Supporting Information

Highly stable Photoelectrochemical Cells for Hydrogen Production using SnO_2-TiO_2/Quantum Dots Heterostructured Photoanode

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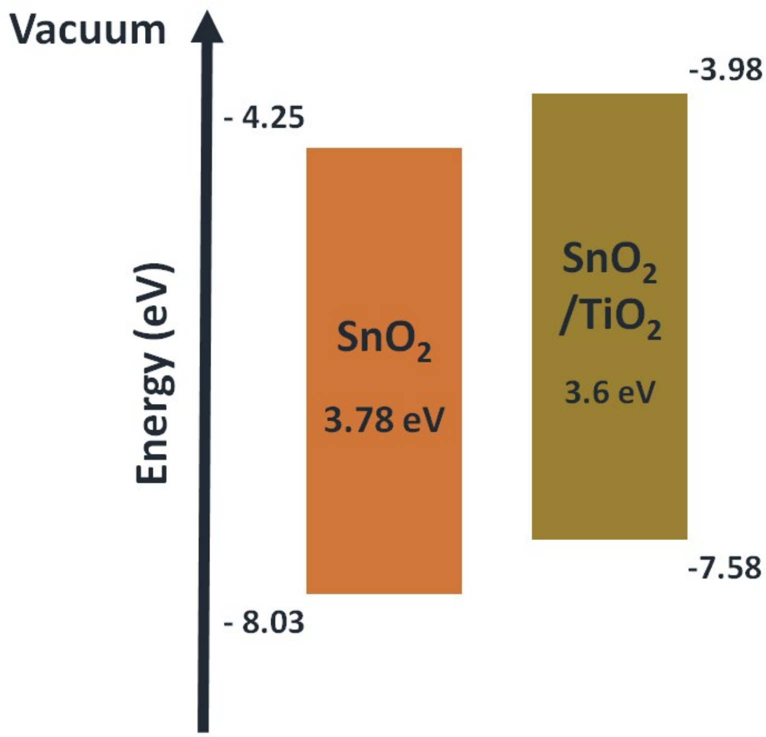

Figure S1 Band diagram constructed by combining the data from UV photoelectron spectroscopy (UPS) and diffuse reflectance spectroscopy (DRS) of the SnO_2 and SnO_2/TiO_2 photoanode.[1]

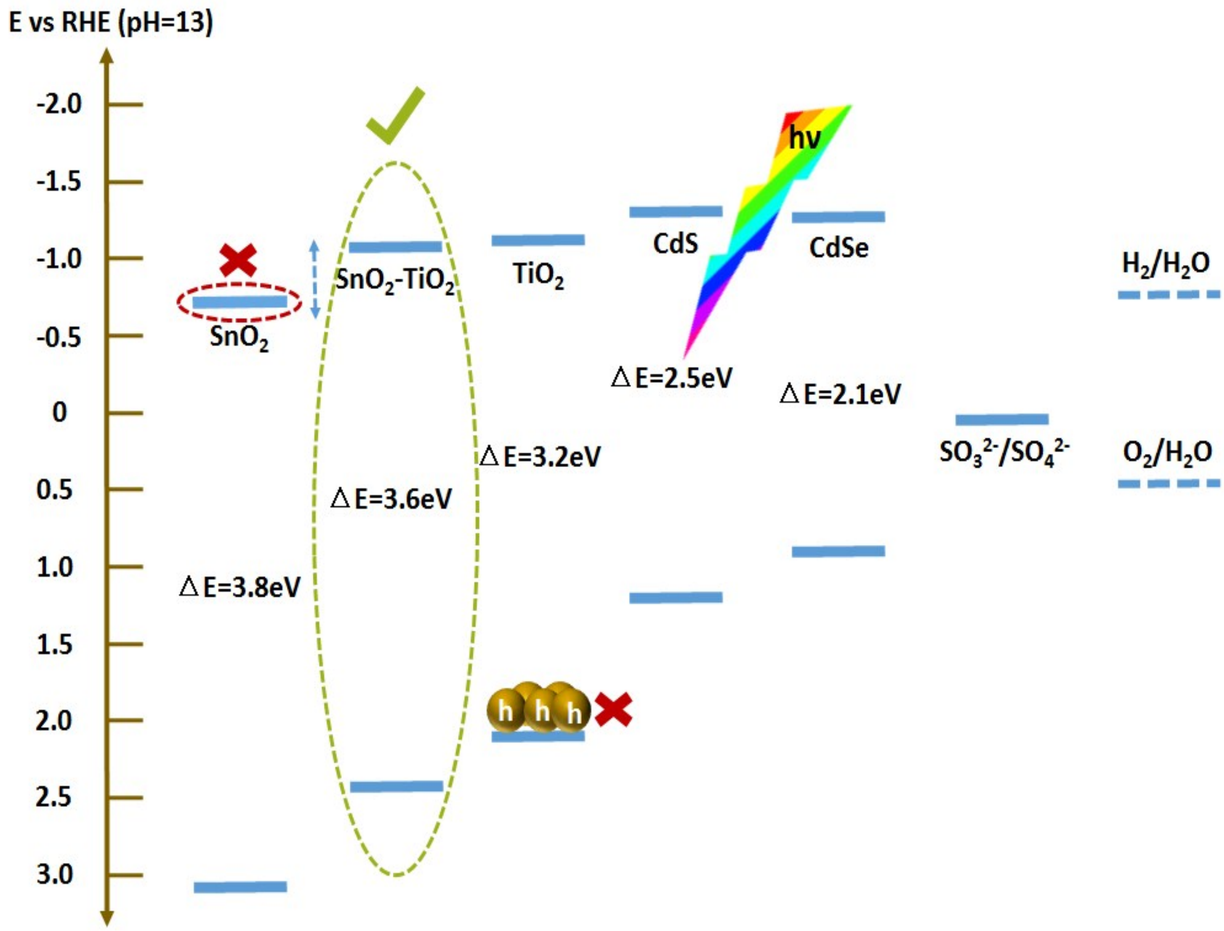

Figure S2 Band diagram depicting the beneficial effect of using SnO_2-TiO_2 over traditional TiO_2 photoanode. Approximate energy levels (corresponding to pH=13) of SnO_2-TiO_2[1], CdSe, CdS, along with related characteristic redox potentials. The band gap value of CdSe and CdS correspond to QD and bulk semiconductors, respectively. The arrows denote the electron and hole transfer mechanisms.

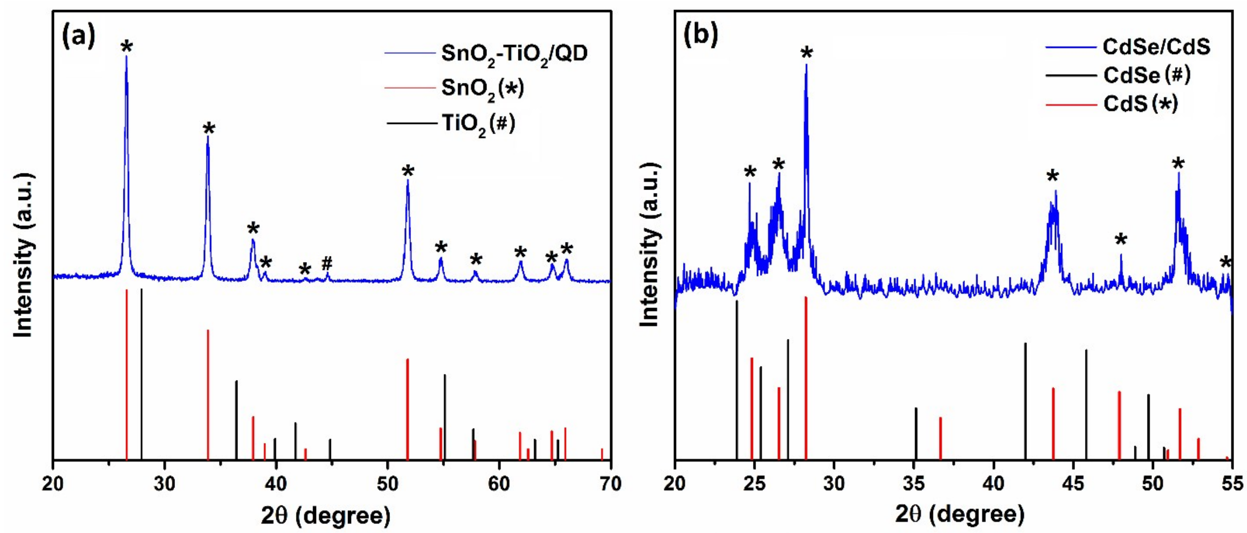

Figure S3 (a) X-ray diffraction patterns of the SnO_2-TiO_2/QD photoanode; (b) Grazing angle X-ray diffraction patterns of the CdSe/CdS core/shell QDs on an Si substrate.

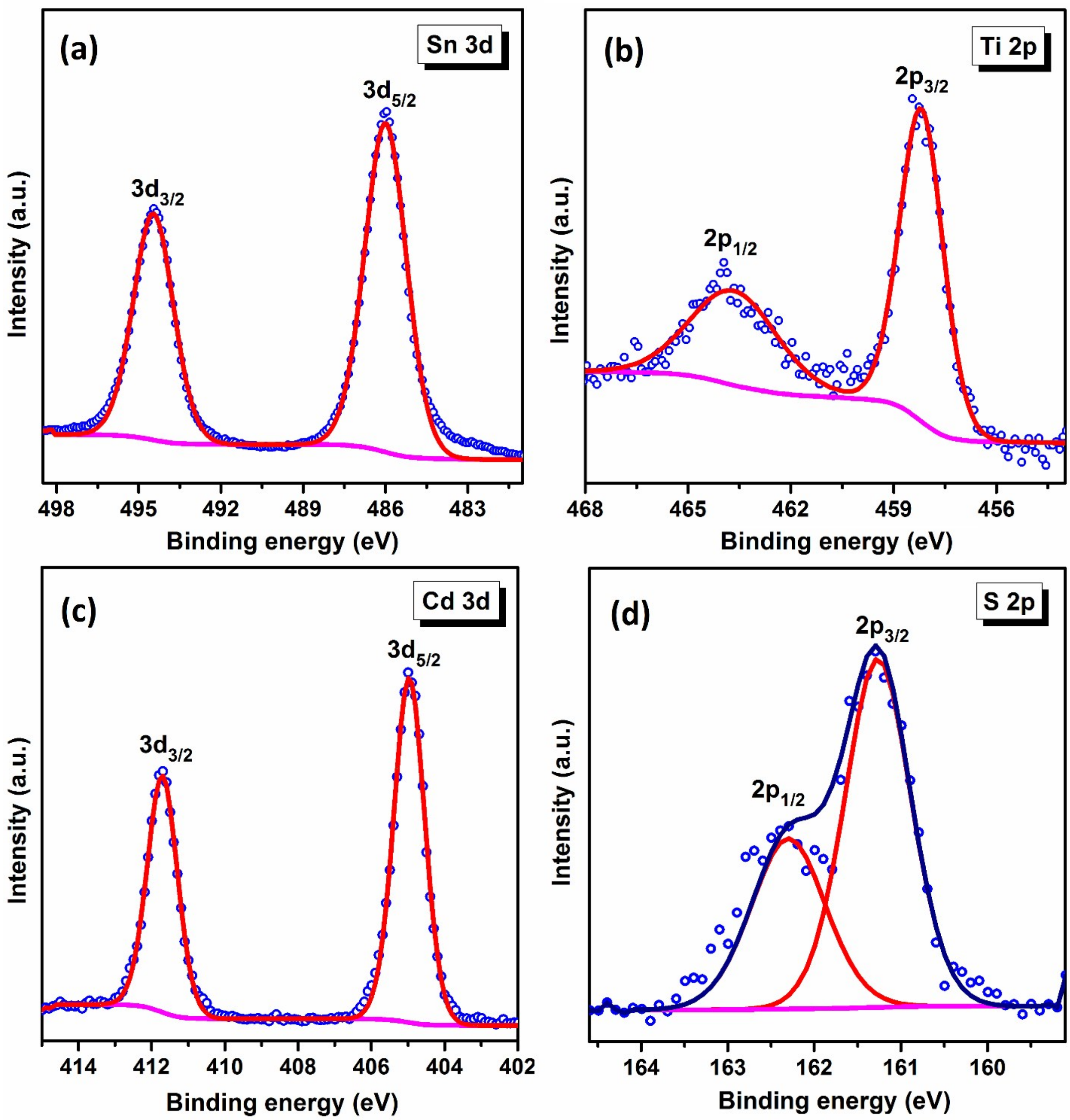

Figure S4 X-ray photoelectron spectra and curve fits of; (a) Sn 3d peak , (b) Ti 2p peak (c) Cd 3d peak, and (d) S 2p peak for the SnO_2-TiO_2/QD photoanode.

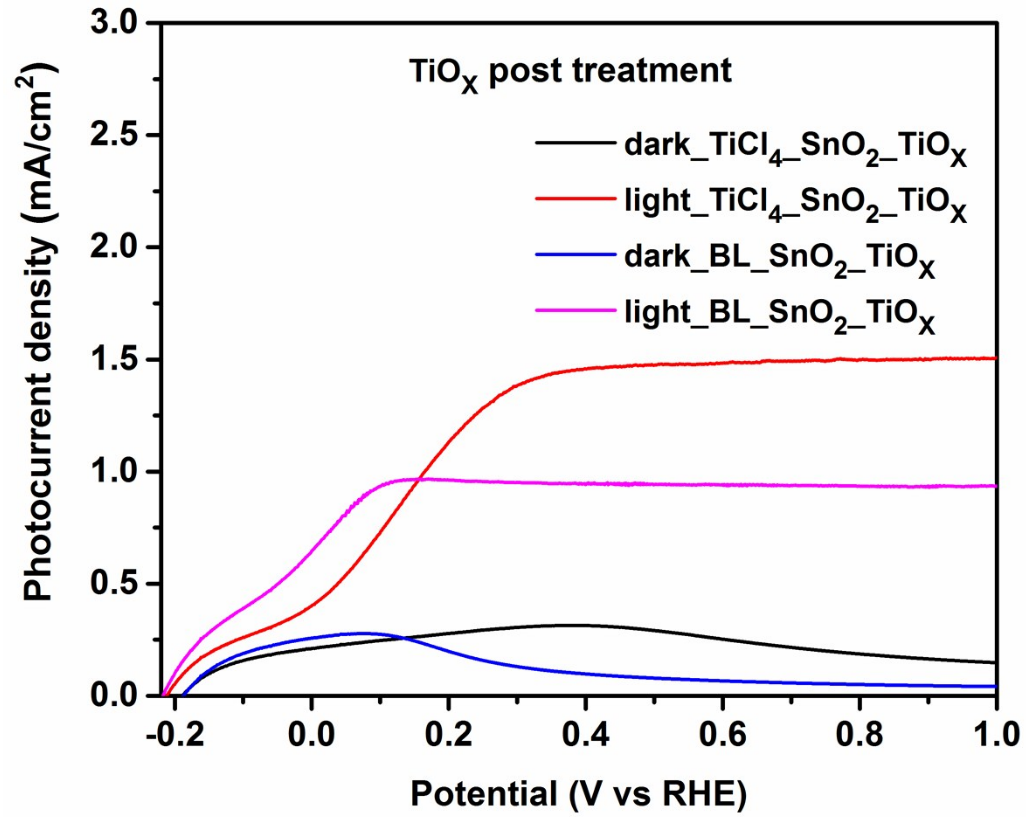

Figure S5 Photocurrent density versus the applied voltage (vs RHE) for SnO_2-TiO_2 photoanode PEC cells with different blocking layers.

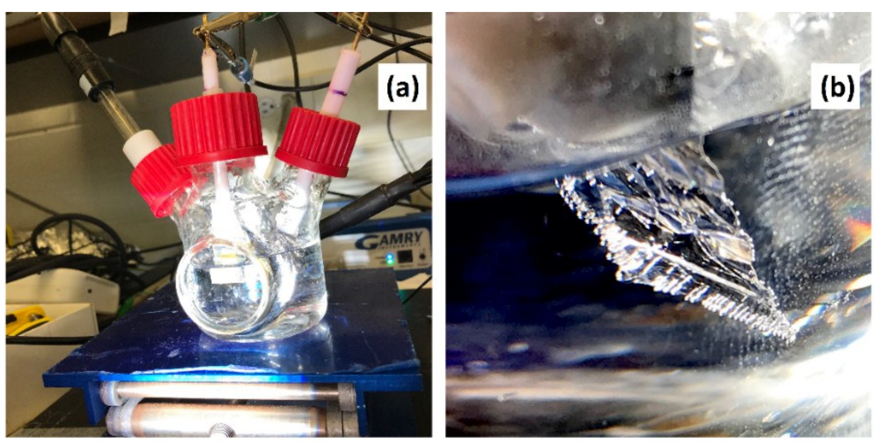

Figure S6 Three electrode experimental setup for PEC measurement. (b) Magnified image of the Pt CE showing the formation of H_2 bubbles on the surface.

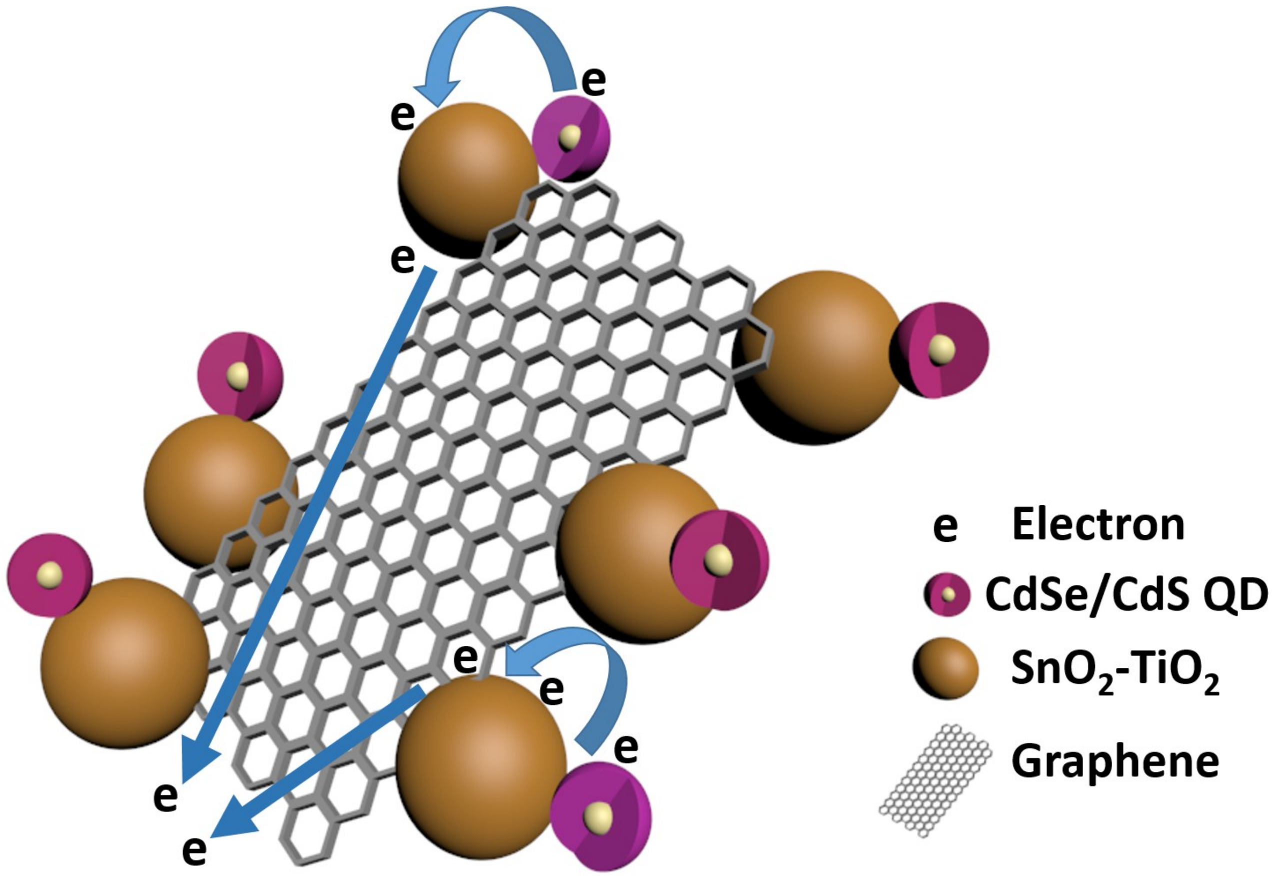

Figure S7 General schematic for efficient photoelectron transfer via graphene conducting pathways in the composite photoanode sensitized with giant QDs, arrows indicate the electron transfer processes.

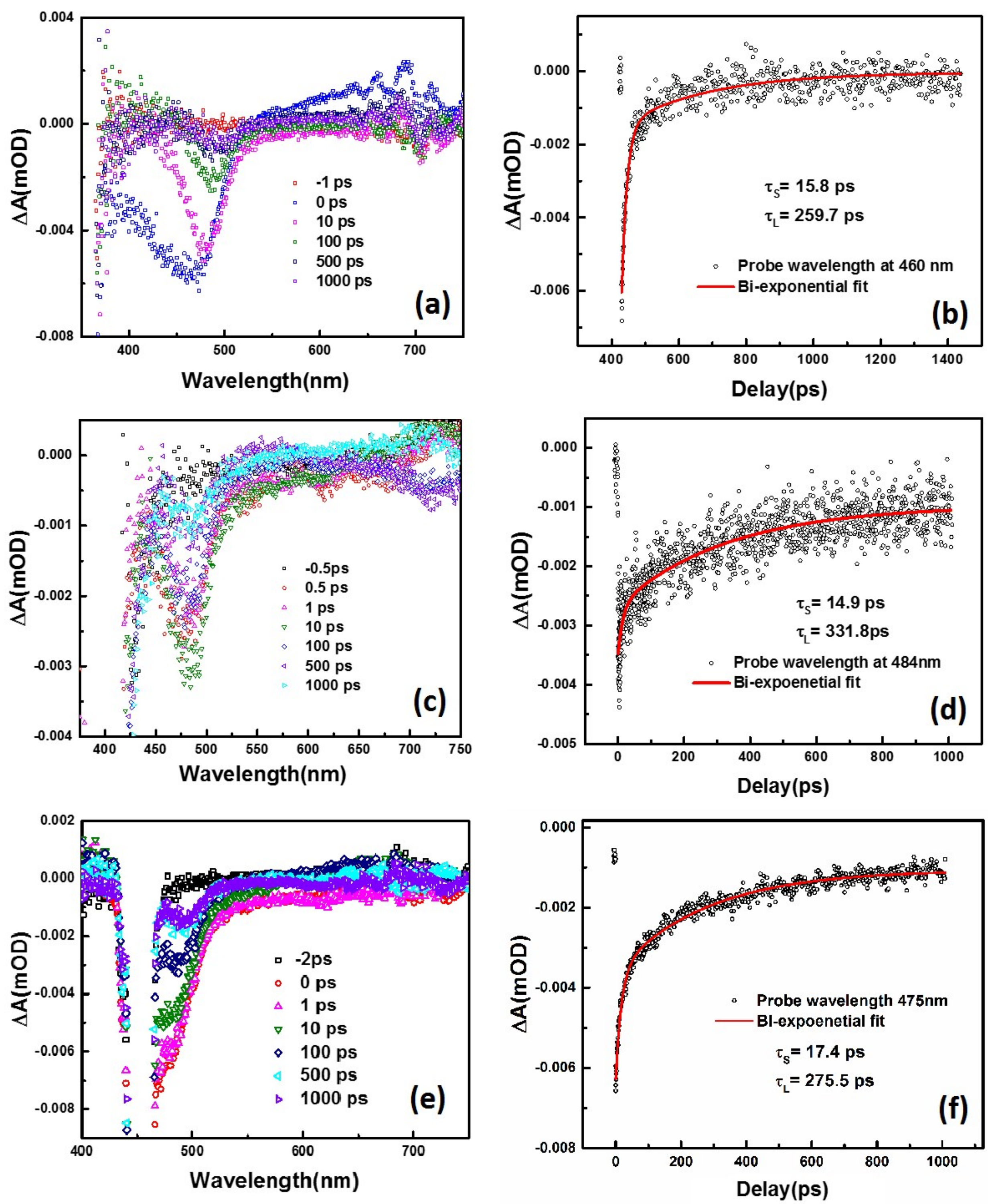

Figure S8 Transient absorption spectra of ZrO_2-QD sample pumped at (a) 350 nm, (c) 400 nm, (e) 450 nm with 0.5 μJ pulse energy; Decay dynamics of ZrO_2-QD sample pumped at (b) 350 nm, (d) 400 nm, and (f) 450 nm.

Note 1

We have estimated the H_2 gas evolution within our CdSe/CdS "giant" QD/SnO_2-TiO_2 photoanode by using the H_2 evolution measurements conducted in a similar system composed of CdSe/CdS "giant" QD /TiO_2 photoanode,[2] Pt as the counter-electrode and a Ag/AgCl saturated reference electrode. The produced H_2 gas in this benchmark system was detected using a Shimadzu GC-8A gas chromatography (GC) device equipped with a thermal conductivity detector. Argon was used as the carrier gas for GC analysis. An air-tight syringe was used for sampling from the vacuum sealed chamber. After 5610, 6280 and 7172 s, the H_2 gas measured was 23.55, 24.65 and 25.61 μmol, respectively. This approach is quite reliable because after 1.5 h, the evolution of the H_2 gas within our benchmark PEC system[2] stabilizes and the photocurrent density is similar to the one produced in this work with the incorporation of 0.1 wt% graphene microplatelets, (~5.6 mA/cm^2).

The Faradaic Efficiency (FE) was calculated using the formula:[3]

$$FE(\%) = \frac{H_2\, evolved\ (mol)\ \times 2 \times F\left(Cmol^{-1}\right)}{Charge\ passed\ through\ WE\ (C)} \times 100\%$$

$$= 81.27\%$$

Where, Faraday constant (F) = 96484.34 C/mol

The solar to hydrogen (STH) conversion efficiency was calculated using the formula:[4]

$$STH = \left[\frac{\left|J_{sc}\left(\frac{mA}{cm^2}\right)\right| \times 1.23\ (V) \times FE}{P\left(\frac{mW}{cm^2}\right)}\right]_{AM\ 1.5G}$$

$$= 5.51\ \%$$

Where J_{sc} is the photocurrent density, P is the input power provided by solar simulator.

When a photoanode for PEC based H_2 generation is used unassisted i.e. without a tandem cell, STH efficiency becomes irrelevant.[4] In such cases, applied bias photon-to-current conversion efficiency (ABPE) may be used to overcome this drawback.[4]

ABPE is defined as:[4]

$$ABPE = \left[\frac{|J_{photo}| \times (1.23 - V)}{P}\right]_{AM\ 1.5G}$$

$$=2.89\%$$

Where, V is the voltage that is applied to the cell from an external power source

J_{photo} is the photocurrent measured at this voltage.

References

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