Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information (SI)

Heterostructured Quantum Dot Architectures for Efficient and Stable Photoelectrochemical Hydrogen Production

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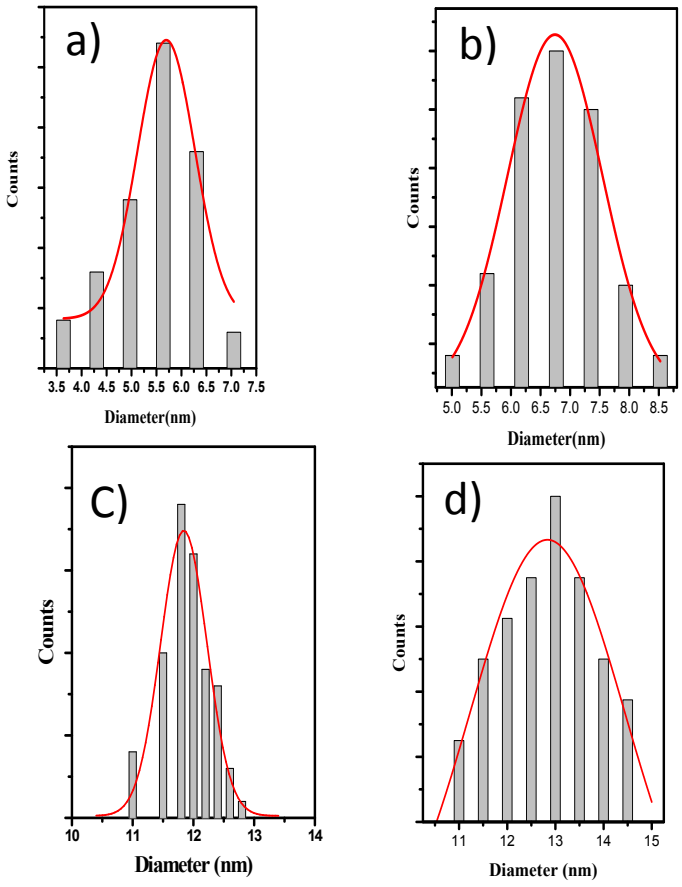

Figure S1. Histogram showing the particles size distribution of the different quantum dots. a) Pure shell-6, b) Alloyed shell-6 c) Pure shell-13 and d) Alloyed shell-13, respectively.

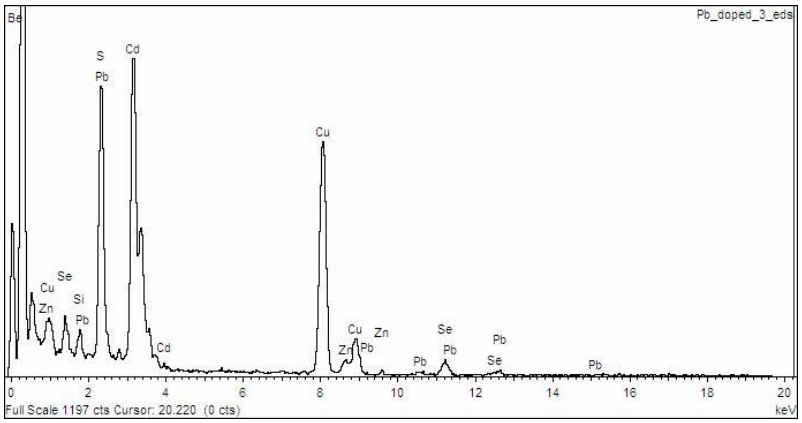

Figure S2 (a). An EDS spectrum of the Alloyed shell-6 quantum dots indicating the presence of Pb in the alloyed shell.

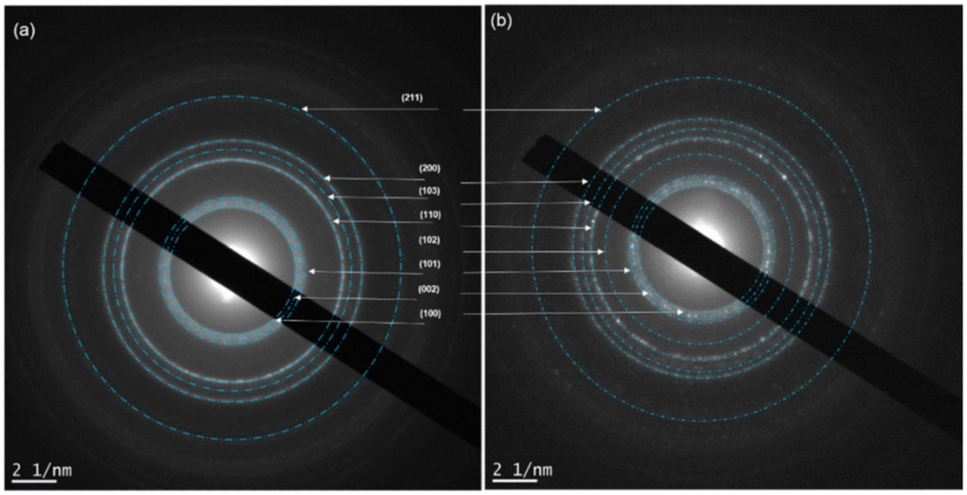

Figure S2 (b). SAED pattern of pure shell-13 and Alloyed shell-13 QDs.[2]

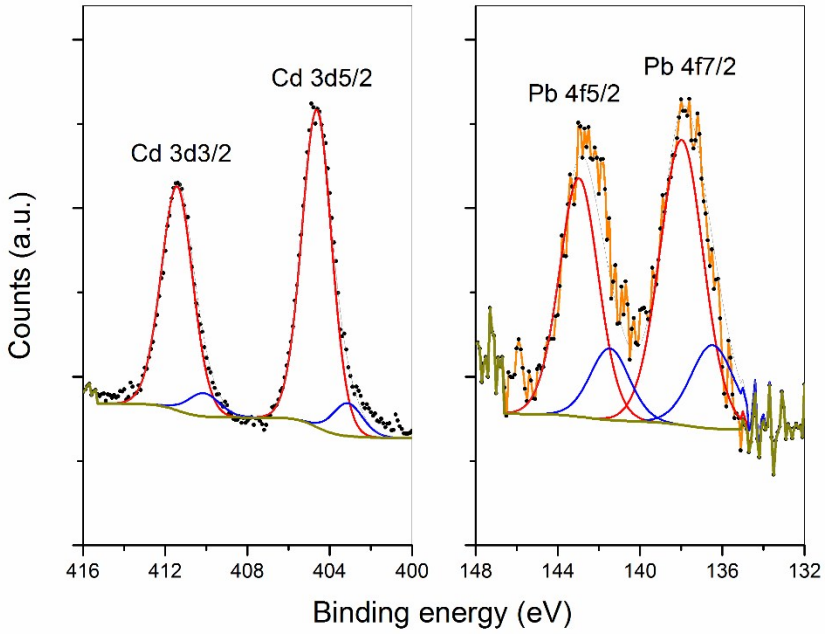

Figure S3 High resolution XPS spectra of Cd 3d and Pb 4f in alloyed shell-13 QDs. The dots represent the experimental data. The thick blue and red lines are the fitting components and the violet line is the overall fitting curve. The dark yellow line is a background curve.

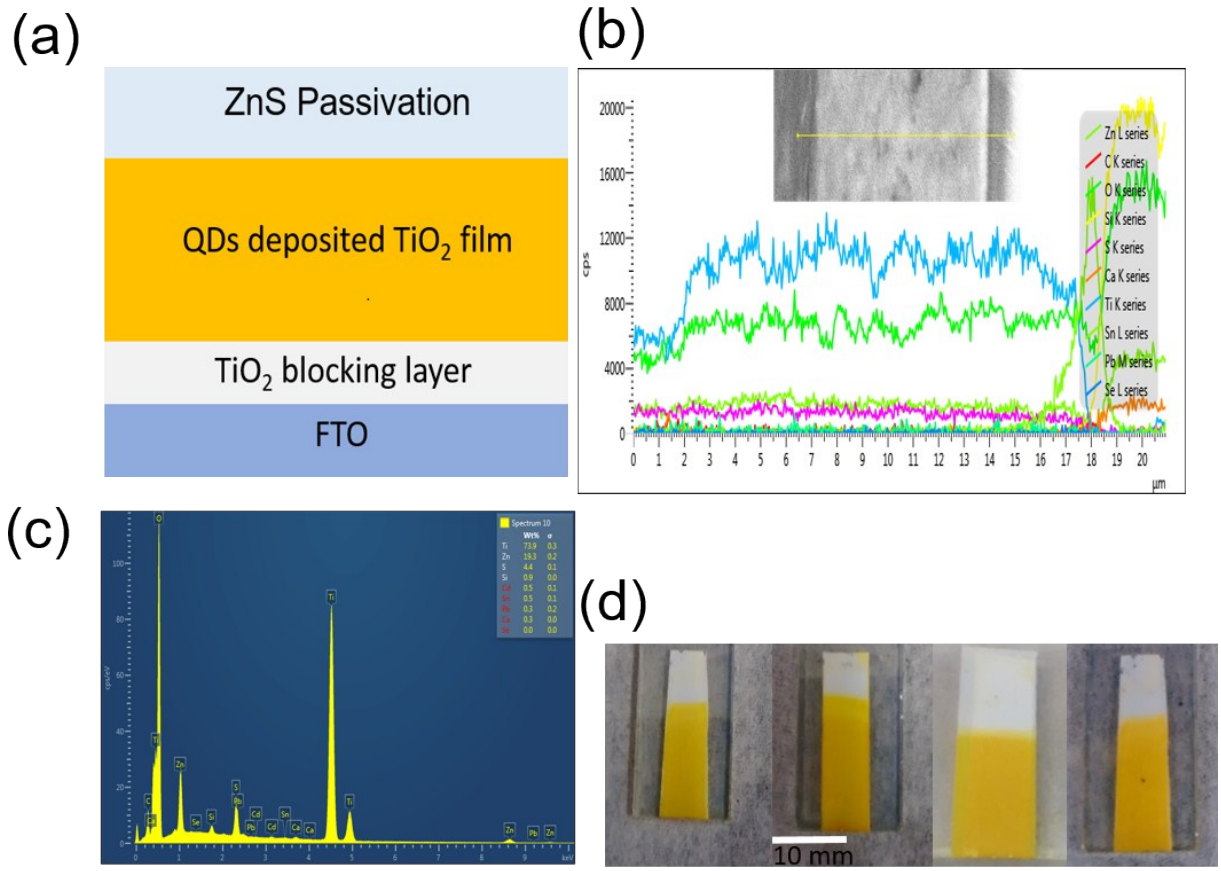

Figure S4. Schematics of the fabrication process and Photoanode architectures finally capped with ZnS passivation layer (a). Line spectra of different elements of alloyed shell-13 QDs deposited TiO_2 film and corresponding EDS spectra (b, c). Photographs of QDs deposited TiO_2 film by EPD process for 2 h (d). Left to right are pure shell-6, alloyed shell-6, pure shell-13 and alloyed shell-13 QDs deposited films, respectively.

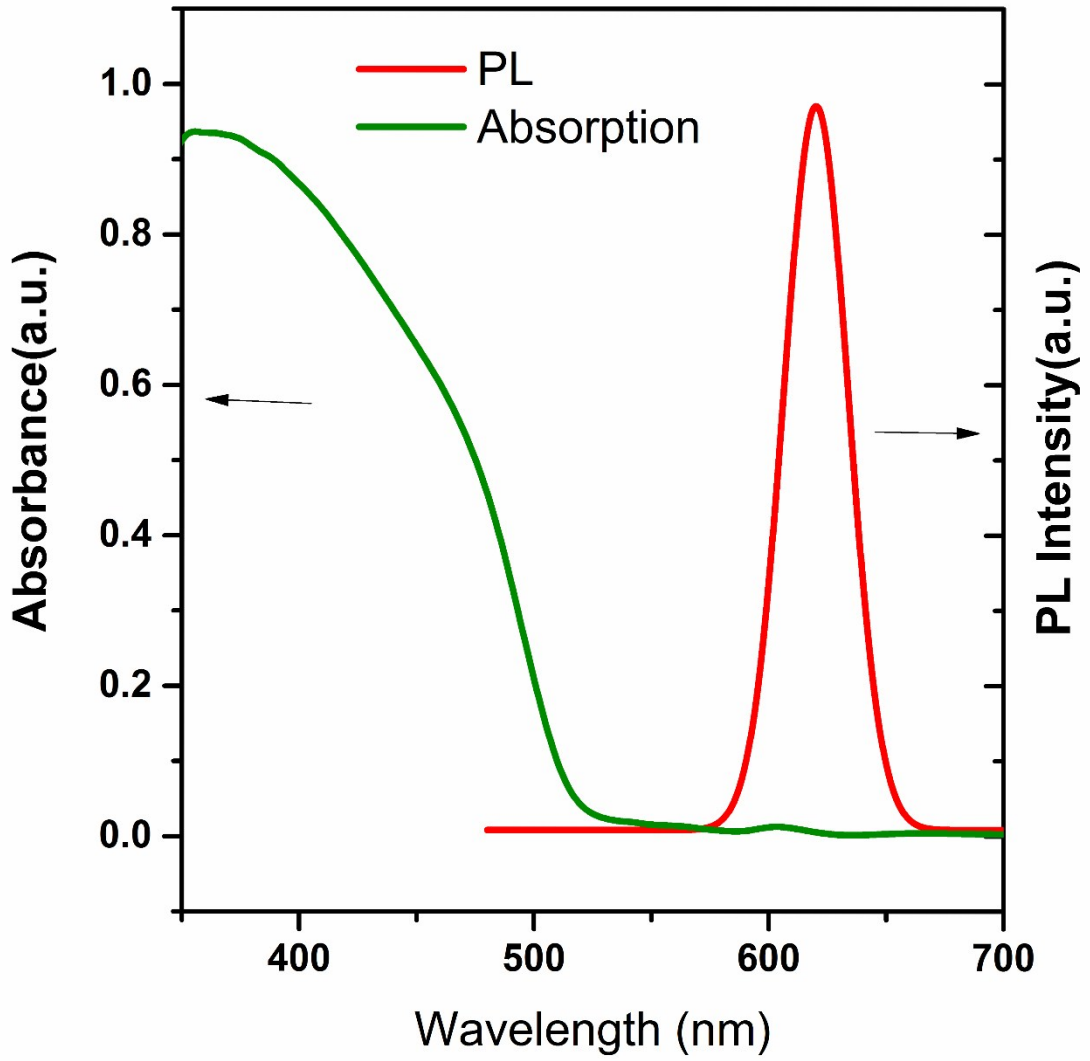

Figure S5. Normalized Absorption and PL spectra of Alloyed Shell-13 QDs in toluene.

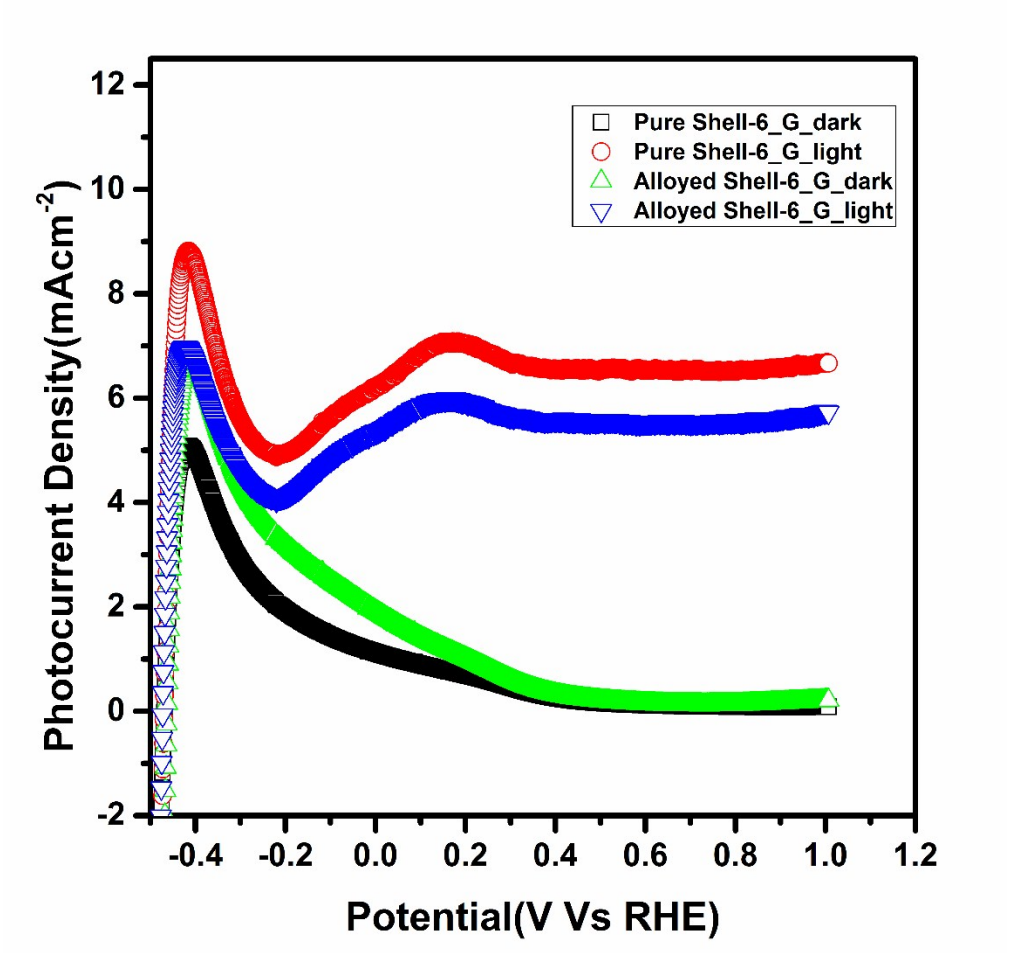

Figure S6. Linear sweep voltamogram of Graphene modified TiO_2 film deposited with pure shell-6 and alloyed Shell-6 QDs. Experimental conditions are similar as explained in the main text.

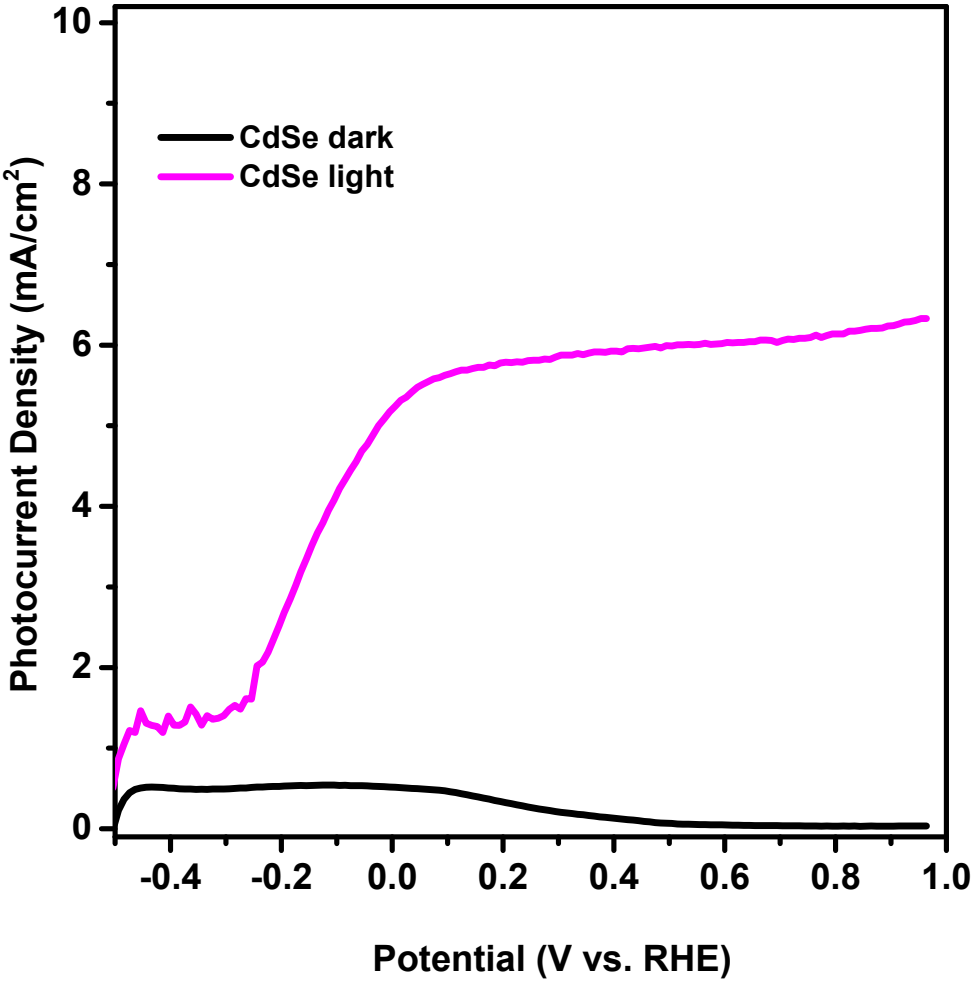

Figure S7a. Linear sweep voltamogram of TiO_2 film deposited with CdSe QDs (size~1.85 nm)[1] after 2 cycle ZnS passivation. Experimental conditions are similar as explained in the main text.

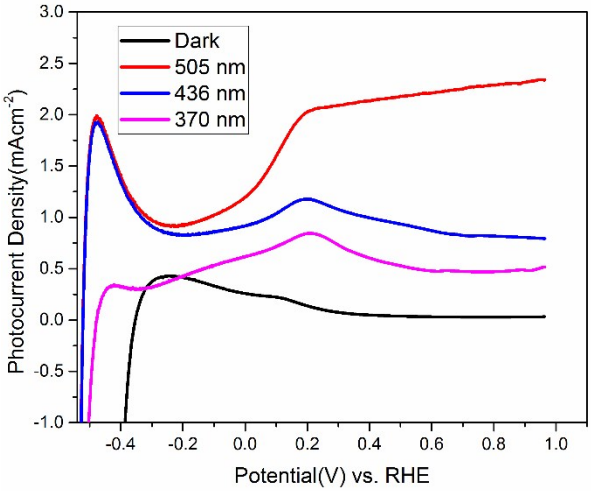

Figure S7b. Photoresponse of TiO_2 films deposited with as prepared core/ shell alloyed QDs at different wavelengths.

Calculation of hydrogen evolution based on the obtained photocurrent

The theoretical number of moles of hydrogen, was obtained according to Faraday's law:

$q=nF$ with the definitions of electrolysis based on the following equations:

$$n=\frac{m}{me} \; and \; q=\int_{t1}^{t2} Idt$$

Where n is the number of equivalents, m is the mass of the substance liberated at an electrode in grams (g), me is the molar mass of the substance in grams per mol (g/mol), i.e. n equals 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:

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

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 Faraday's constant (i.e. 96484.34 C/mole), I is the photocurrent in Ampere (A) and t is time in seconds (s).

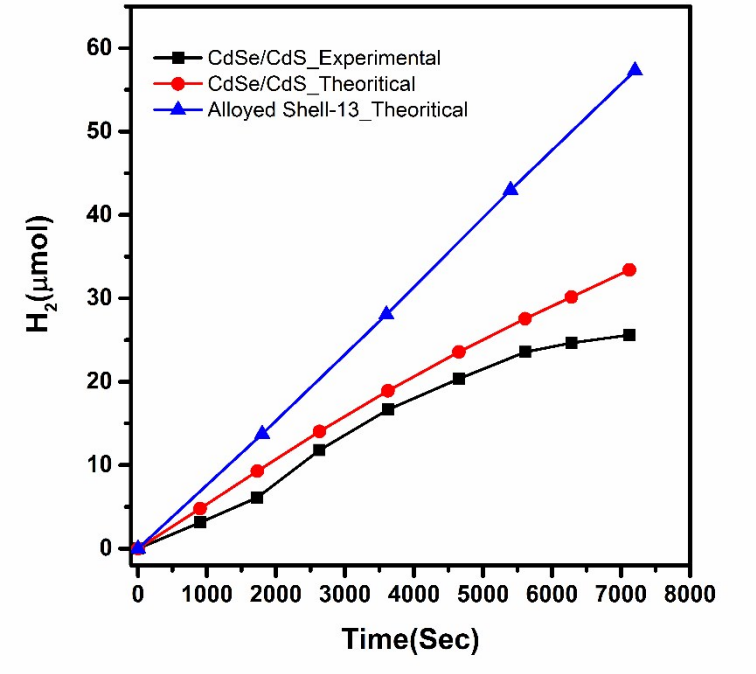

Figure S8. Hydrogen evolution of CdSe@CdS/$(ZnS)_2$ as a function of time at 0.2V vs RHE under 100mW/cm^2, illumination with AM 1.5G filter. The measured evolution of H_2 exhibits nearly a linear increase over time (solid red curve) and the theoretical value was calculated from the measured photocurrent (solid black curve). The same trend was found in the PEC system composed of alloyed shell-13 QDs as the photoanode as displayed by the theoretical calculated H_2 evolution after calibration (solid blue line).[1, 3]

1. R. Adhikari, L. Jin, F. Navarro-Pardo, D. Benetti, B. AlOtaibi, S. Vanka, H. Zhao, Z. Mi, A.Vomiero, F. Rosei, *Nano Energy* 2016, **27,** 265-274.

2. H. Zhao, D. Benetti, L. Jin, Y. Zhou, F. Rosei, A. Vomiero, *Small,* 2016, **12,** 5354.

3. F. Navarro-Pardo, L. Jin, R. Adhikari, X. Tong, D. Benetti, K. Basu, S. Vanka, H. Zhao, Z. Mi, S.H. Sun, V.M. Castano, A. Vomiero, F. Rosei, *Mater. Chem. Front.,* 2017, **1,** 65-72.