# Supplementary Information

## Self-assembly induction of reduced graphene oxide decorated CdS nanoboxes for photocatalytic hydrogen evolution

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**Synthesis of $CdCO_3$ nanocubes**

In a typical synthesis[1], 0.5 mmol of $CdCl_2 \cdot 2.5H_2O$, and 1.5 g of polyvinylpyrrolidone (PVP) were dissolved in 10 mL of deionized water to form a transparent solution A. Then 20 mL of $NaHCO_3$ aqueous solution (0.05 M) was dropwise added into solution A, and stirred for 1 h. Finally, the white precipitates were collected by centrifugation and washed three times with deionized water and ethanol, and dried at 40 °C for 6 h.

**Synthesis of CdS nanoboxes**

Typically, 1 mmol of $CdCO_3$ nanocubes and 2 mmol of thiourea were firstly dispersed in 40 mL of deionized water with stirring for 30 min. Then the mixed solution were transferred into a 50 mL Teflon-lined stainless-lined autoclave, and kept static at 180 °C for 12 h. After naturally cooled down to room temperature, the final precipitation was centrifuged and washed three times with absolute ethanol and water, and dried at 40 °C for 12 h.

**Synthesis of APS-CdS nanocomposites**

Typically, 0.1 g of as-prepared CdS nanoboxes were firstly dispersed into 50 mL of ethanol by sonication for 30 min, followed by the addition of 2 mL of γ-aminopropyltriethoxysilane (APS) and refluxed at 60 °C for 12 h. After naturally cooled down to room temperature, the obtained products of APS treated CdS nanoboxes (APS-CdS) were collected by filtration, washed three times with ethanol, and then dried at 40 °C for 12 h.

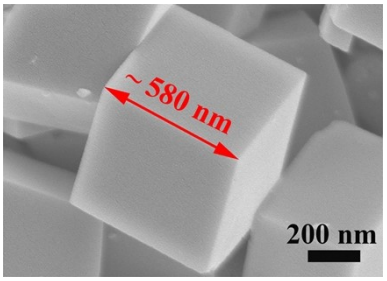


**Fig. S1** SEM image of $CdCO_3$ nanocubes.

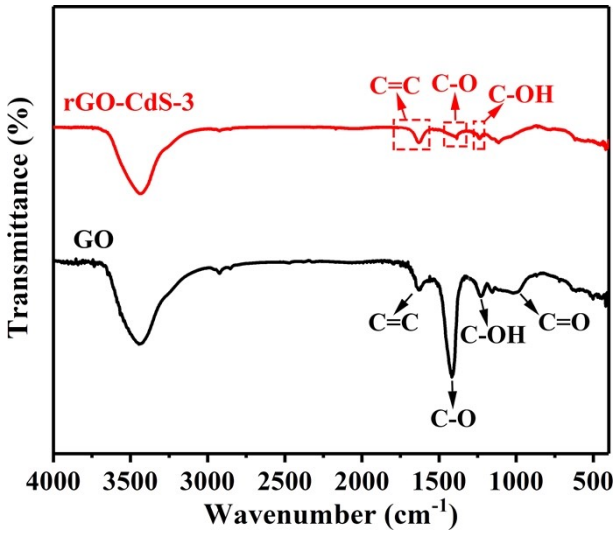


**Fig. S2** FT-IR spectra of GO, and rGO-CdS-3 photocatalysts.

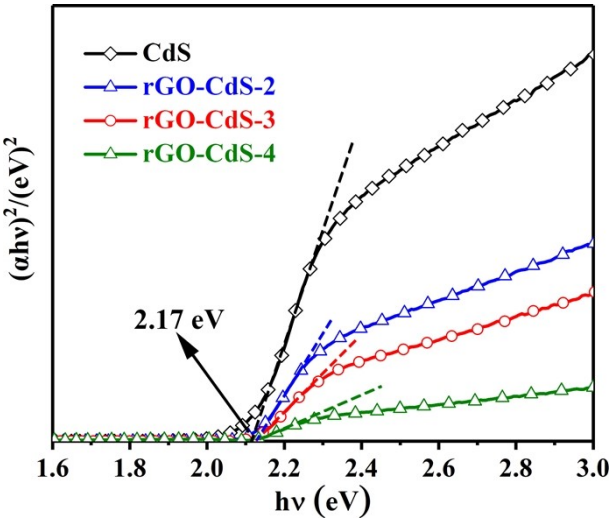


**Fig. S3** Band gap values from the $(\alpha h\nu)^{1/n}$ vs. hν plots of pure CdS nanoboxes, rGO-CdS-2, rGO-CdS-3, and rGO-CdS-4 photocatalysts.

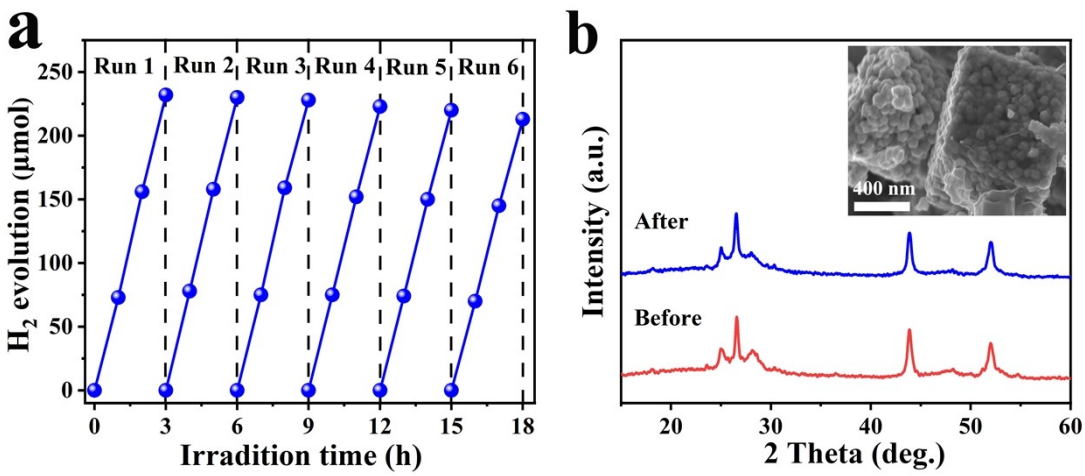


**Fig. S4** (a) Stability test of rGO-CdS-3 in six cycles. (b) XRD patterns of rGO-CdS-3 before and after the durability tests and the SEM image (inset) of rGO-CdS-3 after recycling.

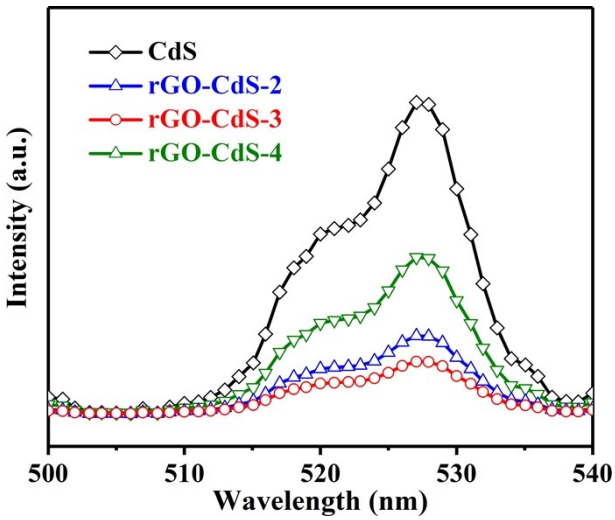


**Fig. S5** PL spectra of pure CdS nanoboxes, rGO-CdS-2, rGO-CdS-3, and rGO-CdS-4 photocatalysts.

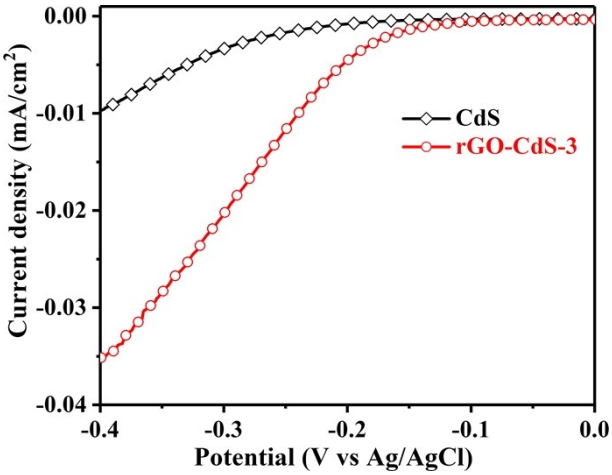


**Fig. S6** LSV curves at a scan rate of 10 mV $s^{-1}$ of pure CdS, and rGO-CdS-3 photocatalysts in 1.0 M KOH solutions.

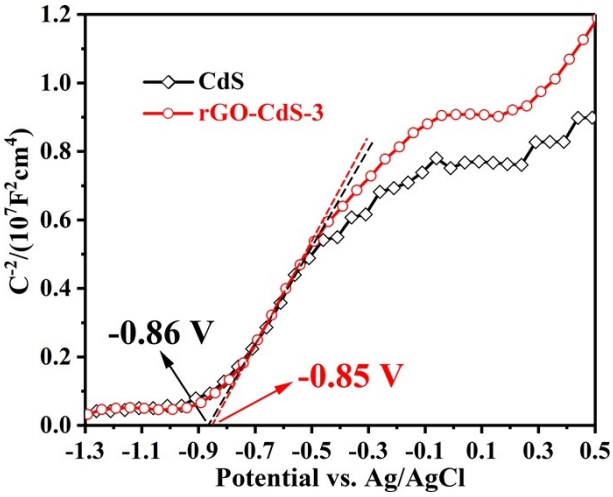


**Fig. S7** Mott-Schottky plots of CdS, and rGO-CdS-3 photocatalysts.

The valence band (VB) edge position and conduction band (CB) edge position of CdS and rGO-CdS-3 are calculated from the following equations [2]:

$$E_{CB} \text{ (NHE, pH = 0)} = E_{fb} \text{ (Ag/AgCl)} + 0.197 \text{ V} \quad (1)$$

$$E_{VB} = E_{CB} + E_g \quad (2)$$

where $E_{CB}$ and $E_{VB}$ are the CB and VB potential, $E_{fb}$ is the flat band potential, and $E_g$ is the bandgap energy. As shown in Fig. S7, the $E_{fb}$ of CdS and rGO-CdS-3 is determined to be –0.86 and –0.85 V. The $E_{CB}$ and $E_{VB}$ of the CdS are calculated to be –0.66 and 1.51 V, while those values of rGO-CdS-3 are –0.65 V and 1.52 V.

**Table S1.** Activity comparison of some representative photocatalysts for photocatalytic water splitting.

| Catalysts | Scavengers | Light source | HER rate ($\mu mol\ h^{-1}\ g^{-1}$) | Ref. |
|---|---|---|---|---|
| rGO/CdS | 15 vol% lactic acid | 300 W Xe ($\lambda>420$ nm) | 1502 | This work |
| CdS-$Co_3O_4$ | 10 vol% lactic acid | 350 W Xe ($\lambda>420$ nm) | 150.7 | S3 |
| $Ag_2S$/CdS | 10 vol% lactic acid | 300 W Xe ($\lambda>420$ nm) | 777.3 | S4 |
| NiPx/$MoS_2$/NiS/CdS | 0.03 M glucose | 300 W Xe ($\lambda>420$ nm) | 297 | S5 |
| CdS/CuS | 10 vol% TEOA | 300 W Xe ($\lambda>420$ nm) | 295 | S6 |
| CdS QDs/$CeO_2$ | 0.31 M $Na_2S$/0.25 M $Na_2SO_3$ | 300 W Xe ($\lambda>300$ nm) | 101.1 | S7 |
| $Ni(OH)_2$/$Ni_3S_2$/$Ni_xS_6$-CdS | 0.1 M $Na_2S$/0.1 M $Na_2SO_3$ | 300 W Xe ($\lambda>400$ nm) | 694 | S8 |
| g-$C_3N_4$/CdS | 0.1 M $Na_2S$/0.1 M $Na_2SO_3$ | 300 W Xe ($\lambda>420$ nm) | 718.6 | S9 |
| CdS/Ni-MOF | 6 vol% lactic acid | 300 W Xe ($\lambda>420$ nm) | 2508 | S10 |

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