Supporting Information

A quantum dot sensitized catalytic porous silicon photocathode

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Experimental Section

Electrochemical measurements were carried out using a PG 310 potentiostat from HEKA Electronics (Germany). Photo-electrochemical measurements were carried out in aqueous 0.1 M H_2SO_4 electrolyte in a Teflon based electrochemical cell at ambient temperature. Working electrodes were produced from *p-type* silicon wafers (Czochralshy, Siltronix Ltd.) with resistivity of 0.5-1 mΩ.cm, orientation (100). The wafers were etched by electrochemical anodisation using in 1:1 ratio 48% hydrofluoric acid: absolute ethanol with a constant current density of 57 mA/cm^2 for 8 minutes. The surface topography and the pore cross-section was characterised using a FEI Quanta 450 Environmental Scanning Electron Microscope (ESEM) instrument, and ToF-SIMS images were obtained on a Phi Trift nanoTOF ToF-SIMS instrument. Freshly etched pSi was quickly transferred to a glove box in an argon atmosphere (M Braun Lab Star, 0.01 ppm O_2). pSi was then subjected to electrografting (Keithley, 2601 source meter) with 0.4 M of methyl iodide electrolyte in acetonitrile at 9 mA/cm^2 for 45 seconds under illumination by a tungsten lamp of 50 mW/cm^2. Finally, the samples were rinsed with glacial acetic acid, acetonitrile and left to dry in the glove box.

InP QDs were synthesized based on the procedure described by Reiss *et al*. with some modifications (see below). The QD size was characterised using a Philips CM200 TEM and a Zetasizer-Nano DLS (Malvern, UK). The PL of the QDs was recorded on a photonics FLS 980 spectrometer from Edinburgh (UK). Irradiation was performed using an Abet Solar Simulator (AM 1.5 – 1 sun) and calibrated against a silicon solar cell (New-Spec). FTIR spectra were recorded using a Tensor 27 FT-IR spectrometer coupled to a Hyperion 3000 FT-IR microscope.

InP QDs were loaded into the pores of the pSi by a physisorption 'drip dry' procedure. Here, 10 µL of InP QDs (dispersed in anhydrous toluene) were loaded into the pores of the silicon wafers, and following evaporation of the solvent, the surface was rinsed with toluene. This

procedure was repeated five times. Finally, the porous photoelectrode was soaked in the $[Fe_2S_2(CO)_6]$ catalyst in toluene for 1 hour. The whole procedure was carried out in a glove box to avoid surface oxidation.

A back contact to the photocathode was formed using In-Ga eutectic applied via a cotton swab. Finally, a copper plate was used as a rigid back contact.

Electrolysis was performed using a sealed three-electrode Teflon photoelectrochemical cell consisting of a Pt counter electrode, an Ag | AgCl 3M KCl reference electrode, and the pSi working electrode. The working electrode was illuminated with a light intensity of 100 mW/cm^2 under air mass (AM) 1.5 conditions with two dark/light cycles to measure the photocurrents as a function of time. The potential between the working and reference electrodes was adjusted between, 0 and -500 mV in 100 mV steps. The hydrogen gas in the headspace above the electrolyte was sampled and analysed using a SRI 310C series gas chromatography (GC) with a thermal conductivity detector and a column held at 50 ^oC in argon as the carrier gas.

Indium phosphide quantum dot synthesis

InP QDs were synthesized based on the procedure described by Reiss *et al.*[1] with some modifications. Briefly, 0.1 mmol of indium acetate ($In(Ac)_3$) and 0.3mmol of myristic acid were dissolved in 4mL octadecene (ODE) at 100 ^oC and left under vacuum for 1 hr to form a clear solution. After the hour had elapsed, the vessel containing the indium precursor was rapidly heated to 250 ^oC. In a connected vessel, 250 mg (1.37 mmol) of calcium phosphide (Ca_3P_2) was reacted with 1.5 mL of 4M HCl to produce phosphine gas. The phosphine gas was immediately transferred across a column containing phosphorus pentoxide (P_2O_5) to our initial reaction containing the indium precursor which was now at 250 ^oC. InP QDs were allowed to grow at 250 ^oC for 90 seconds forming a deep red solution. The QDs were purified from methanol and toluene.

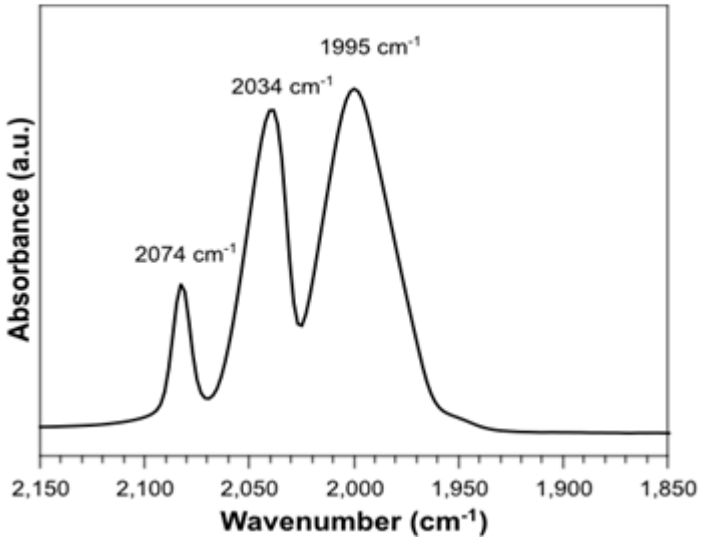


Figure S1. FTIR spectrum of the carbonyl stretching region of the $[Fe_2S_2(CO)_6]$ in toluene[2].

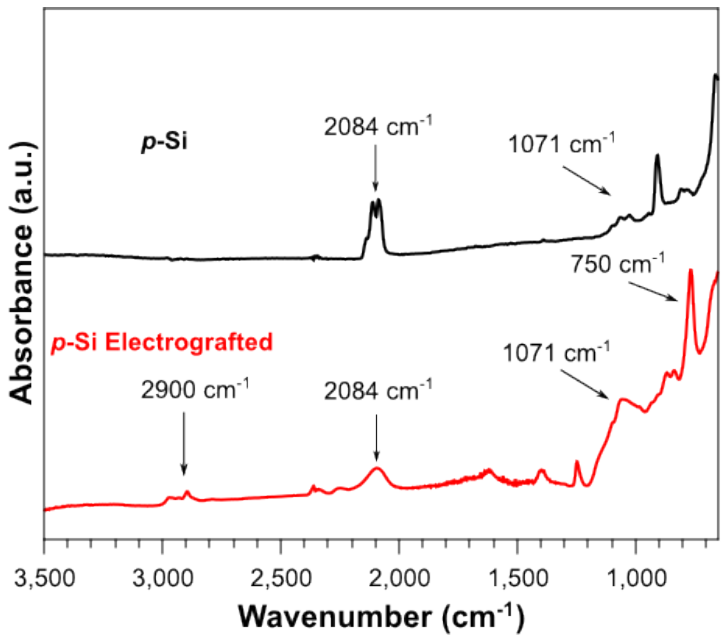
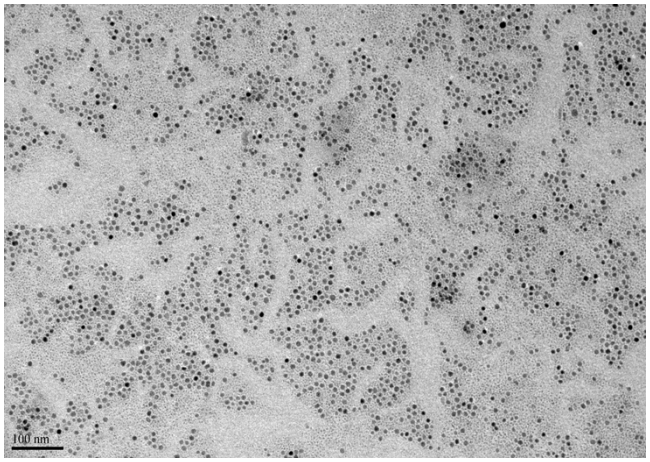
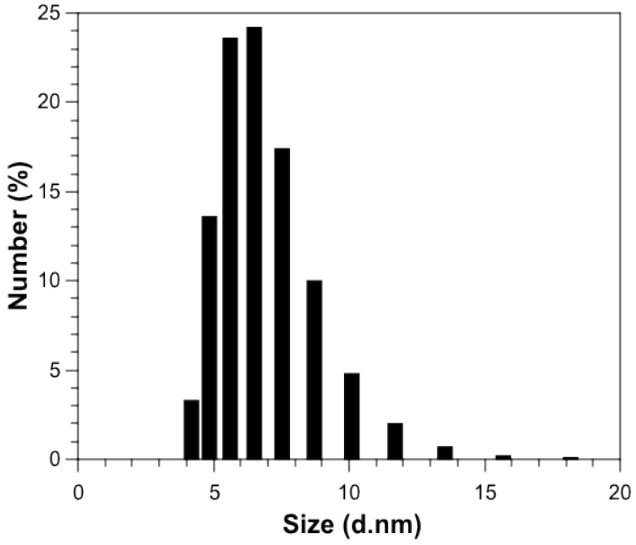


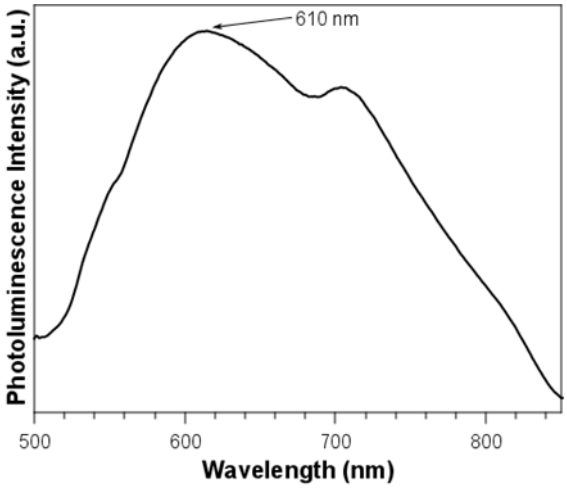
Figure S2. Attenuated total reflectance FTIR spectra of pSi and methyl electrografted pSi. The peaks at 1071 cm^{-1} and 2084 cm^{-1} represent Si-O and Si-H_X stretching modes of pSi, respectively. The peaks values 750 cm^{-1} and 2900 cm^{-1} represents the Si-CH_3 rocking mode and C-H stretching modes, respectively, which confirm the presence of methyl groups on the pSi surface.



(A)

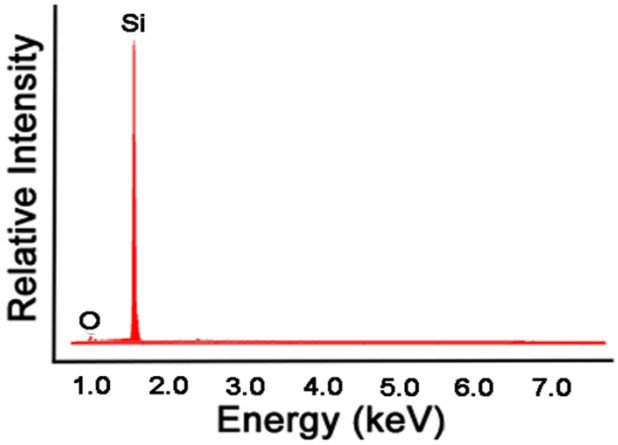


(B)

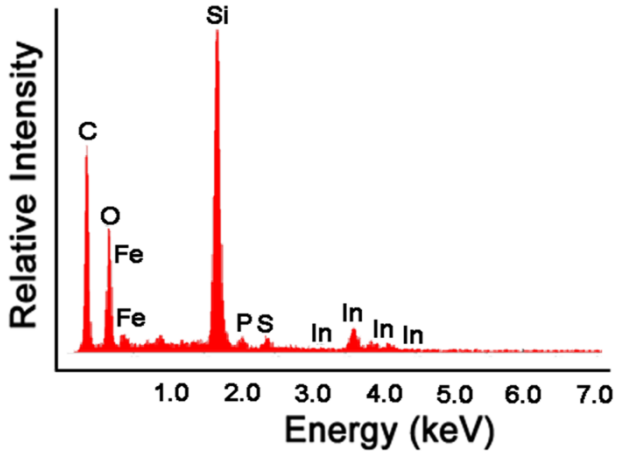


(C)

Figure S3. TEM (A) and DLS (B) show that the InP QDs are approximately 5-9 nm in size and PL (C) shows the intensity peak at 610 nm.

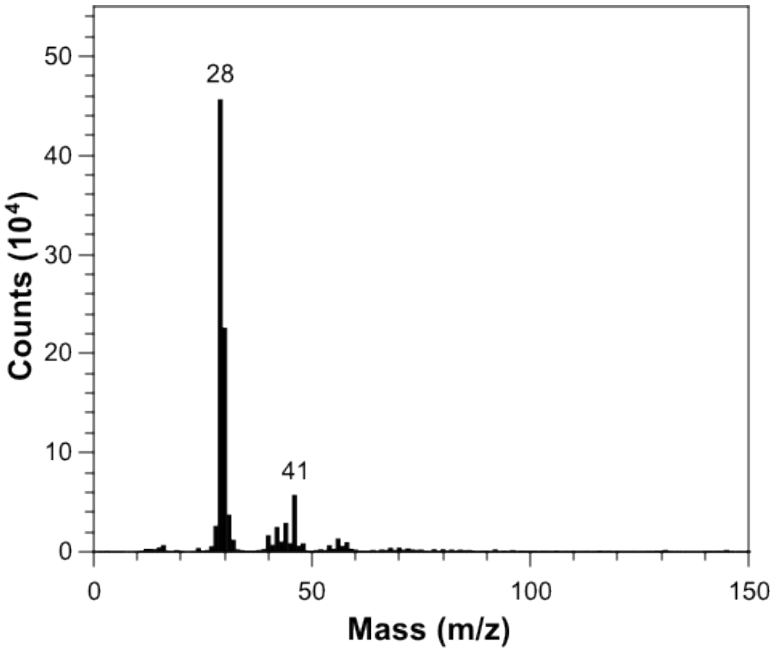


(A)

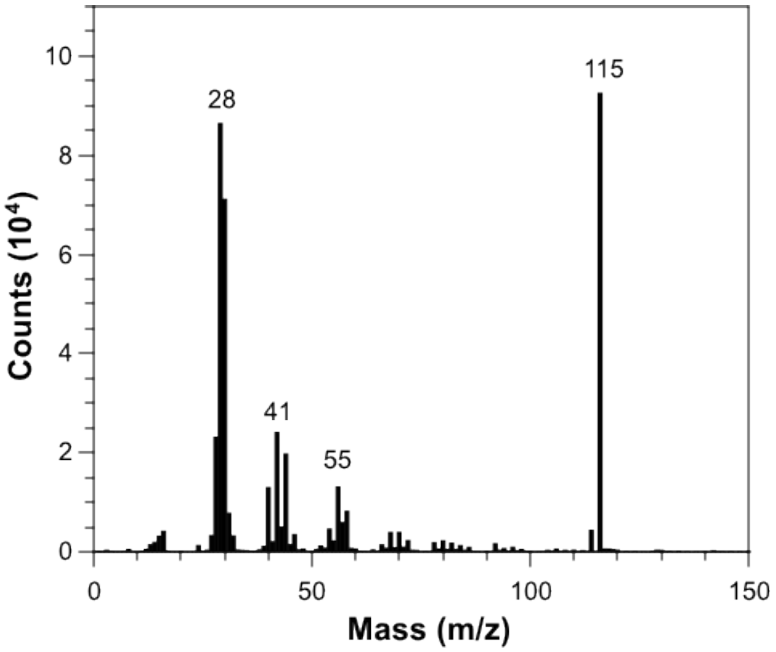


(B)

Figure S4. EDXS spectra of bare pSi (A) and pSi (B) loaded with InP QD_S and $[Fe_2S_2(CO)_6]$ catalyst.



(A)



(B)

Figure S5. ToF-SIMS spectra of bare pSi (A) and pSi (B) loaded with InP QD_S and $[Fe_2S_2(CO)_6]$. The peak values m/z 28, 55 and 115 correspond to Si^+, Fe^+ and In^+. The peak value m/z 41 is attributed to adventitious hydrocarbon.

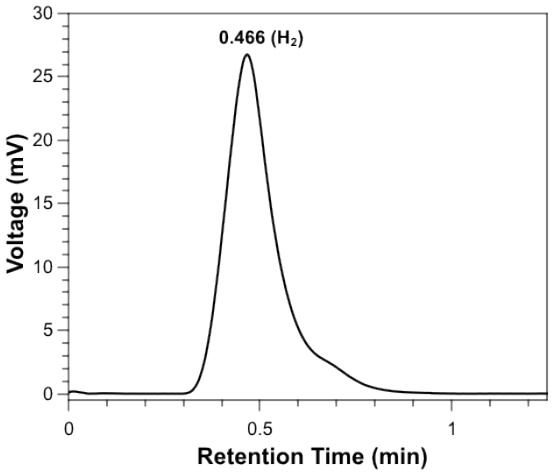


Figure S6. GC showing the presence of hydrogen gas[3]. The hydrogen gas corresponds to the electrografted pSi loaded with InP QDs and $[Fe_2S_2(CO)_6]$ catalyst. And the measured photocurrent density is about -1.2 mA/cm^2 at a bias potential of -500 mV over two light-dark cycles. The cell was irradiated with a calibrated light intensity of 100 mW/cm^2 under air mass (AM) 1.5 conditions.

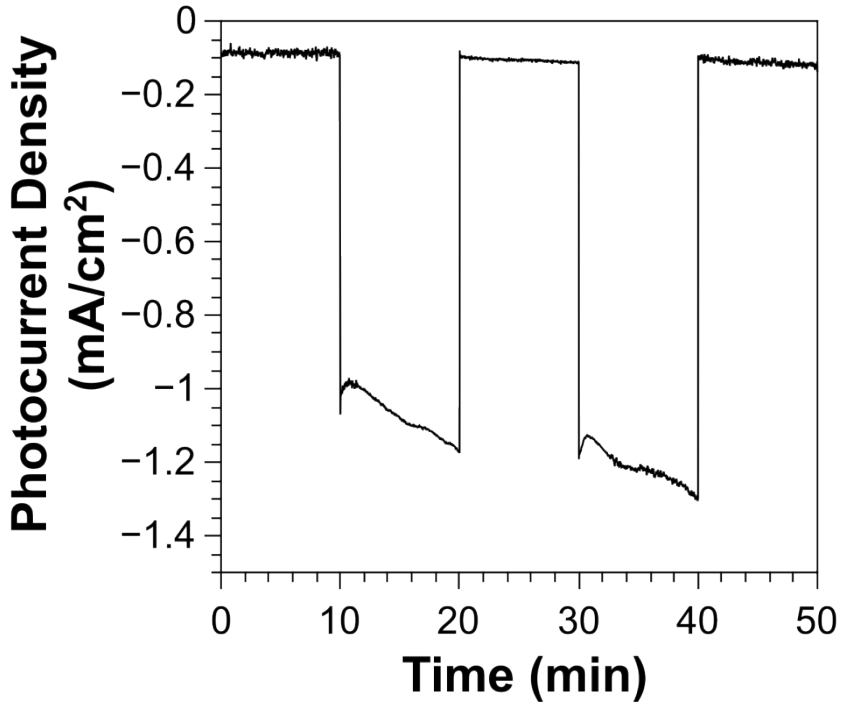


Figure S7. The graph shows photocurrent density measured over 50 minutes with 10 minutes light-dark cycles. The applied bias potential was -500 mV for the electrografted pSi loaded with InP and $Fe_2S_2(CO)_6$ catalyst. The cell was irradiated with a calibrated light intensity of 100 mW/cm^2 under air mass (AM) 1.5 conditions.

References

[1] L. Li, M. Protière, P. Reiss, *Chem. Mater.* 2008, **20**, 2621.

[2] T. Nann, S. K. Ibrahim, P. M. Woi, S. Xu, J. Ziegler, C. J. Pickett, *Angew. Chem. Int. Ed.* 2010, **49**, 1574.

[3] K. Zhang, D. Jing, C. Xing, L. Guo, *Int. J. Hydrogen Energy* 2007, **32**, 4685.