

## Supporting information

### Nanofiber-supported CuS nanoplatelets as a high efficiency counter electrode for quantum dot-based photoelectrochemical hydrogen production

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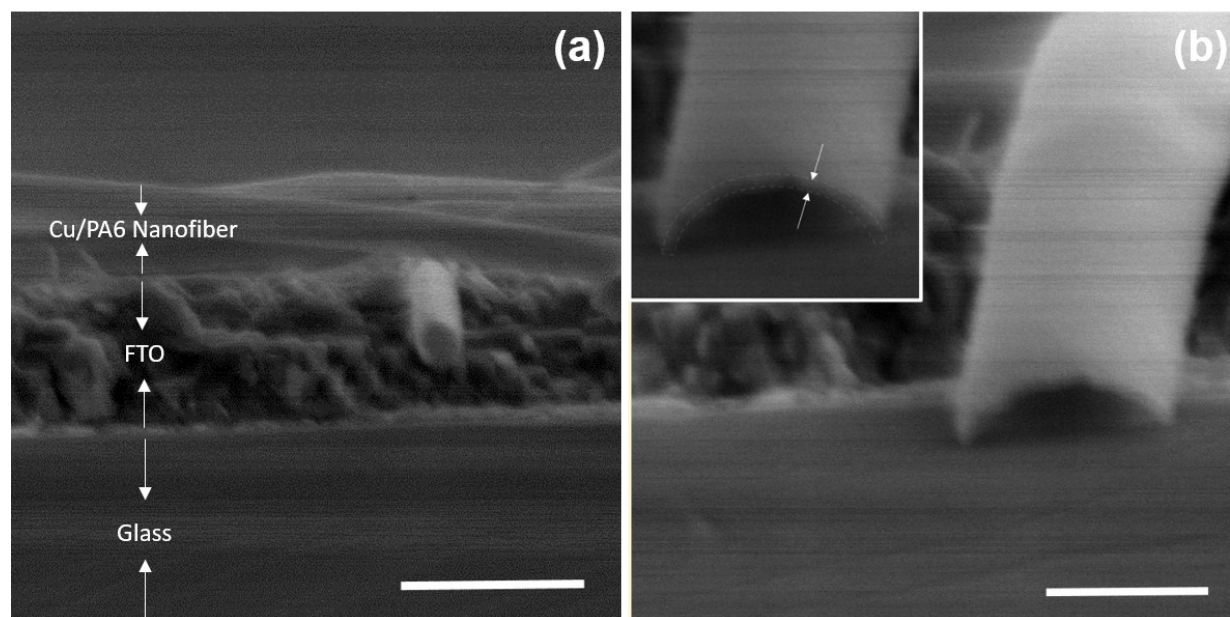
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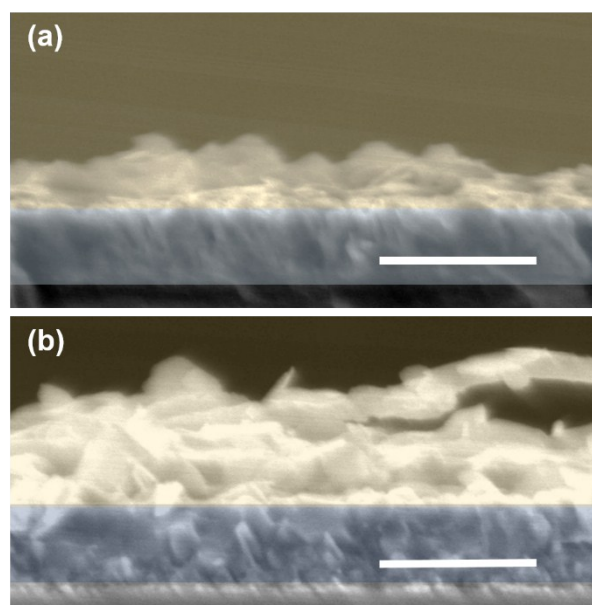
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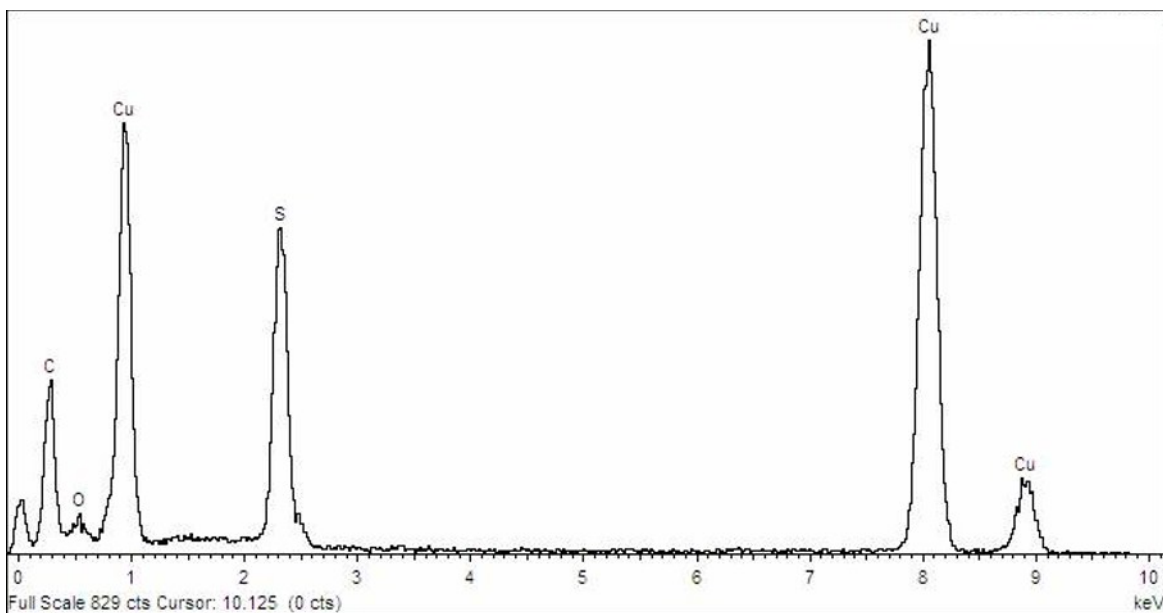
<sup>†</sup> These authors contributed equally to this work.



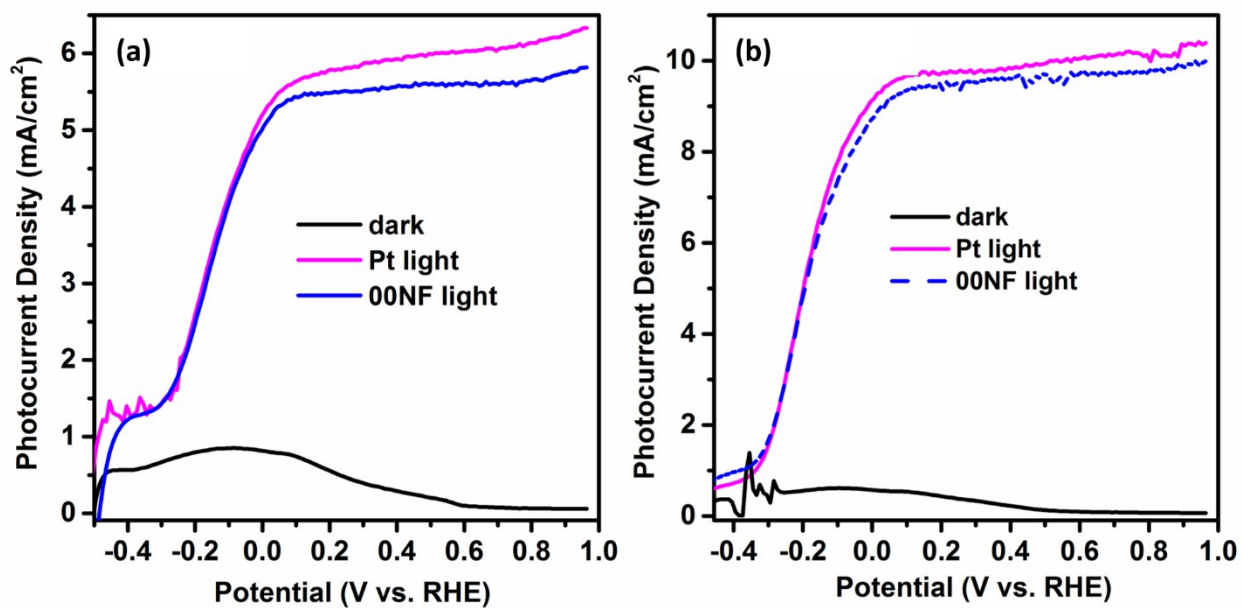
**Figure S1.** SEM images of the sample cross section obtained by electrospinning deposition time of 120 s after sputtering 35 nm Cu: (a) Stacked nanofibers, scale bar equals 1  $\mu\text{m}$ ; (b) Collapsed nanofiber and inset highlighting coating thickness, scale bar equals 0.5  $\mu\text{m}$ .



**Figure S2.** SEM images of the cathode cross-section. (a) Cu<sub>x</sub>S/FTO (00NF) and (b) nanofiber-supported CuS/FTO (120NF). Scale bar equals 1  $\mu\text{m}$ .



**Figure S3.** EDS spectrum of ultrasonically detached  $\text{Cu}_x\text{S}$  nanoplatelets showing their composition.



**Figure S4.** Photocurrent density versus the applied voltage employing (a)  $\text{CdSe}/(\text{ZnS})_2$  or (b)  $\text{CdSe}@(\text{CdS})/(\text{ZnS})_2$  QDs as sensitizers in the  $\text{TiO}_2$  photoanode.

## H<sub>2</sub> evolution calculation based on the obtained photocurrent

The theoretical number of moles of hydrogen, was obtained according to Faraday law<sup>1</sup>:

$$q = nF$$

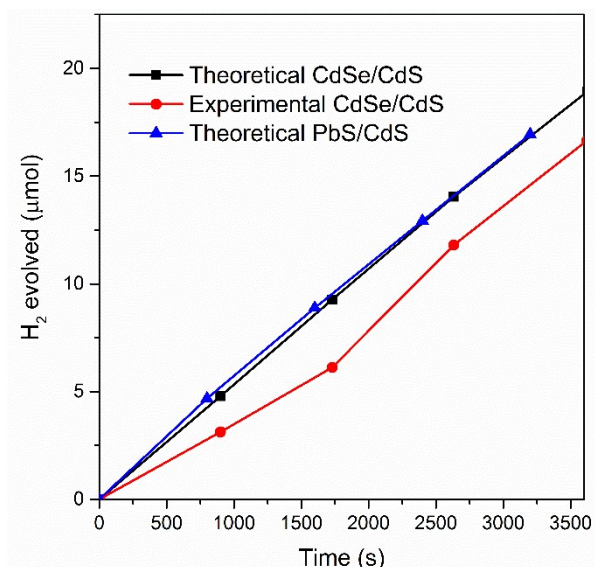
With the definitions of electrolysis based on the following equations:

$$n = \frac{m}{m_e} \quad \text{and} \quad q = \int_{t_1}^{t_2} I dt$$

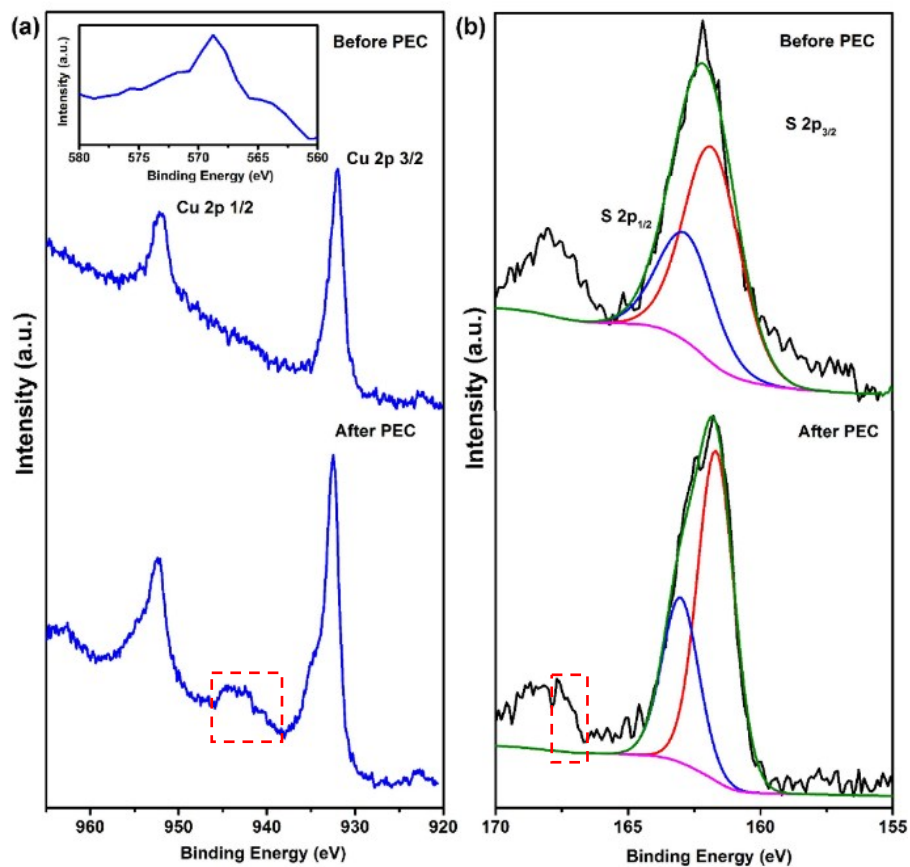
Where  $n$  is the number of equivalents,  $m$  is the mass of the substance liberated at an electrode in grams (g),  $m_e$  is the molar mass of the substance in grams per mol (g/mol), i.e.  $n$  equals to the number of moles. A common assumption on the current being constant over time, allow us to use the mathematical equivalent that can be simplified as<sup>2</sup>:

$$n = \frac{1q}{zF} = \frac{1I \times t}{z F}$$

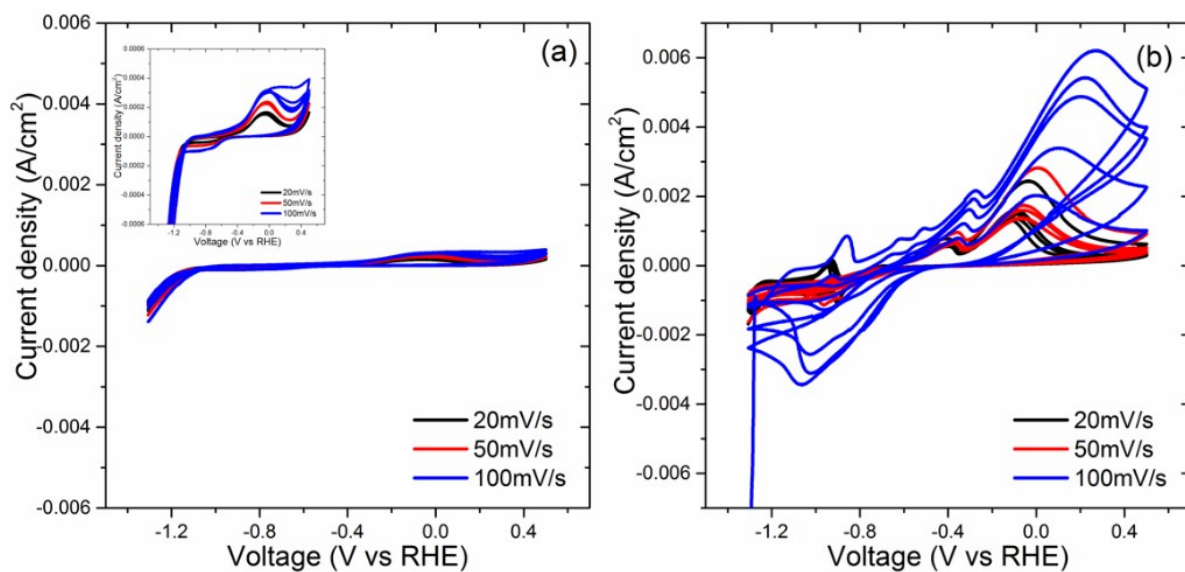
Where  $z$  is the number of transferred electrons per mole of water (i.e.  $z=2$ ),  $q$  is the electric charge in coulombs (C),  $F$  is the Faraday constant (i.e. 96484.34 C/mole),  $I$  is the photocurrent in amperes (A) and  $t$  is time in seconds (s).



**Figure S5.** Hydrogen evolution of CdSe@CdS/(ZnS)<sub>2</sub> as a function of time at 0.6V vs RHE under 100mW/cm<sup>2</sup>, illumination with AM 1.5G filter. The measured evolution of H<sub>2</sub> exhibits nearly a linear increase over time (solid red curve) and the theoretical value was calculated from the measured photocurrent (solid black curve). The same trend was found in the PEC system composed of PbS@CdS QDs as the photoanode and the nanofiber-supported CuS CE, as displayed by the theoretical calculated H<sub>2</sub> evolution (solid blue line).



**Figure S6.** High resolution XPS spectra of Cu 2p (a) and S 2p (b) for nanofiber-supported  $\text{Cu}_x\text{S}$ /brass (120NF) before and after the PEC test.



**Figure S7.** Electrochemical CV measurements of the CEs of (a) Pt and (b) nanofiber-supported  $\text{CuS}$ /FTO (120NF) using electrolyte containing 0.025 M  $\text{Na}_2\text{S}$  and 0.035 M  $\text{Na}_2\text{SO}_3$ .