Wrapping the walls of n-TiO$_2$ nanotubes with p-CuInS$_2$ nanoparticles using pulsed-electrodeposition for improved heterojunction photoelectrodes

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Experimental details

Anodization of TiO$_2$ 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 ºC for 1 h, followed by calcination at 450 ºC for 3 h with a ramping rate of 5 ºC min$^{-1}$ in air.$^{[1]}$

Fabrication of CuInS$_2$-TiO$_2$ 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 CuCl$_2$, InCl$_3$, and Na$_2$S$_2$O$_3$ 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 (λ ≥ 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 (λ ≥ 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-TiO$_2$ array using pulsed-electrodeposition with the moral ratio of Cu : In : S = 1 : 0.8 : 10 and TiO$_2$ 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-TiO$_2$ 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-TiO$_2$ layer. While TiO$_2$ 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