Supplementary Information

Synthesis of 1D CdS/PbS heterostructured nanowires through cation exchange

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1. Supplementary Information 1 (SI_1)

SYNTHESIS

Preparation of Bi seed: Various amounts of zerovalent bismuth seeds were prepared by mixing a 38mM solution of $BiCl_3$ in acetone into the Cd precursor at 270^{o}C. It is to be noted that for preparing CdS, the S precursor was added almost immediately after the Bi seed addition. This allows the Bi salt to undergo reduction and form the catalytic seed and participate immediately for CdS nanowire growth by solution-liquid-solid (SLS) mechanism.

CdS nanowire growth: A solution of 150mL 1-octadecene, 4g cadmium acetate dihydrate, and 8.4 ml oleic acid was heated to 280^{o}C under stirring in a 3-neck flask. Once heated to 280^{o}C, 250µL of $BiCl_3$/acetone (38mM) was injected into the flask. The Bi seeds were followed immediately by an injection of a solution of tri n-octyl phosphine sulfide or TOPS (240mg S, 6ml TOP). The solution turns brown over a period of few minutes and maintained at this condition (temperature and color) for ~5-6 min after TOPS injection and later removed from the heating source. The nanowires are subsequently precipitated by adding methanol to the solution followed by centrifuge-assisted separation.

Ligand exchange with Pyridine: The precipitated nanowires were washed twice in toluene prior to pyridine exchange. 150 mL of pyridine was added to the separated nanowires and heated at 80^{O}C for 1 hour. Finally, the nanowires were centrifuged and separated from the pyridine dispersion. This process was repeated twice and finally the product was collected and stored in methanol.

Ag^{+} treatment using $AgNO_3$ solution: A 30mM solution of $AgNO_3$ in methanol was prepared and was added drop wise to a dispersion of pyridine treated CdS nanowires in methanol until the solution turned dark green. The resultant product was separated and washed with methanol to remove excess Ag^{+} as well as other loosely associated cations from the solution.

Pb^{2+} treatment using $Pb(NO_3)_2$ solution: Pure $Pb(NO_3)_2$ solid was added to a dispersion of CdS/Ag_2S in methanol to attain a molar ratio 1.5:2 $Pb(NO_3)_2$ to $Ag(NO_3)$. 0.4mL of tri-n-butyl phosphine (TBP) was added to this solution and then heated to 65^{O}C for 1 hour with rapid stirring. The resultant product was washed with methanol and stored.

CHARACTERIZATION

Surface and Optical characterization: X-Ray powder diffraction patterns were recorded using a Philips12045 B/3 diffractometer at a scan rate of 1.6°/min using Cu Kα radiation. UV-visible absorbance studies were performed using a Shimadzu UV-2501PC spectrophotometer in the range of 350 nm-900 nm. FT-IR studies were carried out using a PerkinElmer Spectrum RX-1 FTIR spectrometer. Each run consisted of 10 scans in the 400 - 4000 cm^{-1} range using the transmission mode with a resolution of 4 cm^{-1}. The average of the 10 scans was examined. Transmission electron microscopy (TEM) was performed using a JEOL TEM equipped with a LaB6 filament. The TEM samples were prepared using a dispersion of the materials in methanol followed by drop casting it on carbon coated Cu grid. The samples were vacuum dried prior to TEM analysis.

Photoelectrochemical characterization: Photoelectrochemical studies were carried out in a three-electrode quartz cell with Pt wire as the counter electrode, Ag/AgCl (in 3M KCl) as the reference electrode, and CdS on ZnO/ITO glass as working electrode.

Preparation of working electrode: A thin layer of large bandgap n-type ZnO was drop casted on ITO to reduce recombination of photogenerated charges. The working electrodes were prepared by drop casting nanowire dispersion onto the ZnO/ITO. The sample was annealed in a tube furnace at 350°C under N_2 flow for 35 minutes.

Photoelectrochemical analysis was performed using 0.1M Na_2S in water as the electrolyte. I-V characteristics were collected using an Autolab PGSTAT 30 electrochemical analyzer. The working electrode was irradiated with a 500W Newport Xenon lamp equipped with 0.5 M $CuSO_4$ solution as a far UV cutoff filter.

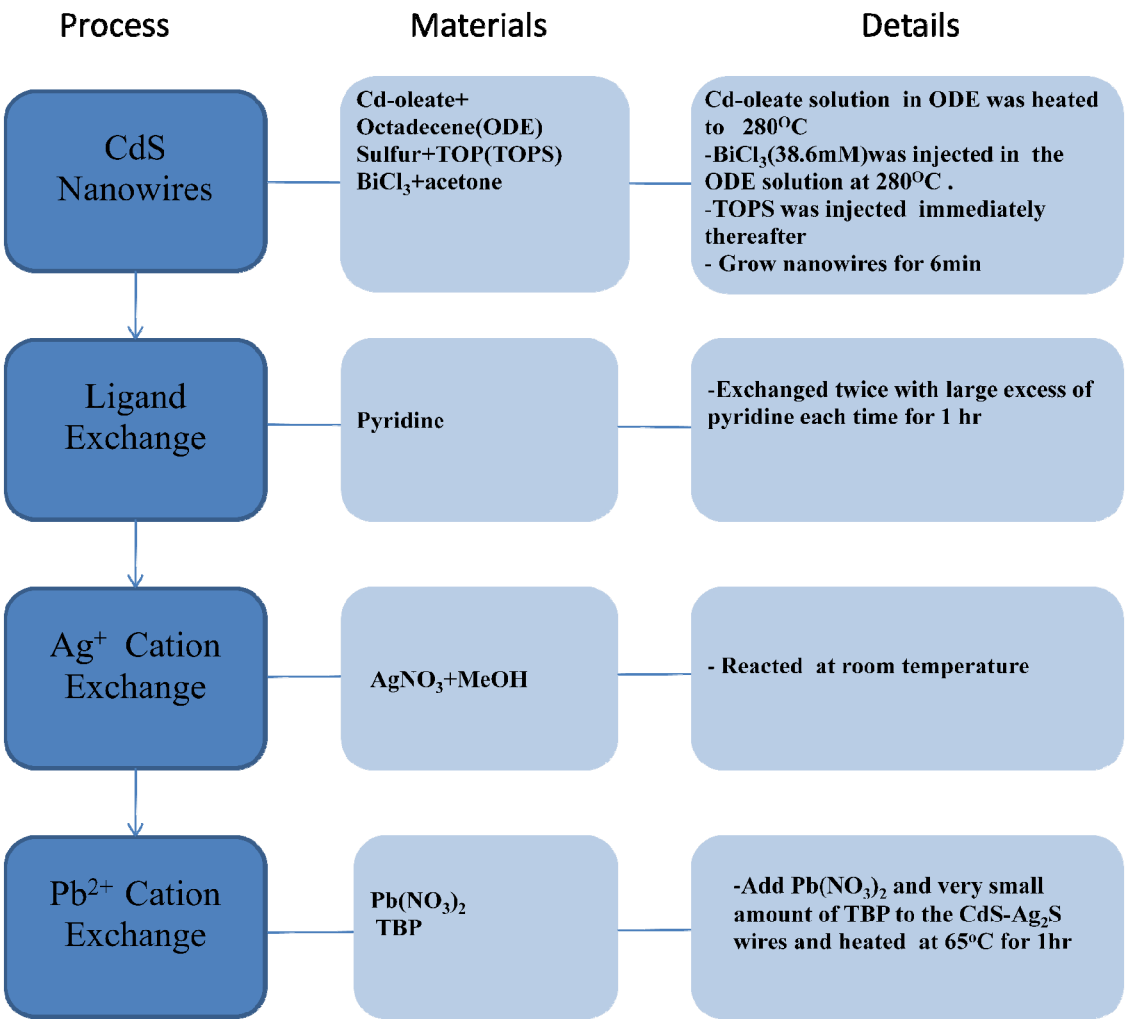


Figure SI_1 A process flow sheet for the synthesis of the 1D CdS/PbS nanowires.

2. Supplementary Information 2 (SI_2)

High resolution transmission electron microscopy (HRTEM) images of a CdS nanowire

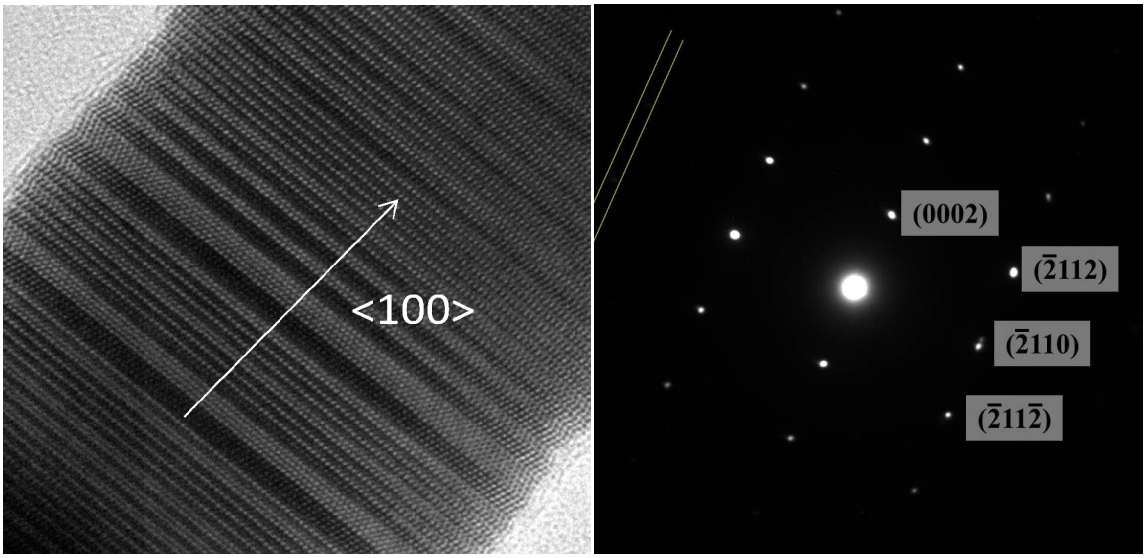
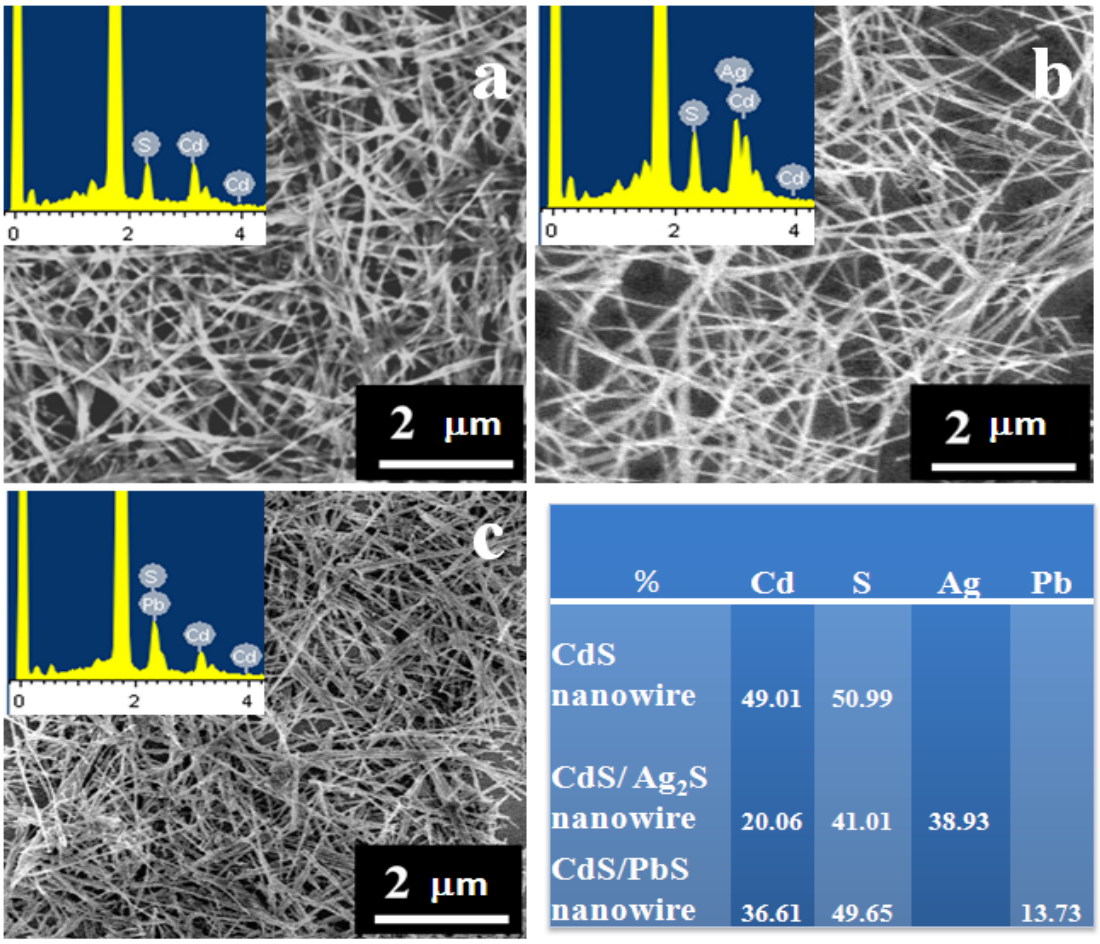


Figure SI_2 Figure SI_2 (left) shows the HRTEM of a single crystalline CdS nanowire prepared using the SLS method. The growth direction of the nanowires matches with <100> of wurtzite CdS. Figure SI_2 (right) shows the SAED pattern from the same nanowire. Points are indexed and matches with hexagonal CdS.

3. Supplementary Information 3 (SI_3)

Scanning Electron Microscopy (SEM) and EDS of different samples



%	Cd	S	Ag	Pb
CdS nanowire	49.01	50.99		
CdS/ Ag_2S nanowire	20.06	41.01	38.93	
CdS/PbS nanowire	36.61	49.65		13.73

Figure SI_3 Figure SI_3(a) shows a low magnification SEM image of a dense CdS nanowire film formed after ligand exchange with pyridine. The inset shows the EDS pattern of CdS nanowires with Cd:S ratio of 49:51. Figure SI_3 (b) shows the SEM of the CdS/Ag_2S nanowires. The nanowires appear to be rough compared to pristine CdS nanowires. Ag_2S cluster are noticed along the length of the nanowires. The EDS (inset) of SI_3(b) suggest ~ 50% of the Cd was replaced by Ag. Figure SI_3 (c) shows the SEM of CdS/PbS. The physical features of the majority of the nanowires appear to be similar to the nanowires before Pb^{2+} treatment. The EDS spectra in the inset show ~27.5 % Pb content on nanowires. [*The table provides the quantitative data of the composition corresponding to the samples shown in the SEM images*].

4. Supplementary Information 4 (SI_4)

Thermogravimetric or TGA Analysis

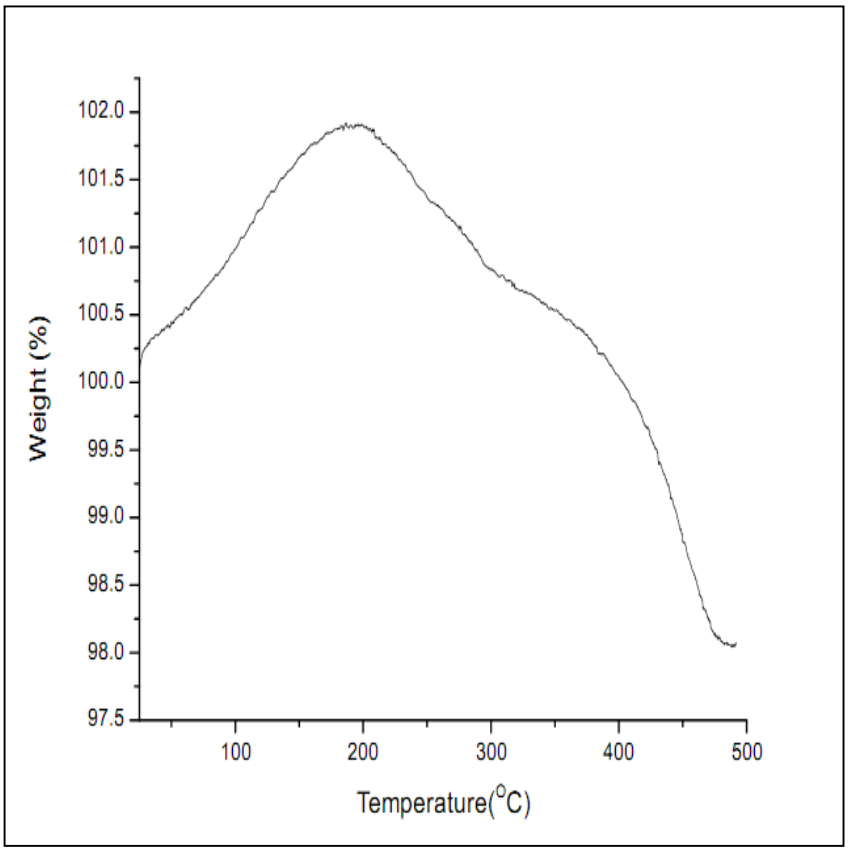


Figure SI_4 The TGA of CdS nanowire after pyridine exchange is shown in the figure. A weight gain of ~2 % is observed until 200°C. Further, beyond 200°C the material starts to lose weight as temperature is ramped up to 500°C.

The key information to be noted from this analysis is the weight loss in the region of 200°C- 350°C. This corresponds to loss of pyridine. Beyond this point the material further start to degrade as indicated by the varying slopes of the TGA. To maintain material integrity, heat treatment temperature was therefore restricted to 350°C.

5. Supplementary Information 5 (SI_5)

Fourier Transform Infra-red spectroscopy or FTIR Analysis

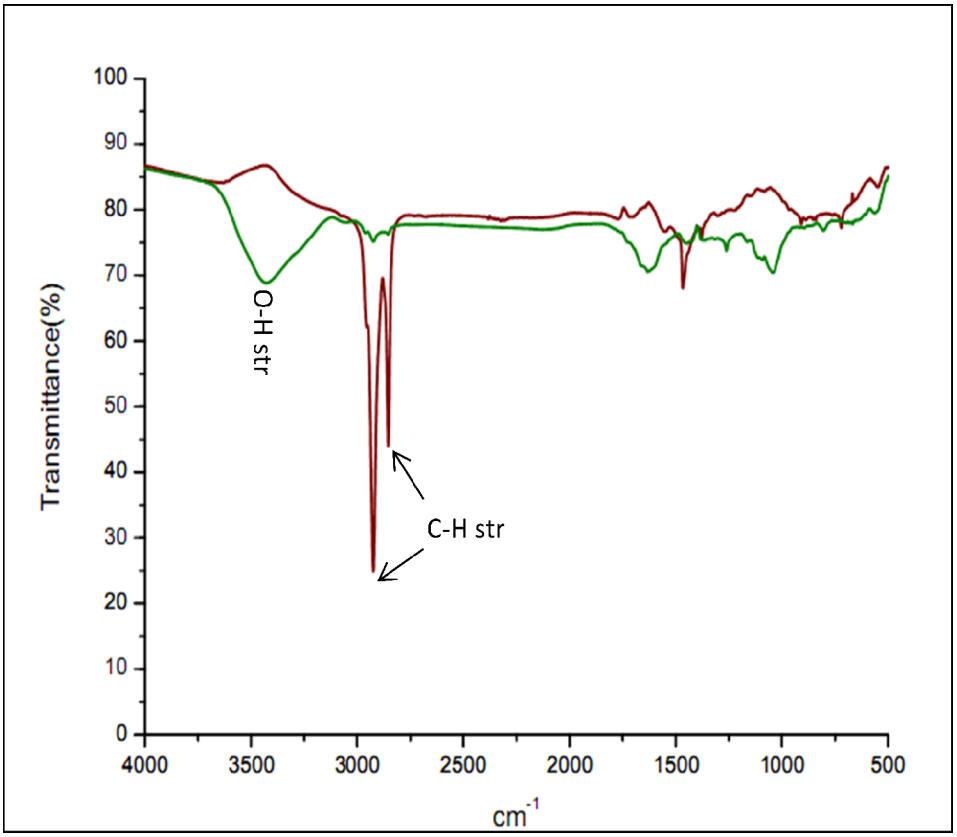


Figure SI_5 FTIR spectra of CdS nanowire before (red) and after (green) pyridine exchange is shown in the figure. The almost complete elimination of the C-H stretching frequency (noted between 3000-2800 cm^{-1}) indicate the success of the ligand exchange.

6. Supplementary Information 6 (SI_6)

UV-Visible Absorption Spectroscopy

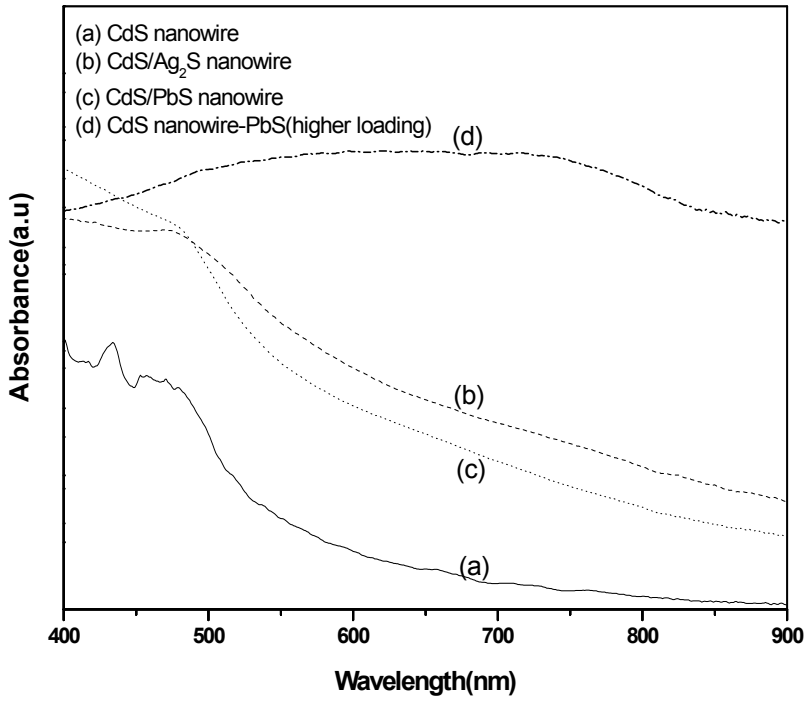


Figure SI_6 The figure shows the UV-visible absorbance spectra of the nanowires samples. SI_6(a) shows the pristine CdS nanowire absorbance with an onset absorbance at 500nm corresponding to 2.48 eV calculated from 1st order derivative of the plot. The bandage for CdS after Ag^{+} treatment shows red shift of onset absorbance. (SI_6(b)). An increase in the absorbance can be noted in the 500nm-900nm region. Absorbance in this region is characteristic to Ag_2S formation. The absorbance values decreases slightly after Pb treatment as shown in SI_6(c). When 70% of the Cd^{2+} is replaced by Pb^{2+},a very broad absorbance profile over the 500-900 nm range is noticed as shown in SI_6(d). This absorbance profile starts to diminish below 500 nm and above 800 nm. PbS nanoparticles are known to display absorbance of this nature. These optical measurements indicate the presence of a large amount of polydispersed PbS nanoparticles on the CdS nanowire framework.

7. Supplementary Information 7 (SI_7)

Mott-Schottky Analysis

The relationship between capacitance and voltage of an electrode in contact with an electrolyte is given by:

$$1/C^2 = 2(V+V_{fb})/(q\varepsilon_0\varepsilon_r n_d)$$

Where the C, V_{fb}, ε_0, ε_r, n_d are capacitance, flatband potential, permittivity in free space, relative dielectric constant of the semiconductor and donor density.

In an ideal case, the linear portion of the plot corresponds to the ideal junction behaviour. One can estimate the apparent flatband potential and donor density from its slope and intercept. One can deduce the p and n characteristics in a composite material from the slopes of this plot. The negative or positive nature of the slope indicates p-type and n-type behaviour respectively. This approach is mostly used to evaluate planer Schottky junction with other considerations such as (i) zero individual resistance, (ii) surface and interfacial traps, and/or (iii) only one type of localized electronic defects. Not many reports are available on spatially distributed p-n junction nanostructures. Our results are discussed based on the linear portion of the curve as described in many other composite porous electrode systems. ZnO-CdS nanowire electrode shows a positive linear slope with flatband potential of -0.74V confirming the n-type nature of the electrode. ZnO-CdS/PbS nanowire samples show the same positive slope and V_{fb} as in ZnO-CdS NW electrode. However, at -0.5 V a change in direction of the slope is noticed giving rise to an overall bell type plot. This clearly indicates the presence and electronic coupling of a p-type material in the matrix. Apparent flat band potential measured from the linear fit of the 2nd part is -0.24 V. Second component from XRD and TEM is confirmed to be PbS but S source for formation of PbS is only limited to CdS nanowire framework. Therefore p-type PbS nanoparticles have to share interfaces with CdS nanowire i.e. formation of p-n junction which can facilitate photogenerated charge separation and may promote efficient photochemical oxidation and reduction in PbS and CdS surfaces respectively.

8. Supplementary Information 8 (SI_8)

Preliminary photocurrent – photovoltage response data

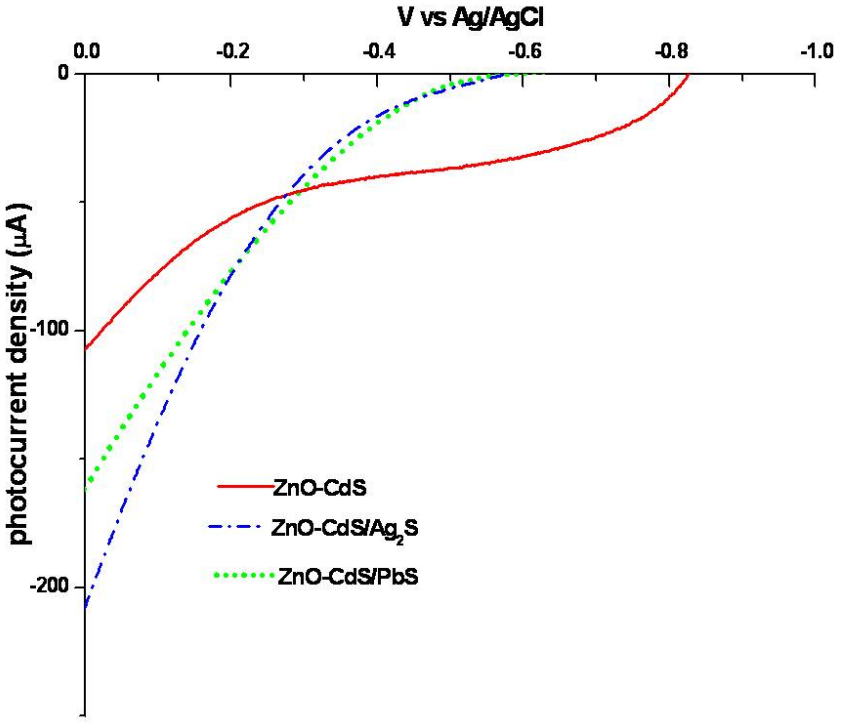


Figure SI_8 The I-V characteristics of the ZnO-CdS nanowire, ZnO-CdS/Ag_2S, and ZnO-CdS/PbS nanowire photoanodes. CdS nanowire-based photoanode shows a short circuit current density of ~ 108 μA and open circuit voltage of -0.83 V vs. Ag/AgCl. After Ag^+ exchange in nanowire framework, photocurrent density increases to ~208 μA but V_{oc} comes down to ~0.58V. With PbS nanoparticle on the nanowire framework at 30% PbS loading the current density reduces to ~160 μA/cm^2. This reduction in photocurrent density is not unexpected as loading of PbS is also reduced compared to Ag_2S loading as can be confirmed from the EDS data. At 70% loading the current density is the highest at ~ 300 μA/cm^2.