Electronic Supplementary Information (ESI)

Catalytically Active and Chemically Inert $CdIn_2S_4$ Coating on CdS Photoanode for Efficient and Stable Water Splitting

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I. Experimental Section

Materials

Table S1. Reagents used in the experiment.

Chemical formula	Specification	Application	Manufacturer
CdS	Analytically pure	Reactant	Alfa Aesar Co. Ltd.
Anhydrous $InCl_3$	Analytically pure	Reactant	Shanghai Aladdin Biochemical Technology Co.,Ltd.
$Na_2S\cdot 9H_2O$	Analytically pure	Reactant	Shanghai Aladdin Biochemical Technology Co.,Ltd.
Na_2SO_4	Analytically pure	Reactant	Shanghai Macklin Biochemical Co.,Ltd
Na_2SO_3	Analytically pure	Reactant	Shanghai Macklin Biochemical Co.,Ltd
CH_3CH_2OH	Analytically pure	Cleaning agent	Shanghai Aladdin Biochemical Technology Co.,Ltd.
CH_3OH	Analytically pure	Reactant	Shanghai Aladdin Biochemical Technology Co.,Ltd.
Pt	Commercial product	Counter electrode	Tianjin AIDAhengsheng Sicence-Technology Development Co.,Ltd.
Ag/AgCl electrode	Commercial product	Reference electrode	Tianjin AIDAhengsheng Sicence-Technology Development Co.,Ltd.

Preparation of CdS NFAs

First, Cd NFAs were grown on fluorine-doped tin oxide (FTO) substrate in a tube furnace by a thermal evaporation process reported in our previous work.[1] Second, Cd NFAs and 0.07 g sulfur were closely placed in the middle of a tube furnace, heated to 280 ℃ and held the temperature for 0.5 h. Resultantly, the Cd NFAs were transformed into CdS NFAs in the same tube furnace. Afterwards, the CdS NFAs were immersed in the $CdCl_2$ saturated methanol solutions for 40 min and annealed at

500 ℃ for 1 h in nitrogen gas.

Preparation of $CdS@CdIn_2S_4$ NFAs

The FTO with CdS NFAs was placed in the center of a quartz tube (60 nm in a diameter), and 0.5 g anhydrous $InCl_3$ was placed 6 cm upstream from the center of the quartz tube. After the quartz tube was evacuated to a negative pressure, N_2 (50 sccm) was flowed in the system. The furnace was heated to 500 ℃ by a heating rate of 10 ℃/min， kept the temperature for 10 min, and then cooled down to room temperature naturally.

Preparation of $CdIn_2S_4$ NFAs

The cation exchange was conducted on the CdS NFAs repeatedly for three times, and all of the parameters are same with these for the preparation of $CdS@CdIn_2S_4$ NFAs. Finally, fully exchanged $CdIn_2S_4$ NFAs can be obtained.

PEC measurements for water splitting

The PEC hydrogen evolution was tested in a standard three electrode system under simulated AM 1.5 solar illumination. The NFAs on FTO substrate served as the work electrode, a Pt plate as the counter electrode, and Ag/AgCl as the reference electrode. The photoelectrode was sealed with nail polish, and the active area was accurately defined as 1 cm^2. An aqueous solution of 0.25 M Na_2S/0.35 M Na_2SO_3 (pH 12.5) was used as electrolyte and sacrificial reagent.[2-4] The linear sweep voltammogram was measured by a Versastat 3 potentiostats electrochemistry workstation at a scan rate of 0.05 V s^{-1}. A 300W Xe lamp calibrated by a standard Si solar cell was used to simulate the 1 sun illumination (100 mW cm^{-2}), and the incident light was irradiated from the FTO side. The hydrogen evolution was detected each quarter using a gas chromatograph (GC-2014C) with a thermal conductivity detector and a molecular sieve 5 A column.

For ease of comparison, the potentials were converted and presented against the reversible hydrogen electrode (RHE) using the following equation:

$$E(vs\ RHE) = E(vs\ Ag/AgCl) + E_{Ag/AgCl}(ref) + 0.0591V \times pH \tag{1}$$

Characterizations

The morphologies of the CdS and CdS@$CdIn_2S_4$ NFAs were observed by a Hitachi S-4800 SEM at an accelerating voltage 5 kV and a Technai G2 F20 TEM with a field emission gun operated at 200 kV. The composition was analyzed by an energy dispersive spectrometer (EDS) module attached on SEM. XRD measurement was carried out using a Bruker D/max 2500 v/pc diffractometer. XPS spectra were obtained from Axis Ultra DLD (Kratos, Japan) equipped with an Al anode X-ray tube and helium lamp (He I radiation), respectively. The diffuse reflectance spectra and transmittance spectra were examined by a Hitachi 3010 UV-vis absorption spectrometer with an integrating sphere. EIS measurements were performed on a Versastat 3 potentiostats electrochemistry workstation with a frequency range from 0.1 Hz to 100 kHz at 0 V *vs.* Ag/AgCl.

II. Calculation Section

Photo-conversion efficiency

The photo-conversion efficiency (η) was estimated by [5]:

$$\eta = I \times (1.23\text{-}V)/P_{light} \tag{2}$$

where I is the photocurrent density, V the bias voltage applied between the working and counter electrodes, and P_{light} the incident light intensity (100 mW cm^{-2}).

Charge separation efficiency $P_{\text{charge-separation}}$

The measured photocurrent density can be described as[6]

$$J^{H_2O}_{photocurrent} = J_{absorbed} \times P_{charge\ speration} \times P_{hole\ \mathrm{injection}} \tag{3}$$

Where $J^{H_2O}_{\mathrm{photocurrent}}$ is the measured photocurrent density, J_{absorbed} is the absorption current density if all absorbed photons by given electrode are converted to electricity, $P_{\mathrm{charge\ seperation}}$ is the charge seperation efficiency and $P_{\mathrm{hole\ injection}}$ is the interfacial hole injection efficiency for photoanode. Since PEC experiments were carried out in the electrolyte of 0.25 M Na_2S/0.35M Na_2SO_3, and the hole scavenger, Na_2S, can consume photogenerated holes rapidly, the hole injection rate is almost 100% (

$P_{\text{hole injection}}$ =1) [6].

The absorption current density (J_{absorbed}) was calculated by the following equation:

$$J_{absorbed} = q\int_{300}^{600} \varphi_{\lambda} A d\lambda \tag{4}$$

where q is the electron charge, φ_λ is the AM 1.5 G solar simulator photon flux in $m^2/s{\cdot}nm$ (data obtained from National Renewable Energy Laboratory, USA), A is the fraction of incident light absorbed over the wavelength range (determined from UV-vis experiments as shown in Fig. S10a). The value of J_{absorbed} for NFAs is derived to be 8.46 mA cm^{-2} based on their absorbance data between 300-600 nm (Fig. S10b). Then, the $P_{charge\text{-}seperation}$ of CdS NFAs and CdS@$CdIn_2S_4$ NFAs can be obtained using the following equation:

$$P_{\text{charge}-seperation} = J_{\text{photocurrent}}^{\text{Na}_2S/Na_2SO_3} \div J_{\text{ab}sorbed} \tag{5}$$

where the $J_{\text{photocurrent}}^{\text{Na}_2S/Na_2SO_3}$ is the measured photocurrent density in 0.25M Na_2S/0.35M Na_2SO_3 as shown in Fig. 2a.

Hole injection rate

The rate of hole injection ($P_{\text{hole injection}}$) can be calculated by using the following equation:

$$P_{hole\ injection} = J_{\text{photocurrent}}^{H_2O} / J_{\text{photocurrent}}^{Na_2S/Na_2SO_3} \tag{6}$$

where $J_{photocurrent}^{H_2O}$ and $J_{\text{photo}current}^{\text{Na}_2S/Na_2SO_3}$ are the photocurrent densities without and with the hole scavengers, as shown in Fig. S5 and Fig. 2a, respectively.

III. Supporting Data

Table S2. Experimental parameters of cation exchange

	(a)	(b)	(c)	(d)	(e)
Temperature(°C)	350	400	450	500	550
Nitrogen flow rate (sccm)	50	50	50	50	50
Reaction time (min)	10	10	10	10	10
Amount of theInCl$_3$ (g)	1	1	1	1	1

Table S3. Reported performance of CdS based electrodes.

Electrode	During time and maintaining potential	J_0 (mAcm^{-2})	Stability (J/J_0)	Reference
CdS@CdIn$_2$S$_4$ NFAs	**10h, 0 V vs Ag/AgCl**	**5.5**	**~0.8**	This work
Nafion-coated CdS IOS	5000s, 0 V vs RHE	5.68	~0.92	7
3D-Branched ZnO/CdS/TiO$_2$ Nanowire Arrays	3000s, 0 V vs Ag/AgCl	half of photocurrent of 3D-Branched ZnO/CdS	~0.80	8
ZnFe$_2$O$_4$/CdS/ZnO Nanowire Arrays	3600s, 0 V vs Ag/AgCl	3.88	—	9
TiO2/CdS/Co–Pi Nanowire Arrays	2h, 0.6 V vs Ag/AgCl	1.1	~0.76	10
carbon-coated CdS core–shell nanostructures	—, -1 V vs Ag/AgCl	0.47	—	11

References

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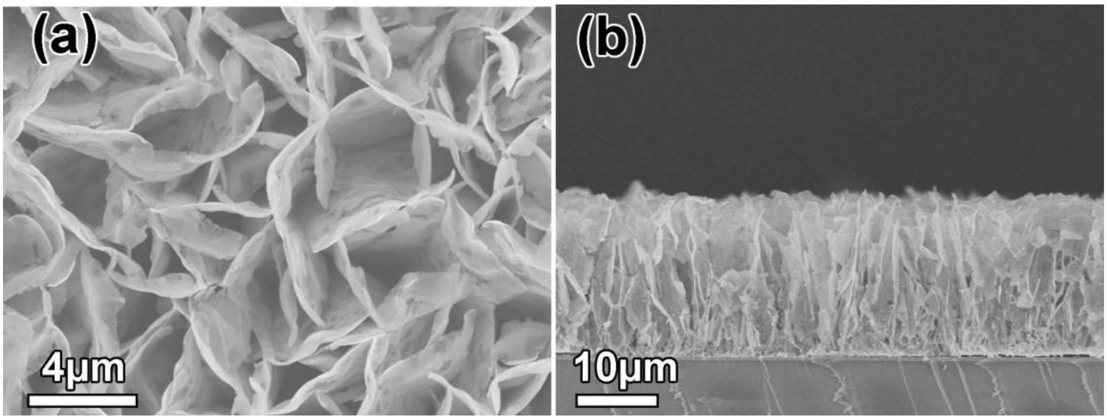

Fig. S1 Top view and cross-sectional SEM images of CdS NFAs.

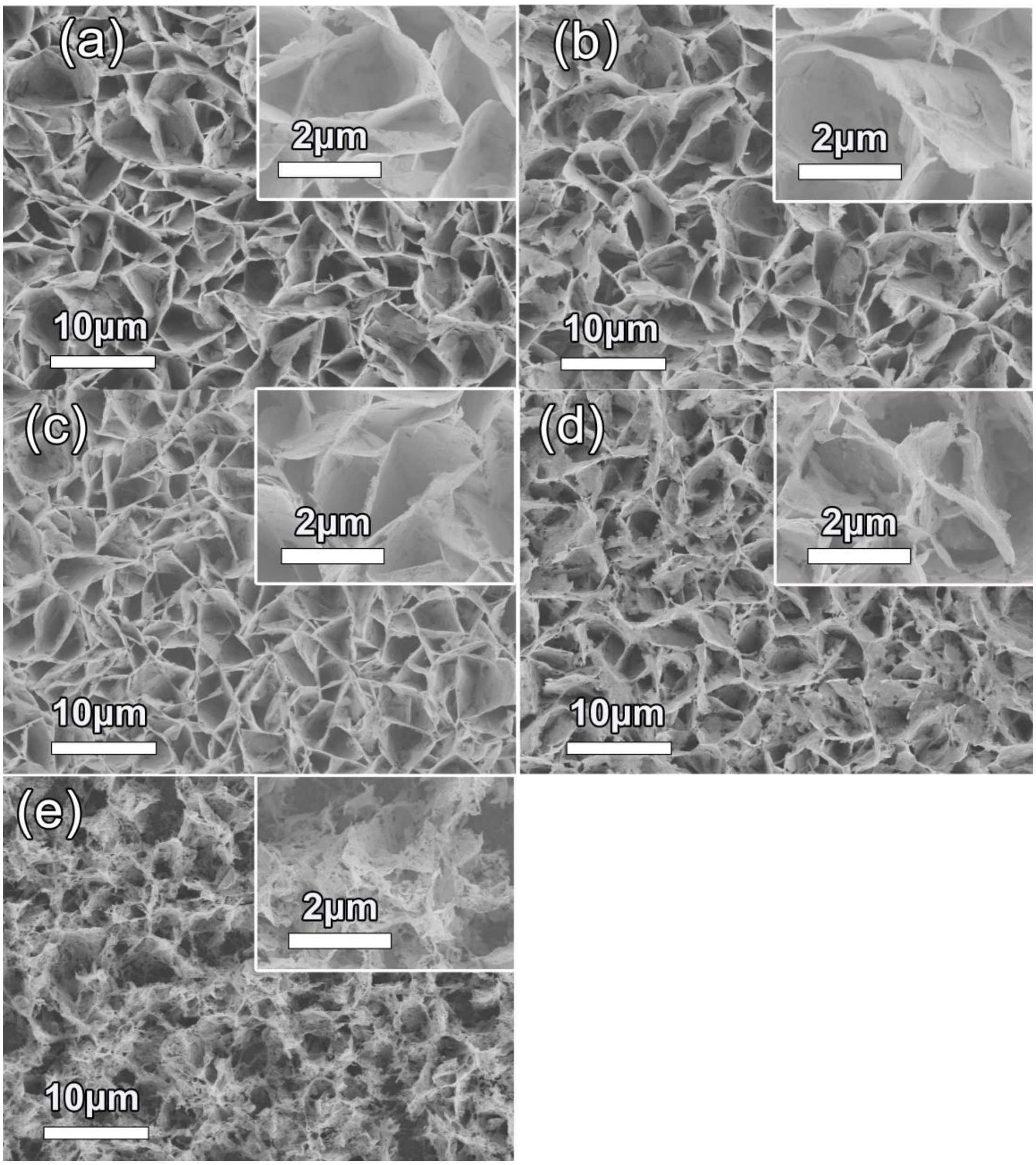

Fig. S2 SEM images of the CdS@CdIn2S4 nanoflake samples after cation exchange at (a) 350 °C, (b) 400 °C, (c) 450 °C, (d) 500 °C, (e) 550 °C.

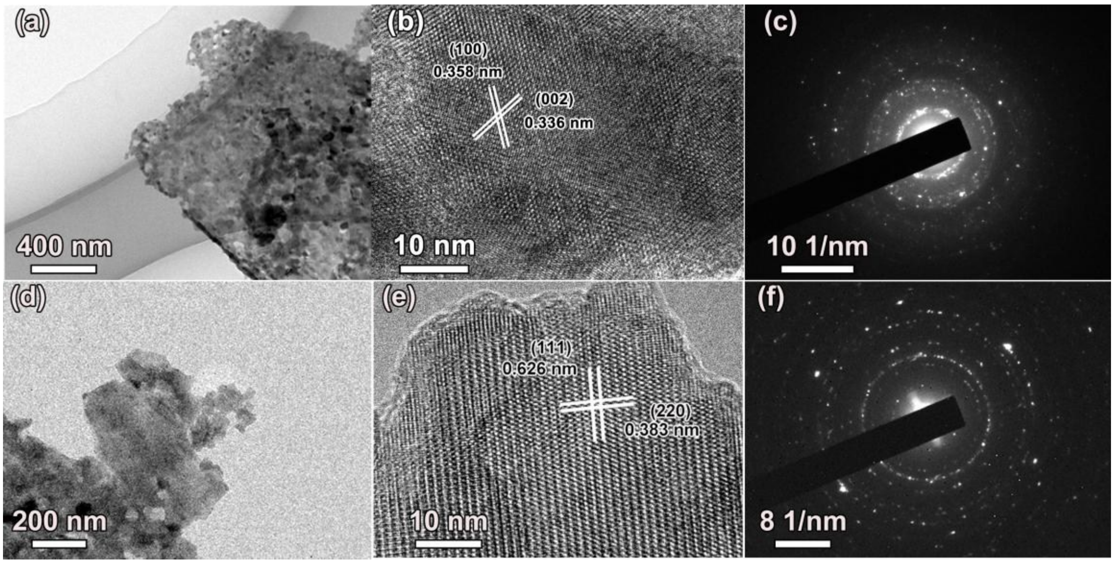

Fig. S3 (a), (b), (c) are Typical TEM, HRTEM, SAED images of CdS NFAs, respectively. (d), (e), (f) are typical TEM, HRTEM, SAED images of CdS@$CdIn_2S_4$ NFAs.

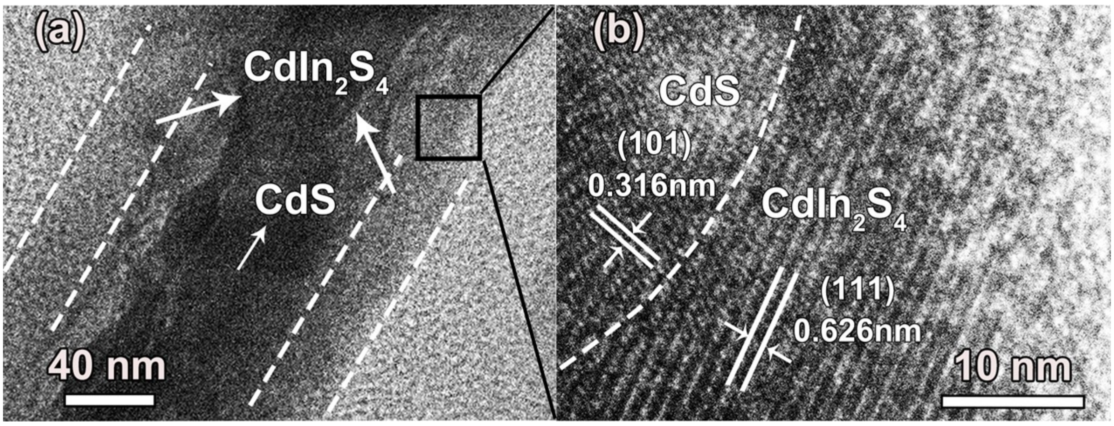

Fig. S4 Cross-sectional TEM image of CdS@$CdIn_2S_4$ nanoflake. (a) Low magnification imgae, (b) high resolution image.

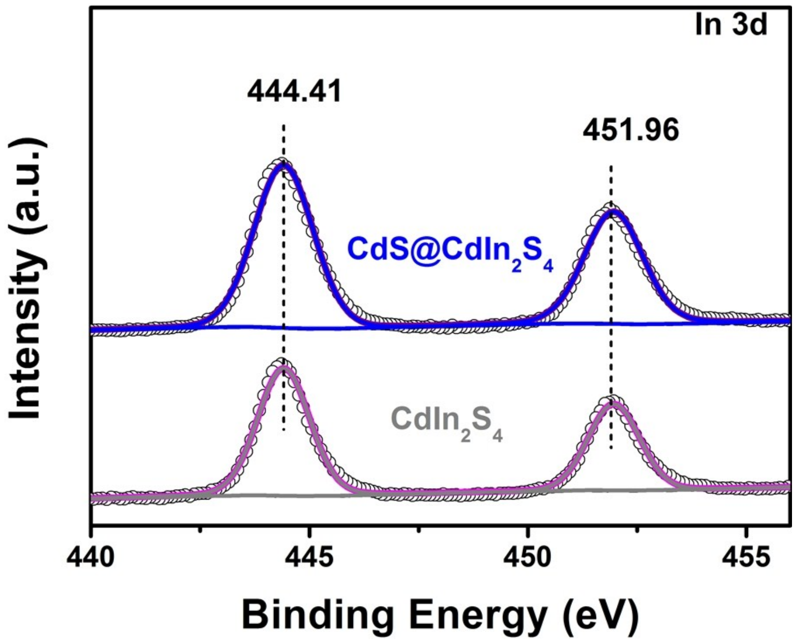

Fig. S5 XPS spectra of In 3d peaks for CdIn$_2$S$_4$ and CdS@CdIn$_2$S$_4$ nanoflake arrays.

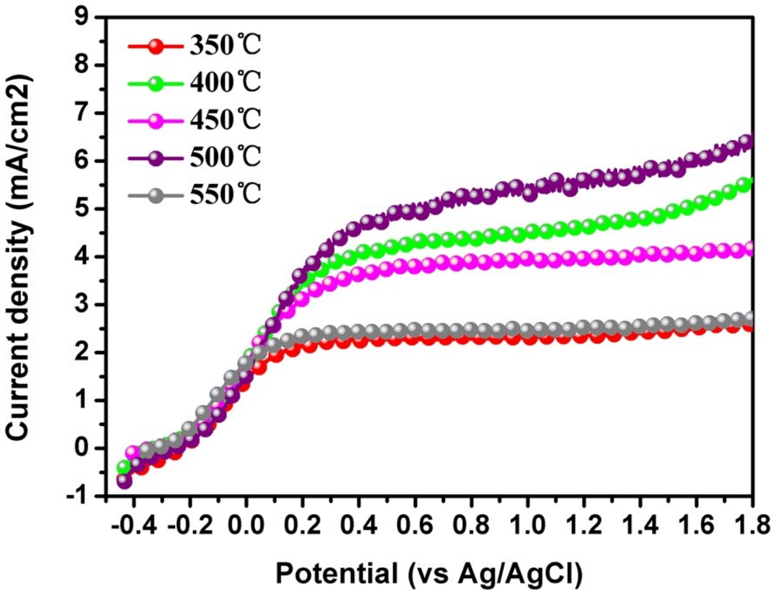

Fig. S6 Photocurrent of CdS@CdIn2S4 NFAs fabricated at different temperatures.

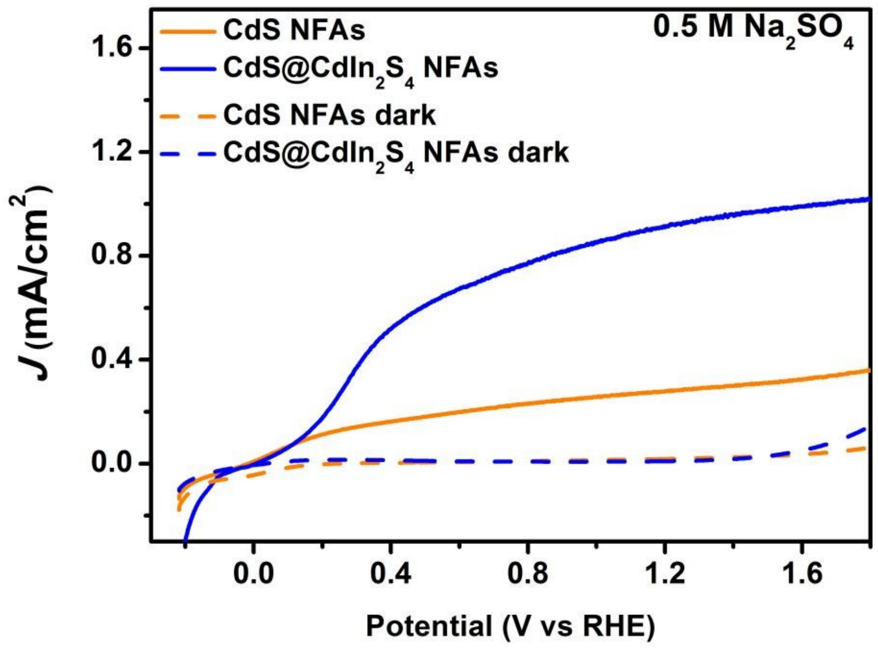

Fig. S7 Linear sweep voltammograms measured in 0.5M Na_2SO_4 under 1 sun AM1.5G illumination.

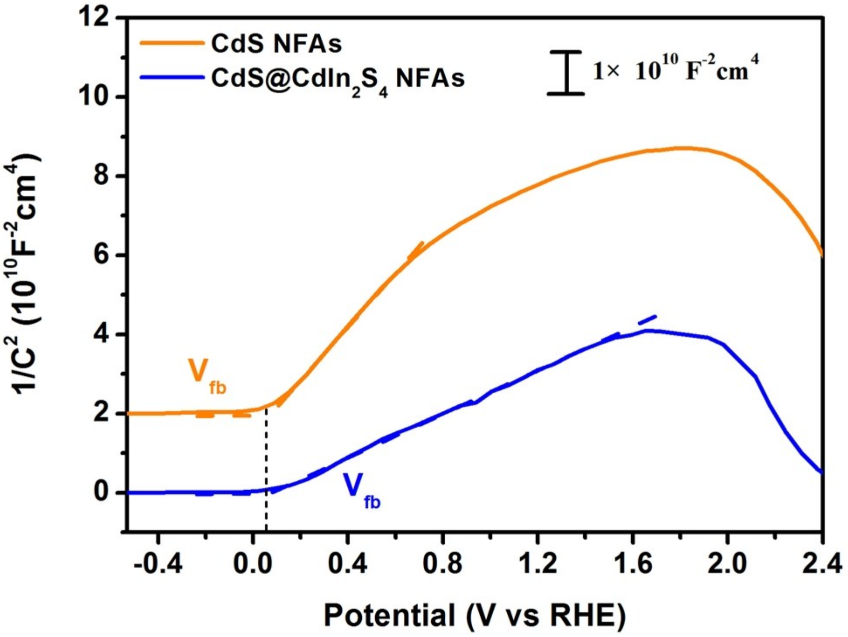

Fig. S8 Mott-Schottky plots of CdS and $CdS@CdIn_2S_4$ electrodes at 1 kHz.

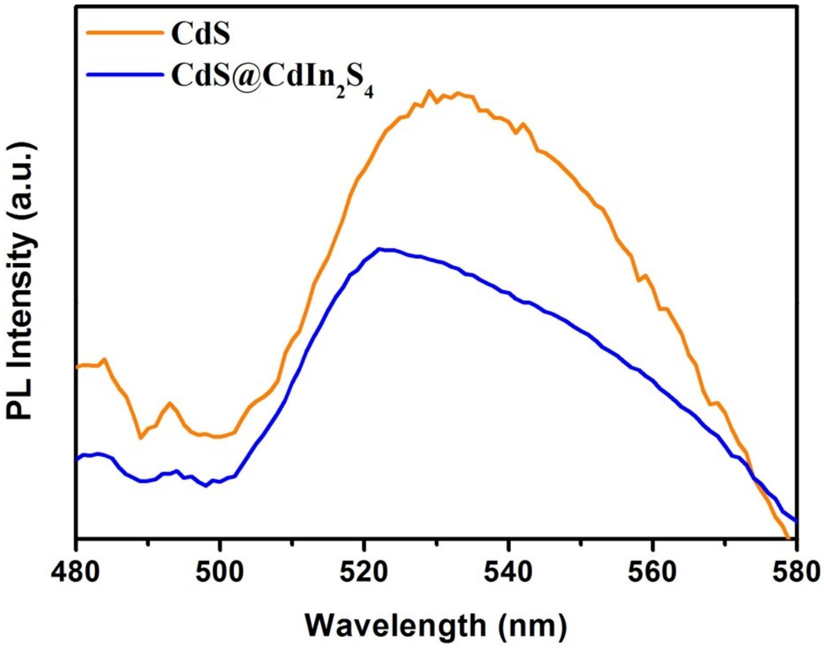

Fig. S9 Room-temperature PL spectra of CdS NFAs (orange line) and CdS@CdIn2S4 NFAs (blue line).

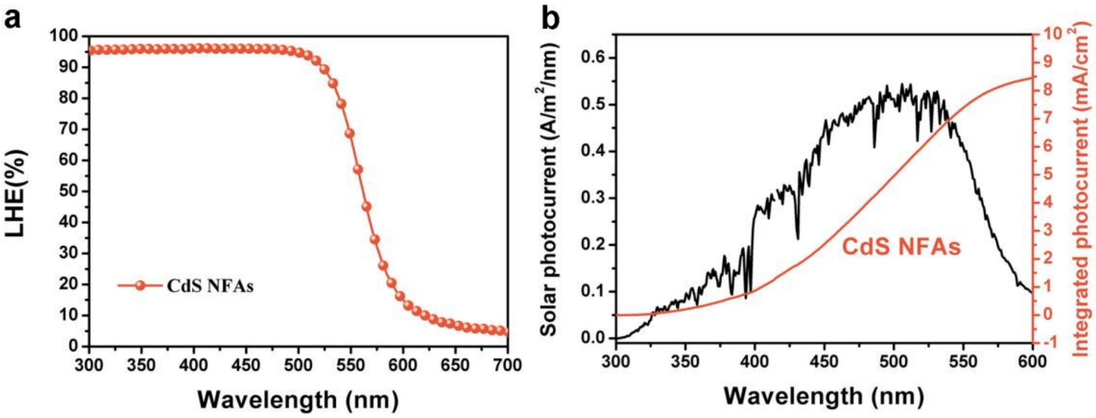

Fig. S10 (a) LHE (light harvesting efficiency) spectra of CdS nanoflake arrays (b) Solar photocurrent spectrum (black) and the corresponding integrated photocurrent density (orange) for CdS NFAs.