

## Electronic Supplementary Information

### **In-situ growth of heterojunction CdS/TiO<sub>2</sub> nanofibers monolithic photocatalyst sheet for enhanced hydrogen evolution**

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## **1. Experimental section**

### **1.1 Chemicals and materials**

All chemicals were analytical grade and used as received without further purification. Ti Foil was purchased from Kunshan Guangjia electronic materials Co., Ltd. NaOH,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and thiourea were purchased from Sinopharm Chemical Reagent Co., Ltd. All aqueous solutions used in the experiments were prepared with ultrapure water (18.2 M $\Omega$ ).

### **1.2 Characterization**

Scanning electron microscopy (SEM) images were obtained using field emission scanning electron microscope (Hitachi SU8010, Japan). Transmission electron microscopy (TEM) images, STEM and EDS elemental mapping analysis were acquired using Talos F200S operated at 200 kV. Powder X-Ray diffraction (XRD) measurement was obtained using Bruker D2 Phaser. The chemical states of the samples were examined using X-ray photoelectron spectroscopy (XPS) with Escalab 250Xi device. All the XPS spectra were corrected according to C 1s line at 284.8 eV. The metal loading amount of Pt was determined with ICP-OES (Prodigy plus). UV-vis diffuse reflectance spectra (UV-vis DRS) were recorded on a PerkinElmer Lambda-750 UV-vis-near-IR spectrometer equipped with an integrating sphere, and  $\text{BaSO}_4$  powders were used as the reflectance standard. Photoluminescence (PL) spectra of selected samples were determined by a Horiba Scientific FluoroMax-4 spectrofluorometer spectrometer.

### **1.3 Preparation of catalysts**

#### **1.3.1 Preparation of NTO nanofibers on TF (NTO/TF)**

NTO/TF was synthesized through a hydrothermal reaction in alkaline condition using TF as Ti sources. Typically, a piece of TF (2 mm  $\times$  30 mm  $\times$  30 mm) was washed ultrasonically using acetone, ethanol and distilled water to remove the surface contaminations. Then the cleaned TF was transferred into a 100 mL Teflon-lined stainless-steel autoclave containing 40 mL of NaOH (8 M) aqueous solution. The hydrothermal growth of NTO nanofibers onto TF was carried out at 180 °C for 12 hours. After reaction, the NTO/TF sample was obtained by rising with distilled water for several times, and

followed by drying in vacuum.

### **1.3.2 Preparation of powder CdS**

$\text{Cd}(\text{NO}_3)_2$  and  $\text{CH}_4\text{N}_2\text{S}$  was dissolved in 40 mL of distilled water (molar ratio of Cd:S = 1:2 ) to form a precursor aqueous solution. And then transferred into a 100 mL Teflon-lined stainless-steel autoclave for hydrothermal reaction at 180 °C for 8 hours. After reaction, the CdS sample was obtained by rising with distilled water thoroughly, and followed by drying in a vacuum oven at 60 °C for 12 h.

### **1.3.3 Preparation of CdS/TiO<sub>2</sub> monolithic photocatalyst on TF (CdS/TiO<sub>2</sub>/TF)**

CdS/TiO<sub>2</sub>/TF was synthesized by a secondary hydrothermal reaction.  $\text{Cd}(\text{NO}_3)_2$  and  $\text{CH}_4\text{N}_2\text{S}$  was dissolved in 40 mL of distilled water (molar ratio of Cd:S = 1:2 ) to form a precursor aqueous solution. Then the as-prepared NTO/TF sample was immersed in the precursor solution for ions exchange, and then transferred into a 100 mL Teflon-lined stainless-steel autoclave for hydrothermal reaction at 180 °C for 8 hours. After reaction, the CdS/TiO<sub>2</sub>/TF sample was obtained by rising with distilled water thoroughly, and followed by drying in a vacuum oven at 60 °C for 12 h.

### **1.3.4 Photodeposition of Pt on CdS/TiO<sub>2</sub>/TF (Pt/CdS/TO<sub>2</sub>/TF)**

Pt nanoparticles cocatalyst were deposited on the surface of CdS/TiO<sub>2</sub>/TF monolithic photocatalyst by traditional photoreduction method. Briefly, CdS/TiO<sub>2</sub>/TF monolithic photocatalyst was fixed on a custom-made Teflon sample holder, and immersed in 50 mL aqueous solution containing  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{SO}_3$  (0.1 M each) as the sacrificial reagent. Then, 0.1 mM of  $\text{H}_2\text{PtCl}_6$  aqueous solution was added under magnetic stirring. The photoreduction was carried out under Xenon lamp (300W) irradiation for 5 h. Finally, these obtained Pt/CdS/TO<sub>2</sub>/TF monolithic photocatalyst was rinsed with distilled water and then dried in a vacuum oven at 60 °C for 12 h.

## **1.4 Photocatalytic hydrogen evolution experiments**

The photocatalytic performance was assessed in an irradiated flat-top 180 mL quartz reactor, which connected to an all-glass automatic on-line trace gas analysis system (Labsolar-6A, Beijing Perfectlight Technology Co., Ltd.). 300 W Xe lamp (PLS-SXE300, Beijing Perfectlight Technology Co., Ltd.) was adopted as the light source for the

photocatalytic reaction. In a typical experiment, monolithic photocatalyst was fixed on a custom-made Teflon sample holder, and immersed in 50 mL aqueous solution containing Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>3</sub> (0.1 M each) as the sacrificial reagents under magnetic stirring. The reaction vessel was initially cooled down to 10 °C by the circulated cooling water. Prior to irradiation, the vessel was evacuated several times to remove ambient air in the reactant suspension. Thereafter, the reactor was irradiated using a Xenon lamp, and the production of H<sub>2</sub> was analyzed by gas chromatography (Shimadzu GC-2014C) with a thermal conductivity detector with 5 °A molecular sieve columns and Ar as the carrier gas.

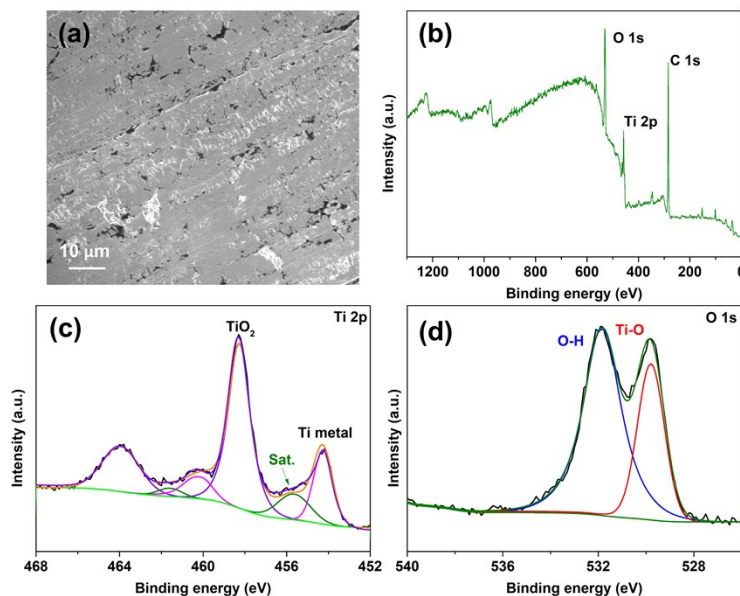
### 1.5 Electrochemical experiments

The electrochemical measurements were carried out in a standard three-electrode electrochemical set-up using a CHI760E potentiostat. The saturated Ag/AgCl and Pt foil (10 mm×10 mm) were used as reference electrode and counter electrode, respectively. The monolithic photocatalyst sheet (10 mm × 10 mm) was used directly as the working electrode. The electrocatalytic activity of CdS/TiO<sub>2</sub>/TF, CdS/TiO<sub>2</sub>/TF and CdS powder towards H<sub>2</sub> evolution was examined by obtaining polarization curves using linear sweep voltammetry (LSV) at a scan rate of 10 mV s<sup>-1</sup> in a mixed aqueous solution (Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>S, 0.1 M each) as the supporting electrolyte and sacrificial reagent. In the photoelectrochemical measurements, Xe lamp was used as the light source, and the photocurrent response was recorded by using an amperometric current-time technique. Electrochemical impedance spectroscopy (EIS) was carried out at a forward bias of 0.7 V with AC amplitude of 10 mV and a frequency range of 10 mHz to 100 kHz in the dark. All the applied potentials are reported as reversible hydrogen electrode potential scale using E (vs. RHE) = E (vs.Ag/AgCl) + 0.197 + 0.059 × pH at 25 °C.

## 2. Additional data

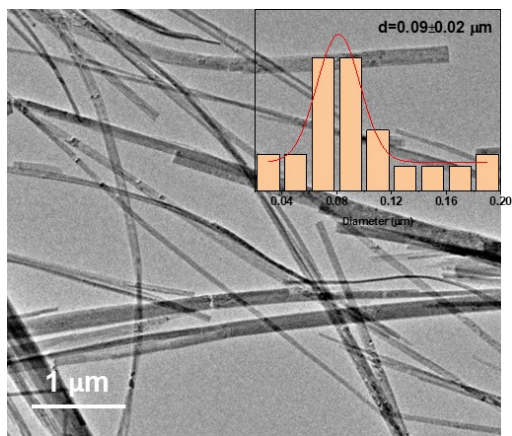
**Table S1** ICP-OES analysis for Pt loading of Pt/CdS/TiO<sub>2</sub>/TF monolithic photocatalyst.

Catalyst	Mass of catalyst (mg)	Concentration of Pt (mg L <sup>-1</sup> )	Pt loading (mg)	Mass percentage (%)
Pt/CdS/TiO <sub>2</sub> /TF	6.13	2.50	0.1425	2.32

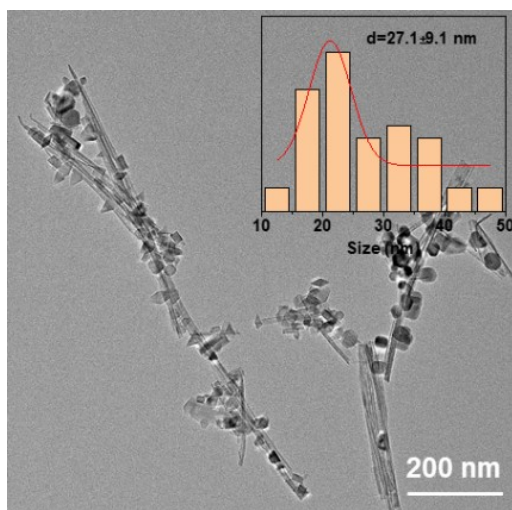


**Fig. S1** (a) SEM image of the pristine TF. (b) Survey XPS spectrum of pristine TF. (c) Ti 2p and (d) O 1s XPS spectra of pristine TF.

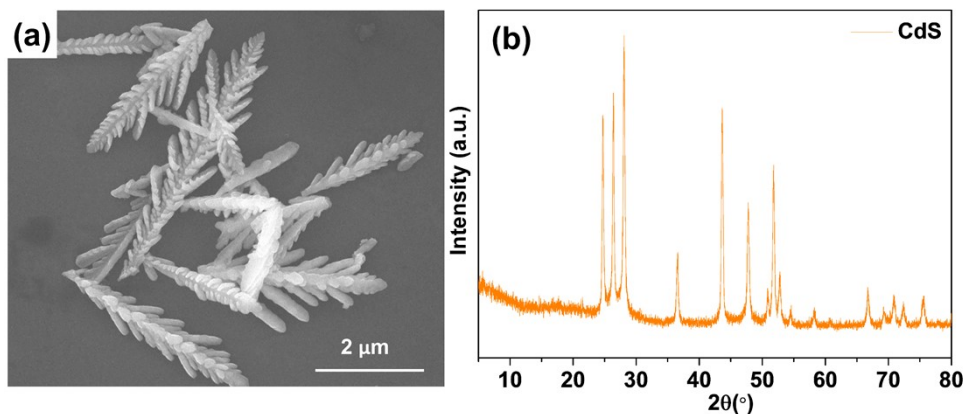
It can be seen in SEM (**Fig. S1a**), the top surface of pristine TF was smooth. XPS measurement was carried out to evaluate the surface chemical states of pristine TF. The XPS survey spectrum (**Fig. S1b**) clearly indicates that pristine TF was composed of Ti and O elements. Meanwhile, Ti 2p<sub>3/2</sub> peak at 454.2 eV could be attributed to metallic Ti, and the peak at 458.2 eV could be attributed to TiO<sub>x</sub> (**Fig. S1c**). The high resolution XPS of O1s at 529.7 eV and 531.8 eV could be attributed to Ti-O and O-H bonds, respectively (**Fig. S1d**). During hydrothermal reaction, the surface TiO<sub>x</sub> layer on TF could be transformed into Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> (NTO) NFs, forming NTO NFs firmly embedded on the TF surface.



**Fig. S2** TEM image of the NTO NFs sample scratched from NTO/TF. Inset shows the diameter distribution statistics of NTO NFs.

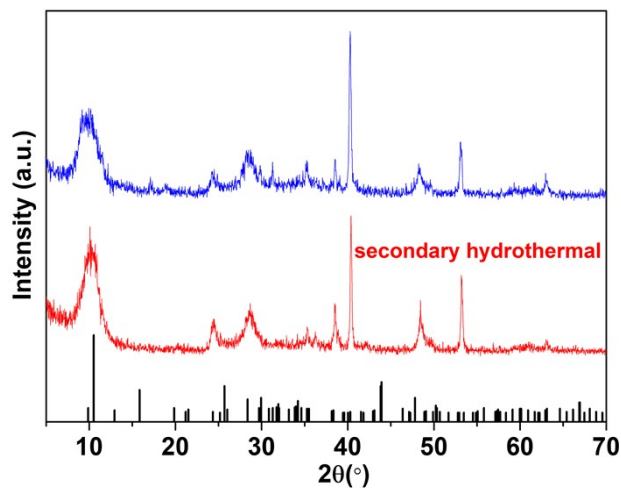


**Fig. S3** TEM image of the CdS/TiO<sub>2</sub> sample scratched from CdS/TiO<sub>2</sub>/TF. Inset shows the size distribution statistics of CdS NSs.

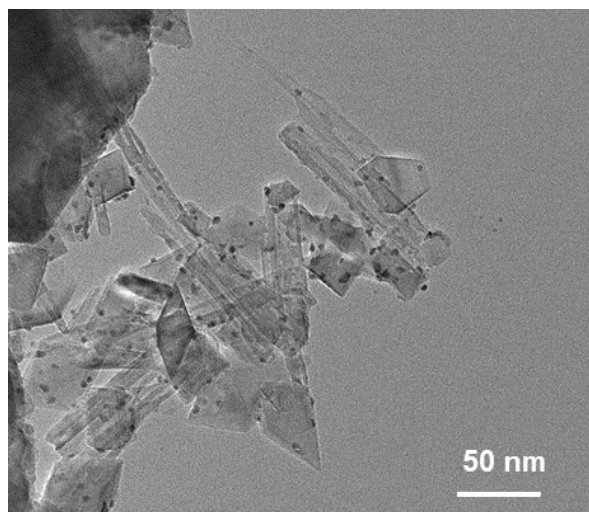


**Fig. S4** SEM image (a) and XRD pattern (b) of CdS powder.

The strikingly difference in the morphology of CdS prepared via the same method is due to the substrate, specifically the presence of  $\text{Na}_2\text{Ti}_3\text{O}_7$  (NTO) nanofibers on Ti foil (TF). During the secondary hydrothermal reaction to prepared CdS onto the NTO/TF substrate, the interlaminar  $\text{Na}^+$  ions of NTO could be exchanged with  $\text{Cd}^+$  ions in the precursor solution, and then the sample underwent sulfidation process with  $\text{CH}_4\text{N}_2\text{S}$  for the in-situ growth of CdS nanosheets. NTO was transformed into  $\text{TiO}_2$  at the same time. This reaction process result in the unique morphology of intimate interfacial heterojunction of CdS/ $\text{TiO}_2$  nanofibers: CdS nanosheets embedded in and CdS thin layers coated on the intertwined  $\text{TiO}_2$  nanofibers. It should be noted that NTO/TF could not be transferred into  $\text{TiO}_2$  without the addition of  $\text{Cd}^+$  and  $\text{CH}_4\text{N}_2\text{S}$  under the hydrothermal reaction process (see **Fig. S5** below). These results indicated that the  $\text{Na}^+/\text{Cd}^+$  ion exchange process is important to deliver the unique morphology of the CdS/ $\text{TiO}_2$ /TF monolithic photocatalyst sheet.

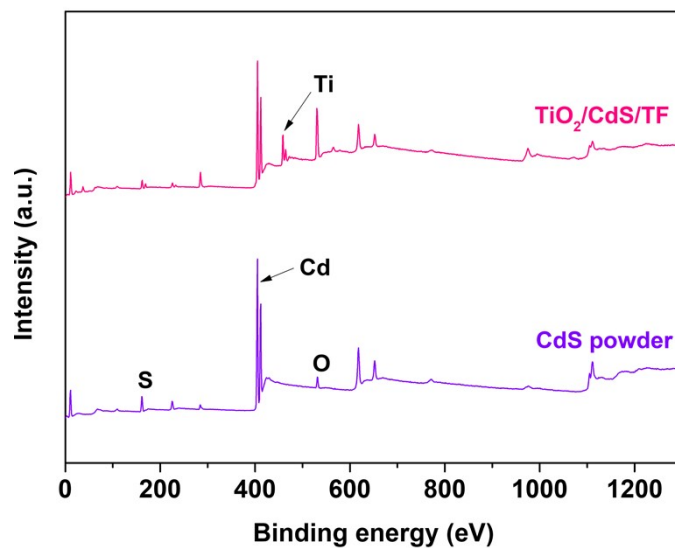


**Fig. S5** XRD patterns of NTO/TF (blue) and after a secondary hydrothermal reaction without the addition of  $\text{Cd}^+$  and  $\text{CH}_4\text{N}_2\text{S}$  (red).

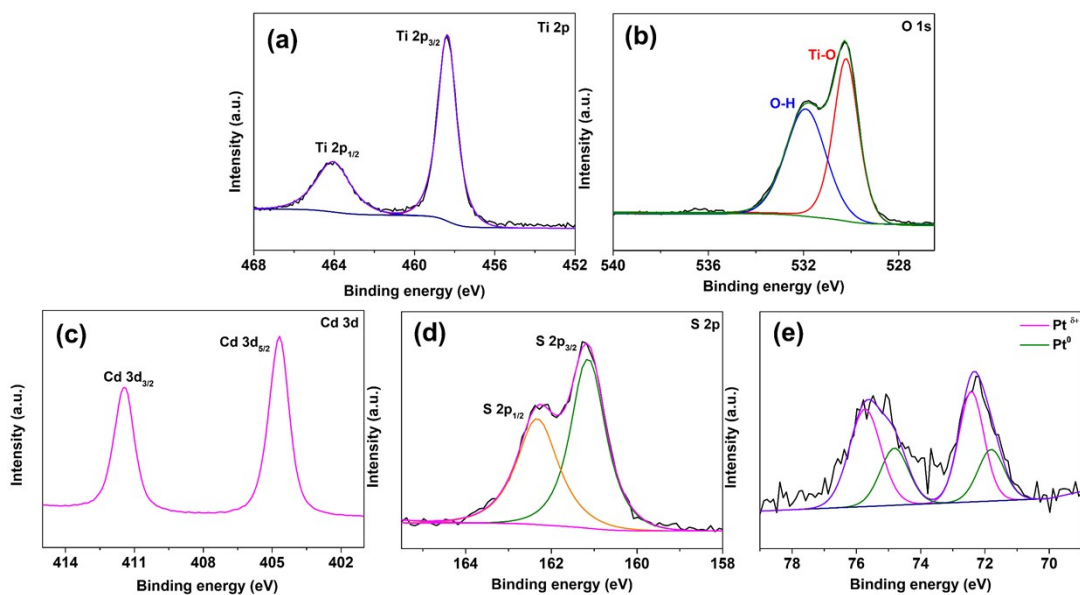


**Fig. S6** TEM image of the Pt/CdS/TiO<sub>2</sub> sample scratched from Pt/CdS/TiO<sub>2</sub>/TF.





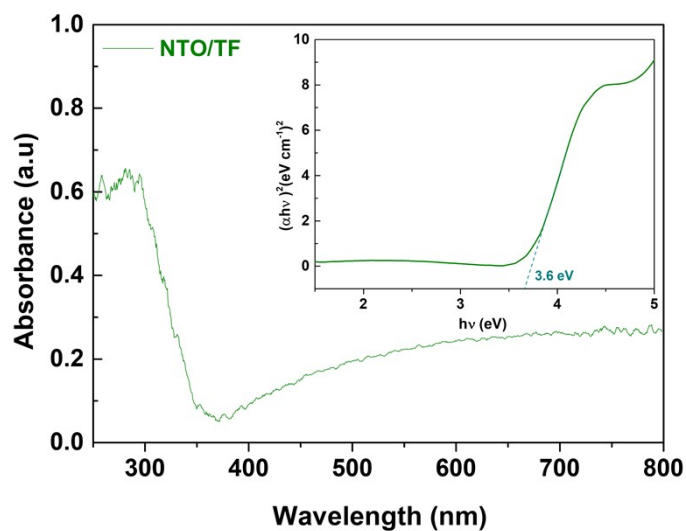
**Fig. S7** Survey XPS spectra of CdS powder and CdS/TiO<sub>2</sub>/TF monolithic photocatalyst.



**Fig. S8** High-resolution XPS spectra of (a) Ti 2p, (b) O 1s, (c) Cd 3d (d) S 2p and (e) Pt 4f of Pt/CdS/TiO<sub>2</sub>/TF monolithic photocatalyst.



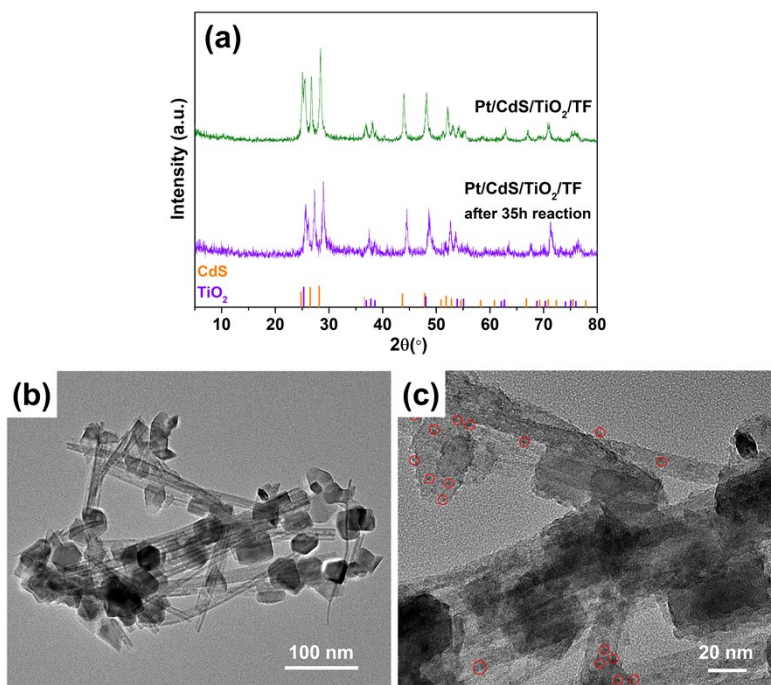
**Fig. S9** A photograph of the photocatalytic reaction setup, and inset shows a photograph of the custom-made Teflon sample holder to hold the photocatalyst sheet for photocatalytic reaction.



**Fig. S10** UV-vis diffuse reflectance spectrum and the corresponding plot of transformed Kubelka-Munk functions versus the photon energy for NTO/TF sample.

**Table S2** Comparison of photocatalytic HER activity of Pt/CdS/TiO<sub>2</sub>/TF monolithic photocatalyst with those of recently reported photocatalyst sheets.

Photocatalyst sheet	Light source	Reaction conditions	HER activity (mmol m <sup>-2</sup> )	Ref.
CdS-NiS <sub>x</sub> /NF	10 W LED Lamp	10 vol.% LA	180	1
Ni <sub>2</sub> P NL/NF	10 W LED Lamp	10 vol.% TEOA, ErB	12.2	2
CdS/Pt@t-GNT	300 W Xe Lamp	(0.125 M) Na <sub>2</sub> S/(0.175 M)Na <sub>2</sub> SO <sub>3</sub>	61.5	3
SrTiO <sub>3</sub> :La,Rh/Au/ BiVO <sub>4</sub> :Mo	300 W Xe lamp	Pure H <sub>2</sub> O	225	4
Pt/CdS/TiO <sub>2</sub> /TF	300 W Xe lamp	(1M) Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	213	This work



**Fig. S11** (a) Comparison of XRD patterns of Pt/CdS/TiO<sub>2</sub>/TF monolithic photocatalyst before and after photocatalytic HER. (b) TEM and (c) HRTEM images of Pt/CdS/TiO<sub>2</sub>/TF monolithic photocatalyst after stability test.

## References

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2. F. Wang, T. L. Liu, Z. T. Liu, Z. G. Zhang and S. X. Min, *Dalton Trans.*, 2022, **51**, 11029-11039.
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