

Supporting Information

A Stable Quantum Dot Photoelectrolysis Cell for Unassisted Visible Light Solar Water Splitting

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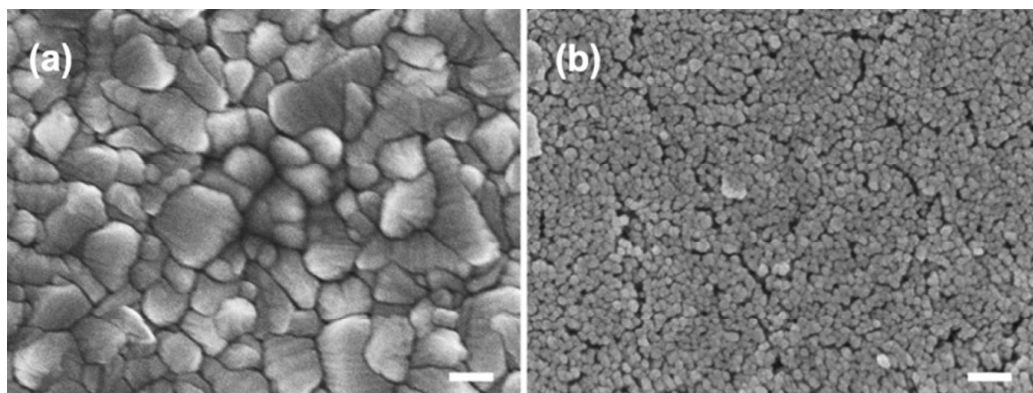


Figure S1. FESEM images of (a) FTO and (b) NiO compact layer coated FTO. Scale bar: 100 nm.

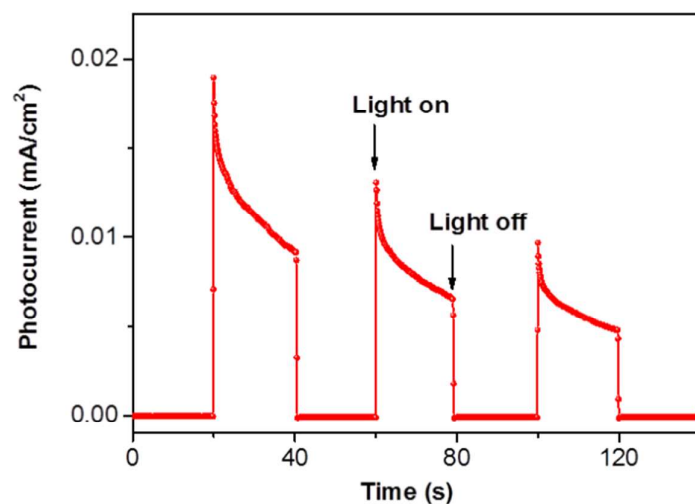


Figure S2. Photocurrent vs. time plot of CdSe/NiO photoelectrode without NiO compact layer at zero bias condition.

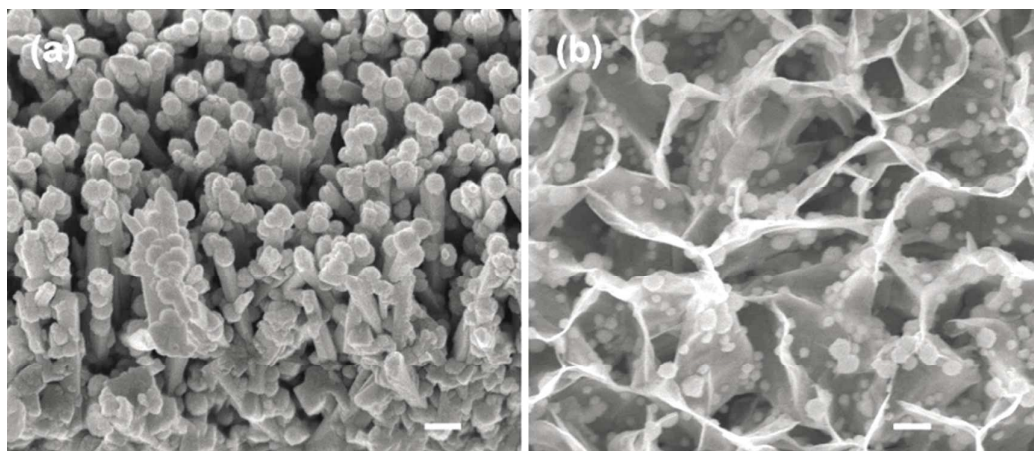


Figure S3. High-magnification SEM images of CdS QDs-modified TiO₂ nanorods and CdSe QDs-modified NiO nanosheets. Scale bar is 100 nm.

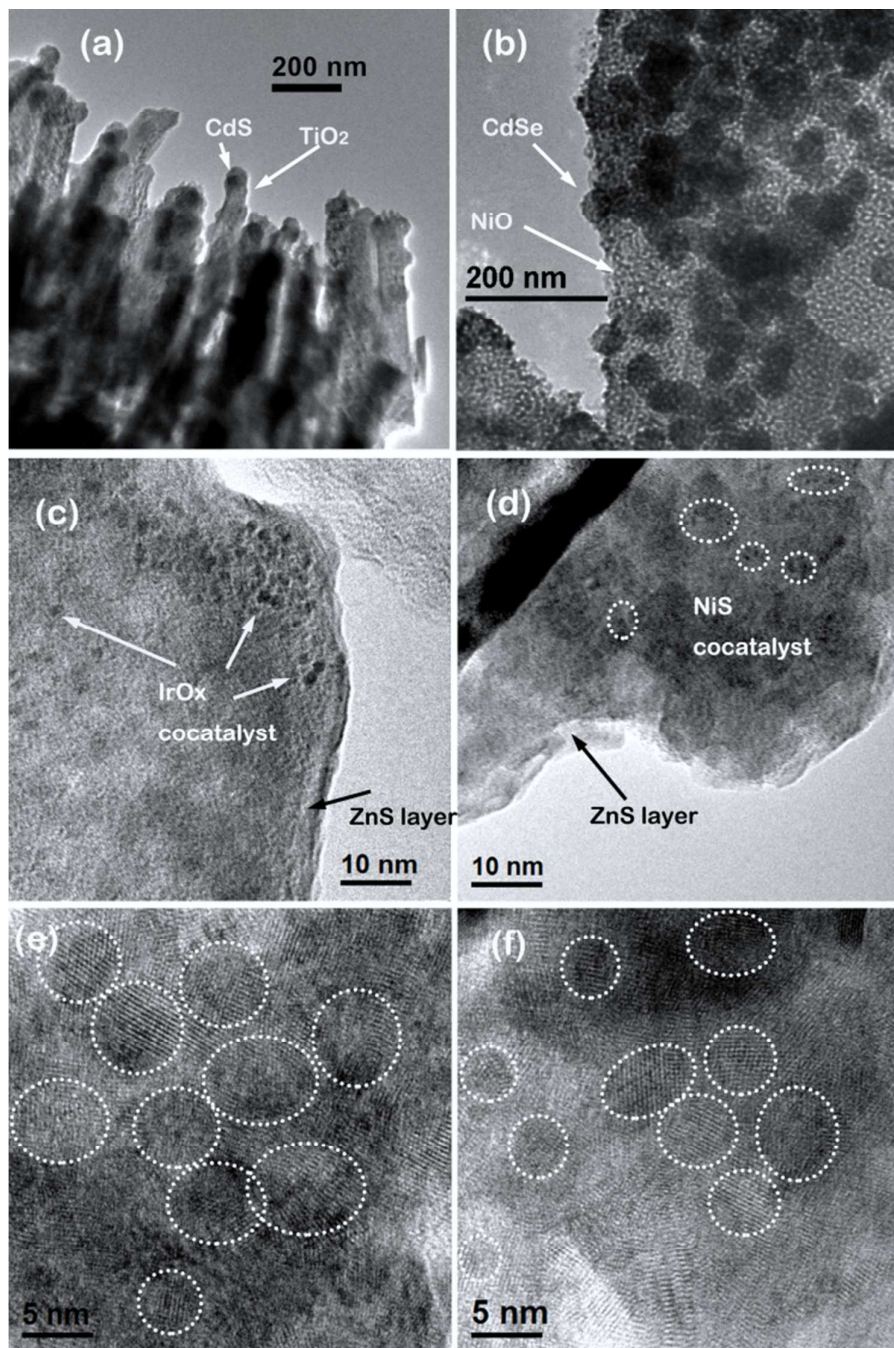


Figure S4. (a) & (b) TEM images of CdS QDs-modified TiO₂ nanorods and CdSe QDs-modified NiO nanosheets. (c) & (d) TEM images showing the decoration of ZnS protective layer and loading of IrO_x and NiS co.catalysts. (e) & (f) HRTEM images showing the crystalline sizes of CdS and CdSe quantum dots.

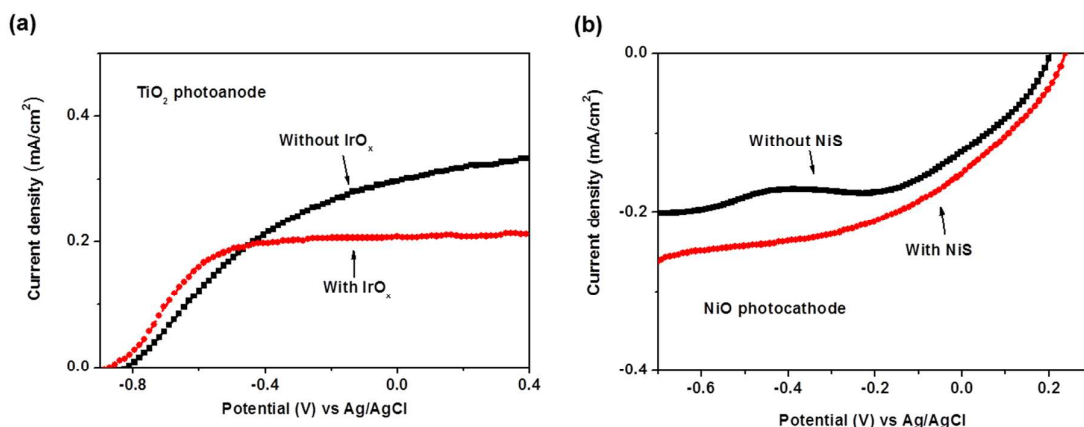


Figure S5. (a) The effect of oxygen-generating $\text{IrO}_x \cdot n\text{H}_2\text{O}$ nanoparticles on $\text{ZnS}/\text{CdS}/\text{TiO}_2$ nanorod photoanode, and (b) the effect of hydrogen-generating NiS nanoparticles on $\text{ZnS}/\text{CdSe}/\text{NiO}$ nanosheet photocathode.

Note: In present condition, the loading of the IrO_x particles on the electrode can significantly improve charge-transfer kinetics to remarkably reduce the overpotential of anodic reaction while the onset potential moved toward lower potential region as compared to that of absence of IrO_x loading, which was consistent with the literature report of co-catalysts loading effect and our observation in the case of NiS co-catalysts loading (as shown in Figure S5b). A lower maximum photocurrent might be attributed to the formation of multiple interfaces including the $\text{IrO}_x/\text{electrode}$ interface and $\text{IrO}_x/\text{electrolyte}$ interface, which might increase the recombination probability of photogenerated carriers. Furthermore, this decrease in photocurrent might be attributed to the inner-filter effect from presence of IrO_x particles upon surface of TiO_2 , which results in competing light absorption by IrO_x particles after their attachment on the photoelectrode.

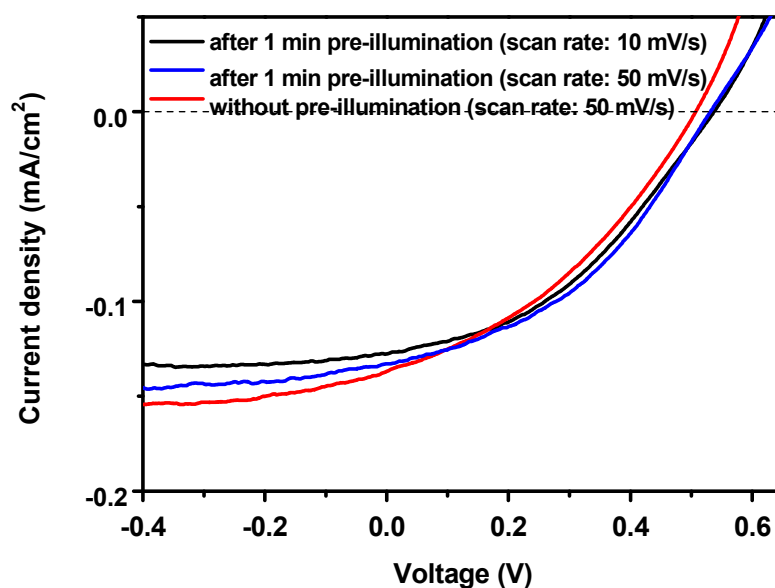


Figure S6. J - V curves of a photoelectrolysis cell with CdS QDs-modified TiO_2 nanorod and CdSe QDs-modified NiO nanosheet photoelectrodes measured at different measurement conditions. a, J - V curve after 1 min pre-illumination (at a scan rate of 10 mV/s). b, J - V curve after 1 min pre-illumination (at a scan rate of 50 mV/s). c, J - V curve after 1 min pre-illumination (at a scan rate of 50 mV/s).

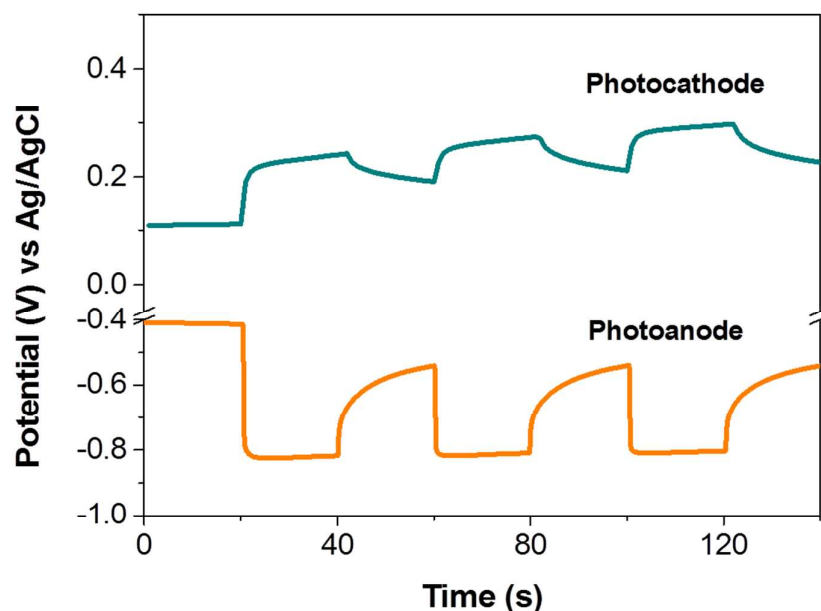


Figure S7. Photovoltage vs. time curves of NiO photocathode and TiO₂ under visible light in 0.5 M Na₂SO₄ electrolyte solution.

Note: The change of open circuit voltage of NiO photocathode can be attributed to the slow kinetics of charge-carriers within NiO since NiO has a very low hole mobility in the range of 0.02-0.8 cm²/(V·s), which considerably leads to an ineffective charge-separation and results in a slow photoresponse. As compared to photoanode case (TiO₂), NiO photocathode exhibited a slow response in both light-on and light-off conditions, while the TiO₂ photoanode can rapidly response to light illumination. Consequently, The NiO nanosheets synthesized in present work have been calcined at 450 °C for 1 hour to improve the crystalline nature, which allow us to improve the carriers mobility and charge separation within NiO.

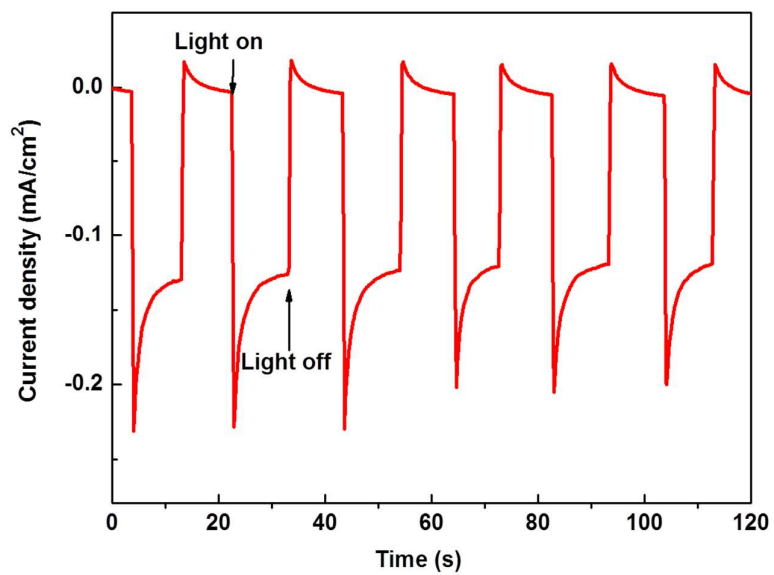


Figure S8. Transient photocurrent response curve of wire linked photoanode and photocathode system at zero bias condition under 1 sun visible light illumination in 0.5 M Na₂SO₄ electrolyte solution.

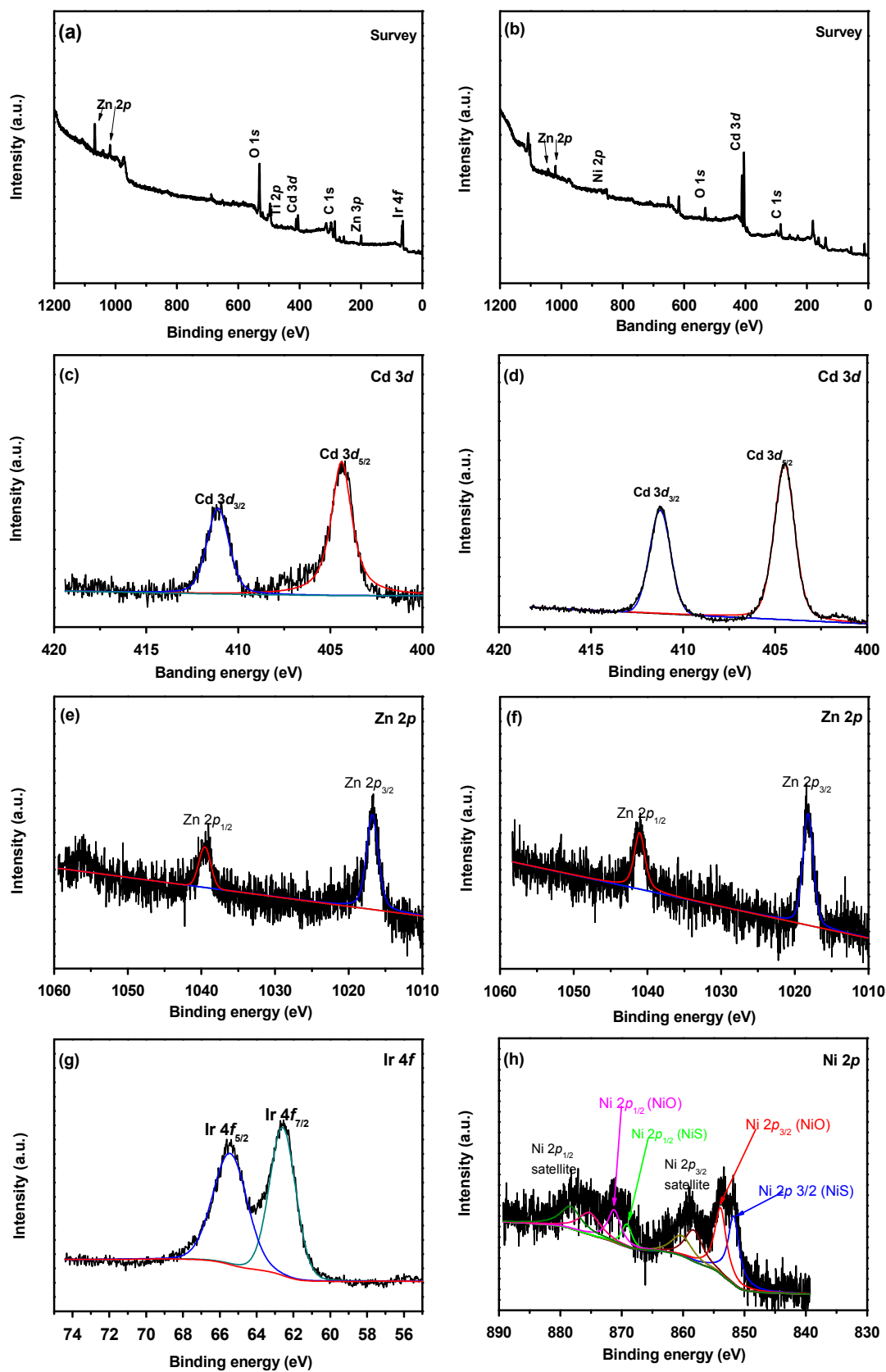


Figure S9. XPS spectra of CdS/TiO₂ photoanode (a, c, e & g) and CdSe/NiO photocathode (b, d, f & h) for various elements after PEC measurement.