

Supporting Information

Double-sided CdS and CdSe Quantum Dot Co-sensitized ZnO Nanowire Arrays for Photoelectrochemical Hydrogen Generation

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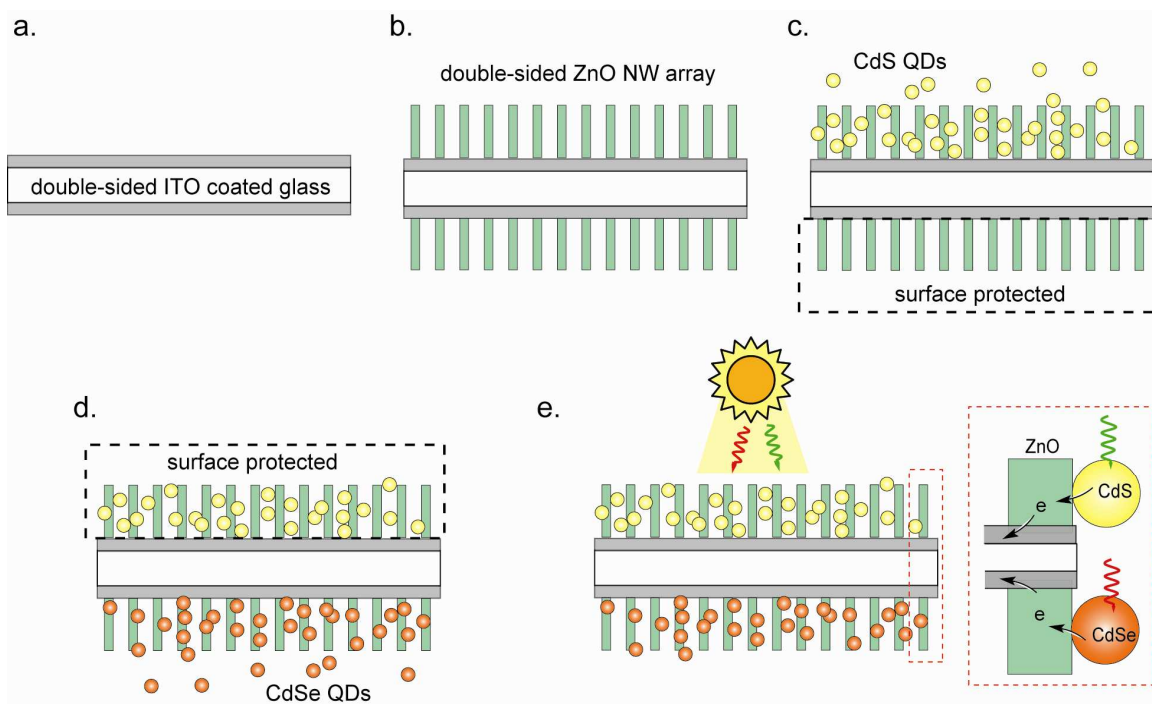
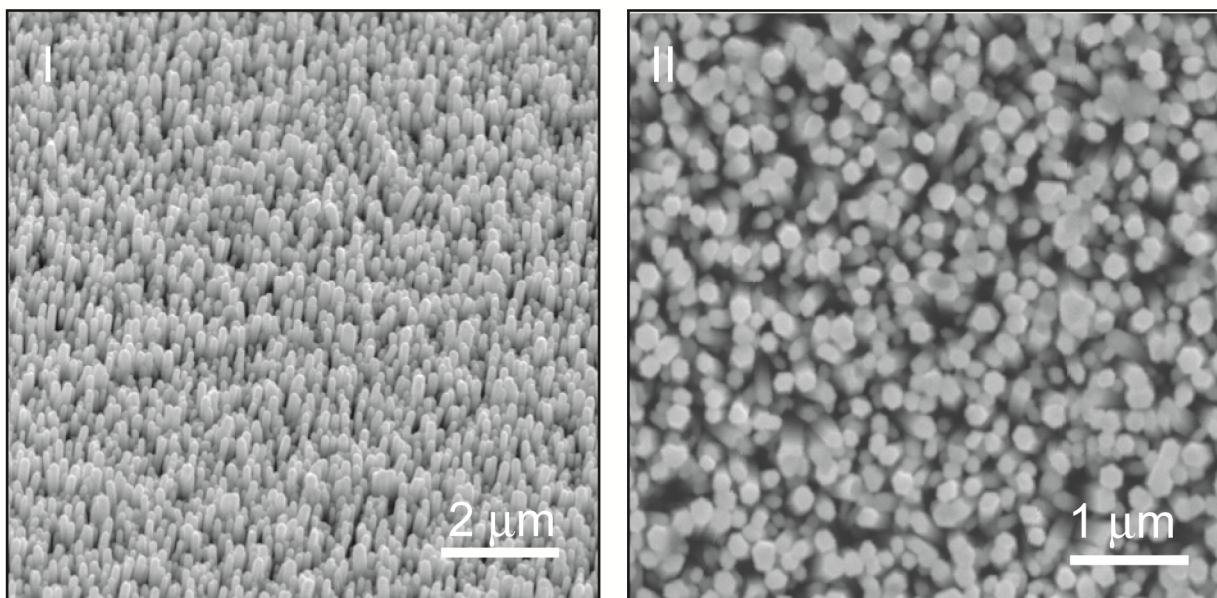


Figure S1. A schematic diagram illustrating the approach for fabricating double-sided QD co-sensitized ZnO NW arrays (CdS-ZnO-ZnO-CdSe). (a) ZnO nanoparticle seeds were deposited on both sides of indium-tin-oxide (ITO) substrates, using previously reported method¹; (b) The substrate was held by a rubber holder and placed vertically into a Teflon-lined stainless steel autoclave, filled with 20 ml 0.05 M zinc nitrate and 0.05 M hexamethylenetetramine aqueous solution, and then heated at 90 °C for 6 hours. Uniform white films were obtained on both sides of the ITO substrate; (c) ZnO NW arrays on one side of the substrate was sensitized with CdS QDs using modified chemical bath deposition method,² while the other side was covered by a parafilm foil and all edges were sealed with adhesive tape; (d) The other side of the substrate was sensitized with CdSe QDs³ using the same method mentioned in (c); (e) The double-sided QD co-sensitized ZnO NW arrays were fashioned into photoanode. The CdS QD sensitized ZnO NWs are faced towards the incident light during all PEC measurements. (The details of synthesis and device measurement please refer to Methods)

a.



b.

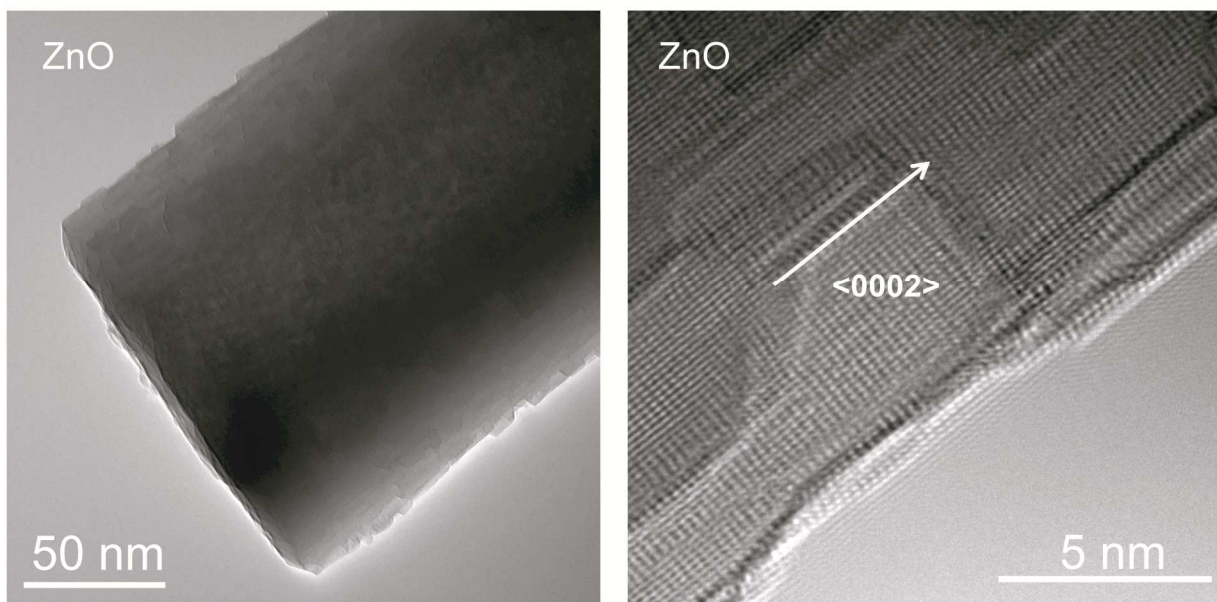


Figure S2. (a) SEM images of ZnO NW arrays on ITO substrate collected at a tilted angle of 30 degree (I) and 0 degree (II); the top view SEM image confirms the nanowires have hexagonal cross-section, indicating the nanowires grow along c axis. (b) TEM images of ZnO NW. White arrow highlighted the NW growth axis of $\langle 0001 \rangle$.

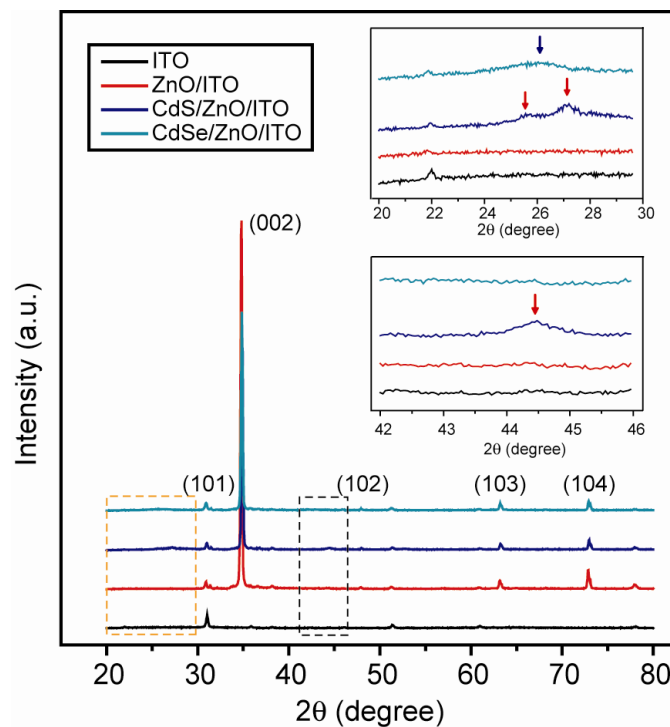


Figure S3. XRD patterns of double-sided ZnO NWs and sensitized ZnO NW samples on ITO substrate. Insets: magnified regions highlighted by the dashed squares. The red and blue arrows highlighted the diffraction peaks of CdS and CdSe, respectively.⁴ Their characteristic diffraction peaks were identified and can be indexed to CdSe cubic and CdS hexagonal structure (standard cards JCPDS No. 41-1049 and JCPDS No. 08-0459) respectively.

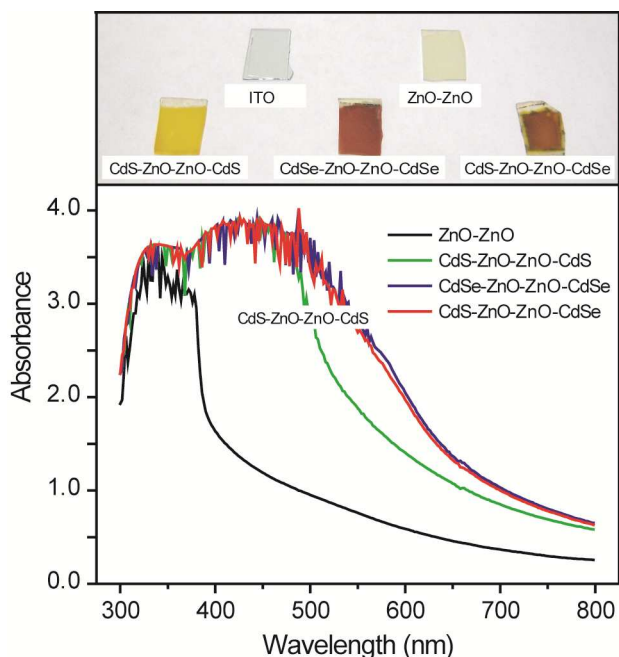


Figure S4. UV-Vis spectra collected from a pristine double-sided ZnO NW sample and QD sensitized ZnO NW structures; Inset: picture of a blank ITO substrate and the four NW samples used for the UV-Vis measurements. The results confirmed the improved visible light absorption of QD sensitized ZnO NWs.

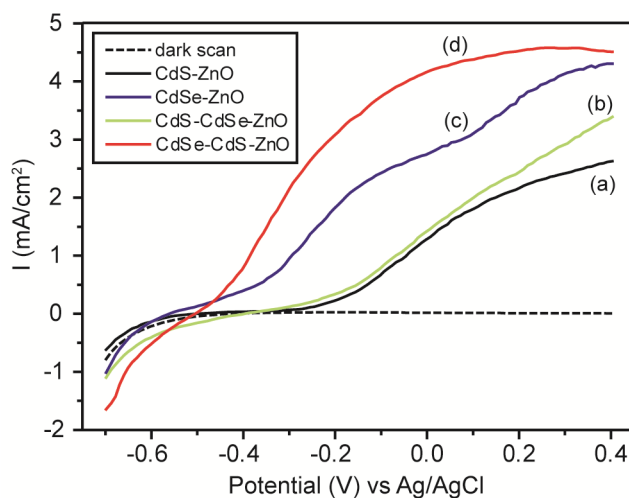


Figure S5. Linear sweep voltammograms, collected at a scan rate of 10 mV/s at applied potentials from -0.7 V to +0.4 V, from photoanodes fabricated from (a) CdS-ZnO; (b) CdS-CdSe-ZnO; (c) CdSe-ZnO; and (d) CdSe-CdS-ZnO nanowire samples at incident light of 100 mW/cm². Dashed line is the linear sweep voltammogram of CdS-ZnO in the dark.

Methods

Synthesis of ZnO NW arrays: ZnO nanowires were grown on a ZnO nanoparticle seeded ITO substrate using hydrothermal method reported elsewhere.¹

ZnO seed coating -- both sides of ITO glass were deposited with zinc acetate ethanol solution, then rinsed by ethanol solution and blew dry. This coating step was repeated five times. Then, the sample was annealed at 350 °C for 30 min. The zinc acetate deposition and annealing processes were carried out twice to ensure a uniform coating of ZnO nanocrystal seeds on ITO glass.

Hydrothermal synthesis -- ITO glass coated with ZnO seeds was vertically put into a rubber holder. The substrate with holder was placed into a Telfon-lined stainless steel autoclave, filled with 20 ml 0.05 M zinc nitrate and 0.05 M hexamethylenetetramine aqueous solution. The sealed autoclave was heated in an electric oven at 90 °C for 6 hours. ITO glass coated with uniform white film on both sides was rinsed with deionized water and air dried.

CdS and CdSe QD sensitization: ZnO NW arrays were sensitized with CdS and CdSe QDs sequentially, using chemical bath deposition (CBD).^{2, 3} For double-sided samples, we first sensitized ZnO NW arrays with CdS QD on one side of the substrate, while the other side was protected by a parafilm foil and all edges were sealed with adhesive tape. Then the other side of the substrate was sensitized with CdSe QDs using the same approach. For single-sided co-sensitized samples, we sensitized ZnO NW sequentially with CdS and CdSe QDs.

CdS QDs were deposited on ZnO NWs with a modified CBD method.² As prepared double-sided ZnO NW array with one side protected was incubated in an aqueous solution of 10 mM $\text{Cd}(\text{NO}_3)_2$ and 10 mM thioacetamide at 40 °C for 10 min. The white ZnO NW film became yellow. The substrate was then washed with deionized water and air dried.

CdSe QDs were deposited on ZnO NWs using a reported CBD method.³ Cadmium nitrate ($\text{Cd}(\text{NO}_3)_2$) was used as Cd source and sodium selenosulphate (Na_2SeSO_3) as Se source. The Na_2SeSO_3 aqueous solution was prepared by refluxing Se powder in an aqueous Na_2SO_3 solution at 80 °C overnight. Freshly prepared 0.1 M Na_2SeSO_3 (8 ml) was mixed with the same volume

0.02 M $\text{Cd}(\text{NO}_3)_2$ and 0.5 M sodium citrate in a 20 ml glass vial. CdS QD sensitized ZnO NW sample with CdS side protected was placed into the vial, and heated in water bath at 60 °C for 15 min. The process above was termed as a CBD cycle. We carried out two CBD cycles, the color of ZnO NW arrays were changed from white to deep red.

Electron microscopy: SEM images were collected in a Hitachi 2700 SEM. NWs were dispersed in ethanol solution and then transferred onto Cu/lacey-carbon TEM grids. TEM images were collected in a FEI monochromated F20 UT Technai TEM/STEM operated with a 200 kV electron beam.

Powder X-ray diffraction: The NW films on ITO substrate were characterized by PXRD with a Rigaku Americas Miniflex Plus powder diffractometer. Diffraction patterns were recorded from 20 to 80° 2 θ with a step size of 0.04° at 1°/min.

UV-vis spectroscopy: The UV-vis absorption spectra of NW films were taken on a Hewlett-Packard 8452A diode array spectrophotometer at room temperature.

Fabrication and PEC measurement of NW photoanodes: NW arrays were fashioned into photoanodes by securing a copper wire onto a bare portion of ITO substrate with silver conducting paint. Both sides of the substrate were connected to the same copper wire by soldering. The substrate was then sealed on all edges with epoxy resin except for a working area of 0.18 cm² on both sides. All PEC measurements were carried out in a three-electrode electrochemical cell in a stirred solution bubbled with nitrogen, with a coiled Pt wire as a counter electrode and an Ag/AgCl electrode as a reference. The electrolyte was a mixture of 0.25 M Na_2S and 0.35 M Na_2SO_3 aqueous solution with a pH of ~9.5, which were used as sacrificial reagents to maintain the stability of CdS and CdSe. I-V measurements were made on a Solartron 1280B potentiostat coupled to an infrared water-filter (Oriel no. 6127) using a 1000 W Xenon Arc Lamp as the white light source. The light power of 100 mW/cm² was measured with a power

meter (Molelectron, PM5100). IPCE characteristics were measured with a monochromator (Oriel Cornerstone 130 1/8m).

Further specifications of the PEC setup include:

Focal Length	130 mm
F/#	F/3.7
Usable Wavelength Range	180 nm to 24 μ m with interchangeable gratings
Spectral Resolution	With 1200 l/mm grating, 10 μ m x 2 mm slit
Wavelength Accuracy	0.50 nm
Wavelength Precision	0.08 nm

References

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