Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Enhanced photoelectric performance of CdS/CdSe co-sensitized TiO_2 Nanosheets Array Film

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Experimental

Preparation of vertically aligned TiO_2NSs array film 15 mL deionized water was mixed with 15 mL concentrated hydrochloric acid (mass fraction 36.5-38 %) and stirred at ambient condition for 5 min. 0.5 mL titanium butoxide was added into the mixture and stirred for another 5 min. Next, 0.25 g ammonium hexafluorotitanate was also added and further stirred for 15 min. Then, two pieces of cleaned Fluorine-doped SnO_2 glass plates (FTO) were put into a teflon-lined stainless steel autoclave of 100 ml and the mixture was transferred into it. The hydrothermal reaction was conducted at 170 ^oC for 12 h in an electric oven. After reaction, the autoclave was cooled to room temperature, the samples were were taken out and rinsed with deionized water thoroughly and annealed at 550 ^oC for 2 h in air atmosphere.

Preparation of TiO_2NSs/CdS array film photoelectrodes CdS QDs were deposited onto TiO_2NSs array film by CBD method. The samples were kept vertically in the alkaline mixture aqueous solution containing 0.02 M $CdCl_2 \cdot 2.5H_2O$, 0.5 M KOH, 1.5 M NH_4NO_3 and 0.2 M CH_4N_2S. The deposition was conducted at 80 ^oC for 0–40 min. After thoroughly washed by deionized water, the samples were soaked in anhydrous cadmium chloride saturated methanol solution for 10 s and annealed at 300 ^oC for 1 hour in air atmosphere.

Preparation of TiO_2NSs/CdS/CdSe array film photoelectrodes CdSe QDs were assembled onto the TiO2NSs/CdS array film by SILAR method. Typically, 0.5 M $Cd(NO_3)_2 \cdot 4H_2O$ in ethanol was used as cation source and Na_2SeSO_3 aqueous solution as anion source. The desired amount of CdSe QDs was obtained by manipulating the number of SILAR cycles. Each cycle of SILAR consists of successive immersion of the electrodes in cadmium ion solution for 10 min and selenide anion solution in water bath at 50 ^oC for 30 min. After each step of immersion, the samples were rinsed with deionized water and ethanol. Then, all the samples were annealed at 300 ^oC for 1 hour in air atmosphere.

Characterization: The crystal structure of the as-prepared films were characterized by a Rigaku D/max-ray diffractometer (XRD) with Cu Karadiation (λ = 1.5418 Å). The morphology and elemental analysis of the samples were characterized using field-emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDS) on a FEI MAGELLAN 400 Scanning Electron Microscope. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) were obtained through a JEM-2100F transmission electron microscope operating at 200 kV. UV–vis diffuse reflectance absorption spectra of the films were performed using a UV-3150 double-beam spectrophotometer. External quantum efficiency (EQE) was obtained through QTest

Station 1000A (CROWNTECH, INC.).

Photovoltaic measurements:

The samples were sealed in sandwich structures with a 25 μm spacer by using Pt as counter electrode, which were prepared by dropping 5mM H_2PtCl_6 in isopropanol onto the FTO substrate, followed by heating at 400 ^oC for 15 min. The liquid electrolyte composed of .1 M S and 1 M Na_2S solution was injected into the internal space of the two electrodes. The active area was 0.15 cm^2. Photocurrent–voltage measurements were carried out by a Keithley model 2400 Source Meter. The sun illumination (AM 1.5 G) was simulated by a 500W xenon lamp.

Figure S

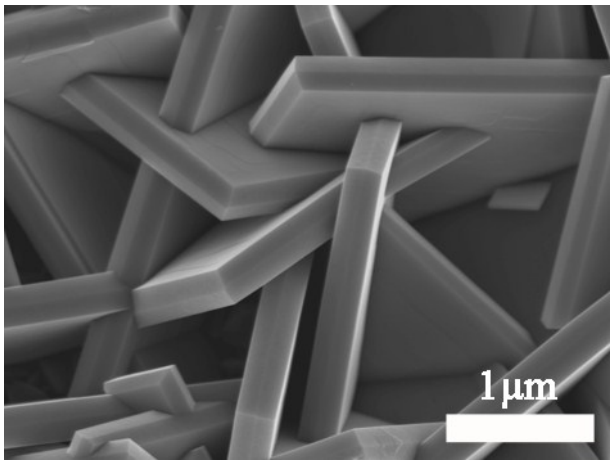

Figure S1. the magnified FESEM image of TiO_2NSs;

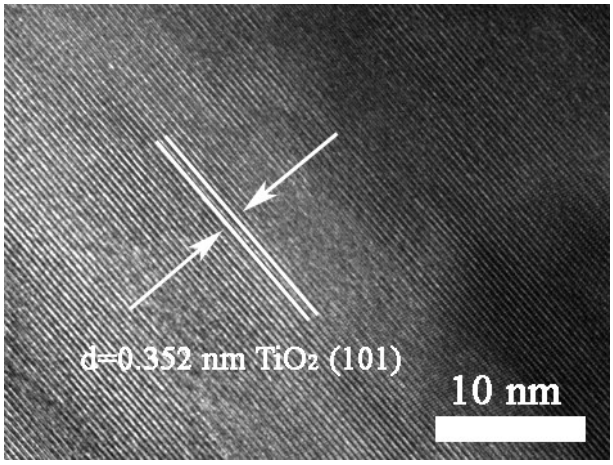

Figure S2. HRTEM image of bare TiO_2NSs;

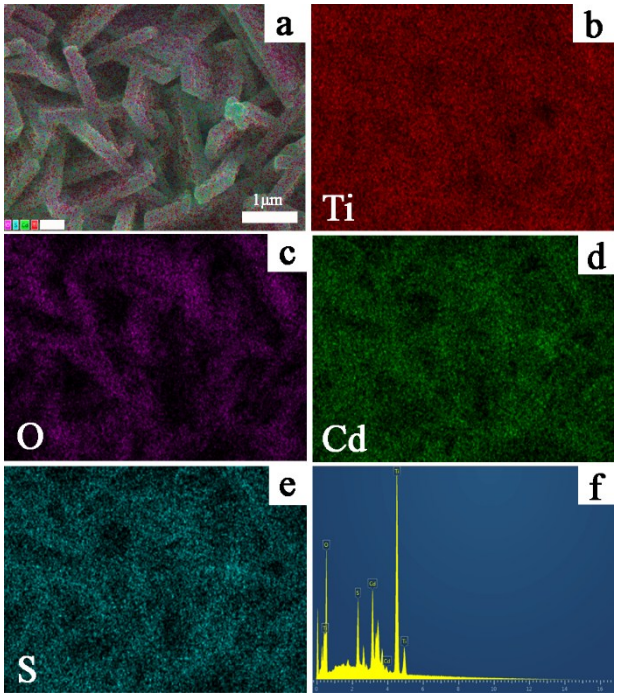

Figure S3 (a), (b), (c), (d) and (e) SEM image and Ti, O, Cd and S EDS mapping from TiO_2NSs/CdS(30 min); (f) EDS spectrum of TiO_2NSs/CdS(30 min).

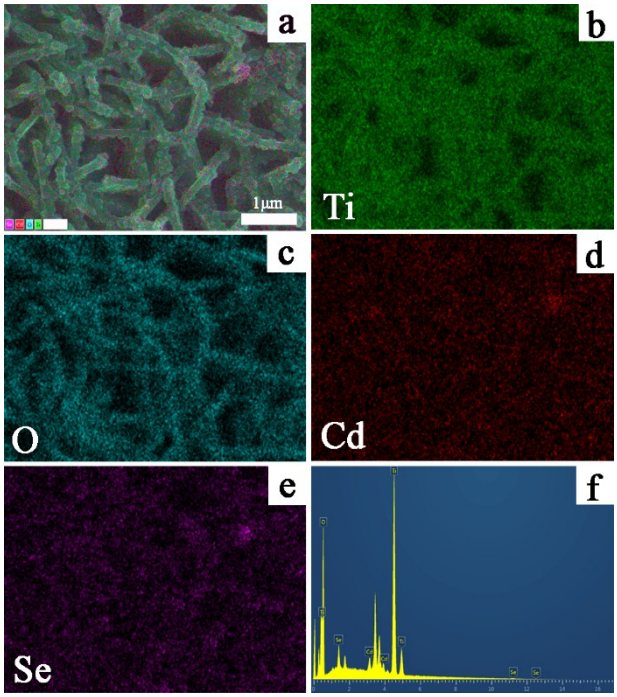

Figure S4 (a), (b), (c), (d) and (e) SEM image and Ti, O, Cd and Se EDS mapping from TiO_2NSs/CdSe(10 C); (f) EDS spectrum of TiO_2NSs/CdSe(10 C).

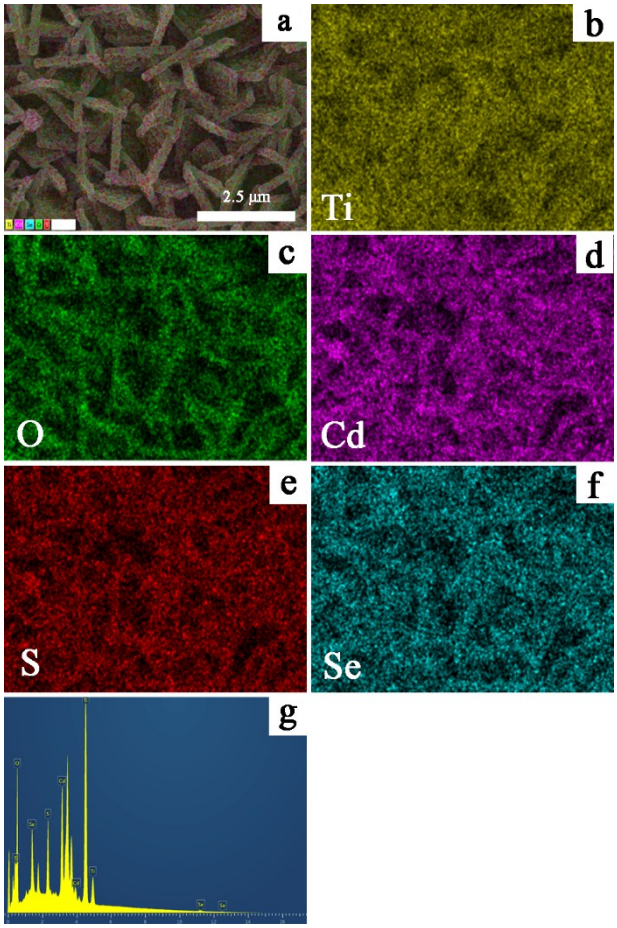

Figure S5 (a), (b), (c), (d), (e) and (f) SEM image and Ti, O, Cd, S and Se EDS mapping from TiO_2NSs/CdS(30 min)/CdSe(10 C); (g) EDS spectrum of TiO_2NSs/CdS(30 min)/CdSe(10 C).

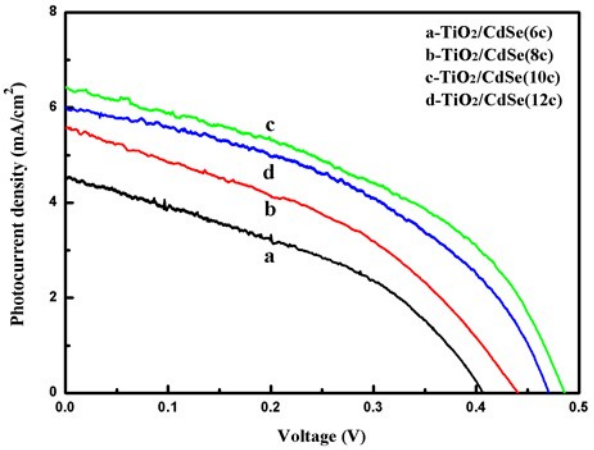

Figure S 6. J-V curves of TiO_2NSs/CdSe with different CdSe SILAR cycles (6 C, 8 C, 10 C, 12 C).

Table S1 The photovoltaic parameters of the devices.

Devices	condition	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)
TiO_2/CdS(X)	0 min	0.25	0.37	0.33	0.03
	10 min	1.01	0.48	0.50	0.24
	20 min	4.78	0.50	0.52	1.24
	30 min	7.68	0.52	0.52	2.09
	40 min	6.31	0.51	0.45	1.43
TiO2/CdSe(X)	6 C	4.52	0.41	0.40	0.73
	8 C	5.57	0.44	0.40	0.97
	10 C	6.42	0.48	0.44	1.36
	12 C	5.99	0.47	0.44	1.24
TiO_2/CdS(30 min)/CdSe(X)	6 C	12.68	0.50	0.51	3.22
	8 C	15.41	0.50	0.48	3.69
	10 C	18.22	0.51	0.52	4.77
	12 C	16.54	0.48	0.49	3.96