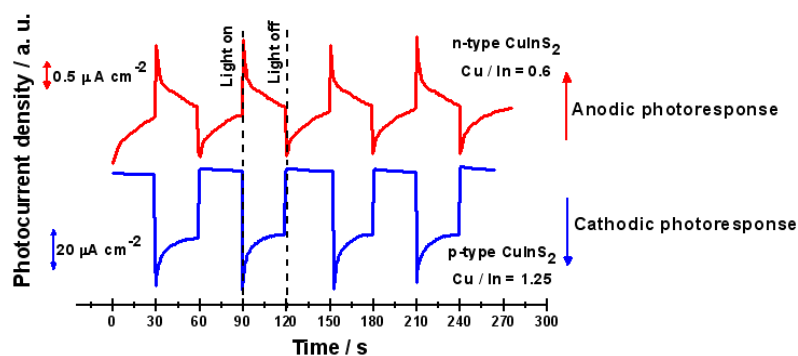


Figure S1. Visible light responses of CIS layers coated on FTO conductive glass with different molar ratio of CIS precursors in 0.1 M LiCl under short circuit condition (The light source was 300 W Xe-lamp with UV cut off filter ($\lambda \geq 420$ nm)).

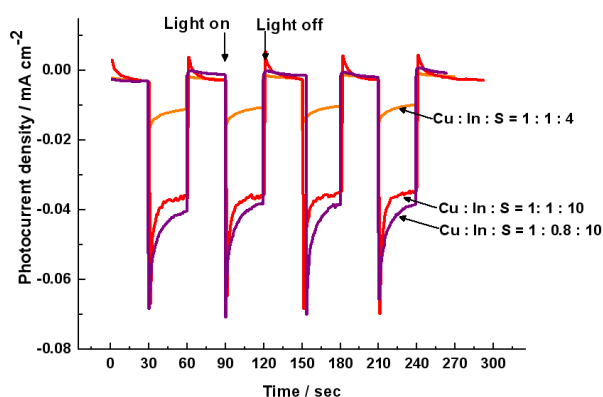


Figure S2. Photocurrent density of CIS layers controlled by electrodeposition with different molar ratio of Cu : In : S in CIS precursor solution. in 0.1 M LiCl under short circuit condition (The light source was 300 W Xe-lamp with UV cut off filter ($\lambda \geq 420$ nm)).

Although the concentration of S in the precursors is not critical in determining the type of semiconductor, the presence of a higher amount of S generates higher photocurrent density.

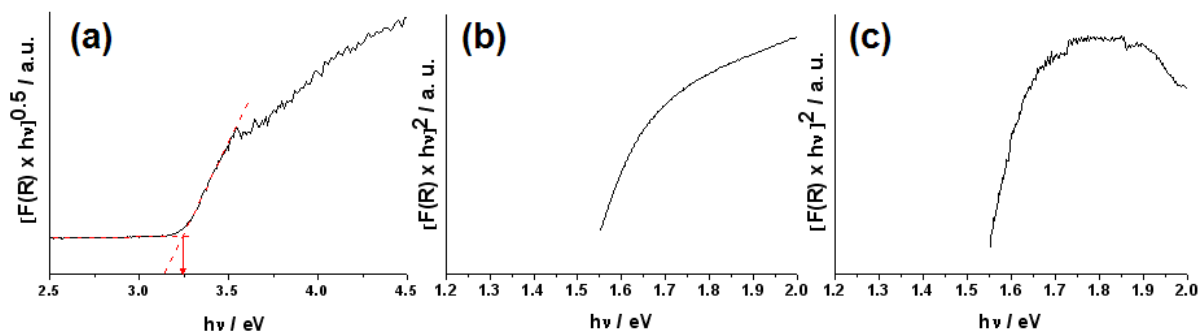


Figure S3. Diffuse reflectance UV spectra of (a) pure TNT array, (b) pulsed-electrodeposited-pure CIS layer on Ti foil, and (c) pulsed-electrodeposited CIS-TNT array in molar ratio of Cu : In : S = 1 : 0.8 : 10 in CIS precursor solution.

The pure TNT exhibits wide band gap energy with UV-only activation while CIS-TNT shows extended absorption into visible light region, similar with that of the pure CIS sample.

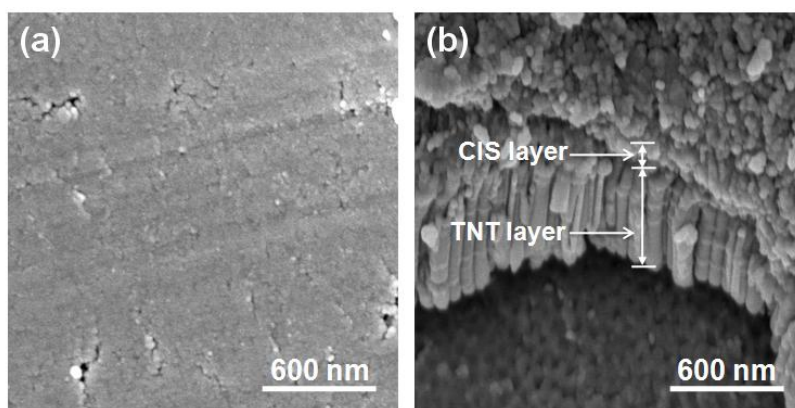


Figure S4. (a) Top and (b) cross-section SEM images of CIS-TNT array by non-pulsed electrodeposition.

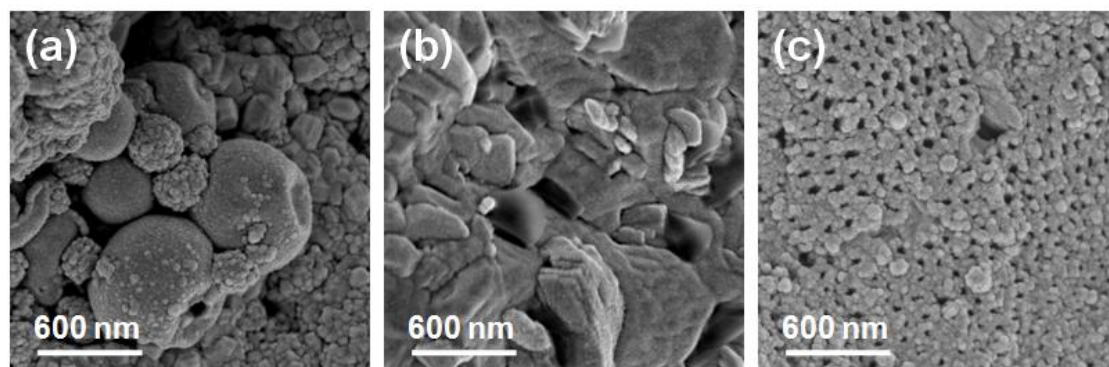


Figure S5. Top view SEM images of CIS-TNT array with different pulse relaxation in pulsed-electrodeposition with the molar ratio of Cu : In : S = 1 : 0.8 : 10 in CIS precursor solution : (a) 20 ms pulse, (b) 50 ms pulse, (c) 200 ms pulse.

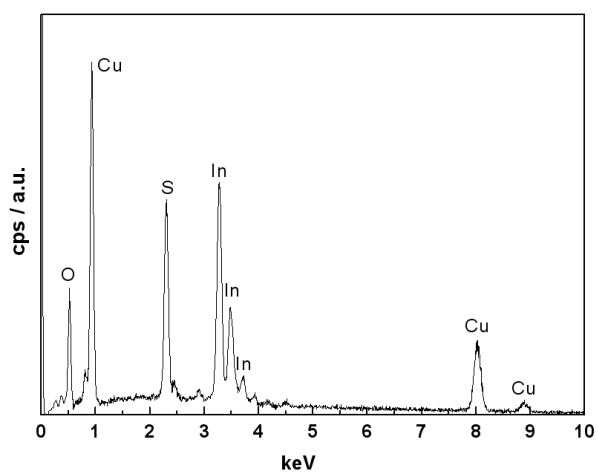


Figure S6. EDX analysis of the pulsed-electrodeposited CIS-TNT array with the molar ratio of Cu : In : S = 1 : 0.8 : 10 in CIS precursor solution.

Energy dispersive X-ray (EDX) spectrum was obtained from the bulk CIS-TNT bundle. This reveals that the nanoparticles deposited on the nanotubes are mainly composed of Cu, In and S.

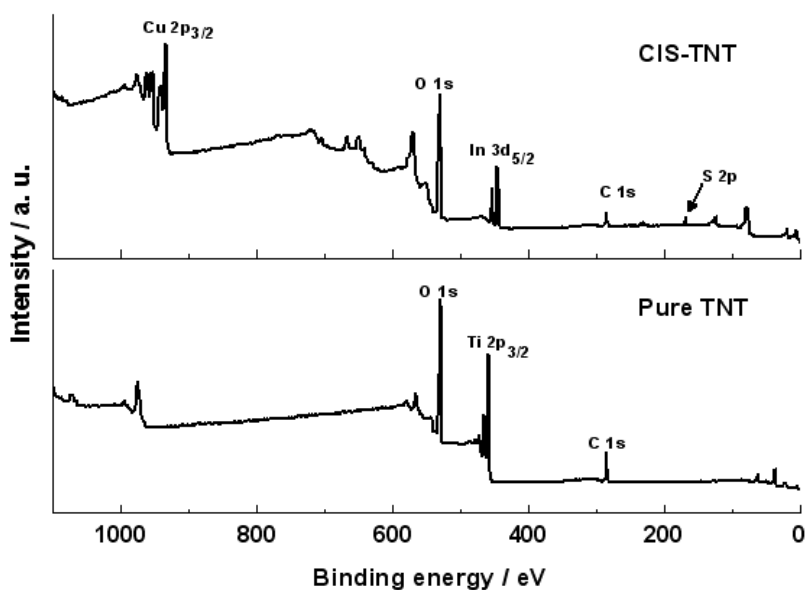


Figure S7. XPS survey spectra of CIS-TiO₂ array using pulsed-electrodeposition with the molar ratio of Cu : In : S = 1 : 0.8 : 10 and TiO₂ array prepared by anodising condition of 60 V and 1 h in ethylene glycol based-electrolyte containing 0.5 wt. % NaF and 5 wt. % water.

In **Figure S7**, XPS survey spectra of CIS-TiO₂ shows the existence of Cu, In, S, C, and O elements. Binding energies of Cu 2p_{3/2}, In 3d_{5/2}, S 2p, C 1s and O 1s are 932 eV, 952 eV, 169 eV, 286 eV, and 531 eV, respectively. The binding energies of Cu 2p_{3/2}, In 3d_{5/2}, and S 2p indicate a good agreement with those of CIS composite.^[2] On the other hand, Ti 2p was not detected in the XPS spectrum of CIS-TiO₂ layer. While TiO₂ is detected in the bulk crystal structure analysis in XRD, the absence of Ti element in XPS surface analysis confirms the CIS layer is covered on the TNTs.

References

1. J. -H. Yun, Y. H. Ng, C. Ye, A. J. Mozer, G. G. Wallace, R. Amal, *ACS Appl. Mater. Interfaces.*, 2011, **3**, 1585.
2. A. Katerski, A. Mere, V. Kazlauskienė, J. Miskinis, A. Saar, L. Matisen, A. Kikas, M. Krunkas, *Thin Solid Films*, 2008, **516**, 7110.