Electronic Supplementary information


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Experimental section

**Materials:** Cadmium nitrate tetrahydrate (Cd(NO$_3$)$_2$·4H$_2$O, 99%, aladdin), zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O, 99%, Sinopharm), thiourea (TU, 99%, Sinopharm), Diethylenetriamine (DETA, 99%, Sinopharm), oleylamine (OLA, 80-90%, aladdin), hydrogen tetrachloroaurate (III) (HAuCl$_4$·4H$_2$O, ≥47.8%, Sinopharm), absolute ethanol (C$_2$H$_5$OH, AR, 99.7%, Tianjin Fuyu). All reagents were used in experiments as received without further purification.

**Preparation of GO:** Graphene oxide (GO) was prepared from natural graphite powder using the improved method (ACS Nano 2010, 4, 4806), and redispersed in ultrapure water for stock with the concentration of about 6.0 mg mL$^{-1}$.

**Preparation of CdS/ZnS-RGO heterostructures (denoted as Cd$_x$Zn$_{1-x}$G$_2$):** CdS/ZnS-RGO was obtained by a facile one-pot hydrothermal method. In detail, 0.3 mmol Cd(NO$_3$)$_2$·4H$_2$O and 0.7 mmol Zn(NO$_3$)$_2$·6H$_2$O were dispersed in 35 mL ultrapure water and stirring for 1 h, followed by the addition of 2 mL of the stocked GO suspension. After stirring for 1 h and ultrasonication for another 1 h, the obtained mixture was kept stirring overnight. 0.1 g TU was added and stirred for 3 h. Then, the introduction of 1 mL DETA was applied and continuously stirred for another 2-3 h. Finally, the resultant suspension was transferred into a 50 mL Teflon-lined autoclave and maintained at 180 °C for 12 h. Via the centrifugation, the product was collected, washed with water and ethanol each for three times and freeze-dried for 3 days. The final sample prepared above is labeled as Cd$_{0.3}$Zn$_{0.7}$G$_2$, in which 0.3, 0.7 and 2 refer to 0.3 mmol Cd(NO$_3$)$_2$·4H$_2$O, 0.7 mmol Zn(NO$_3$)$_2$·6H$_2$O and 2 ml GO, respectively. The following samples also accord with the nomination rule and generalized as Cd$_x$Zn$_y$G$_z$ tuned by changing the molar amount of Cd(NO$_3$)$_2$·4H$_2$O as well as Zn(NO$_3$)$_2$·6H$_2$O and the volume of GO suspension.

The self-standing CdS and CdS/ZnS (denoted as Cd$_x$Zn$_y$ for convenience of comparison with Cd$_x$Zn$_y$G$_z$) samples were prepared based on the above procedures except no addition of GO suspension.

**Preparation of Au-CdS/ZnS-RGO:** 50 mg of the as-prepared Cd$_{0.3}$Zn$_{0.7}$G$_2$ and a
certain amount (1, 2, 5 mg) of HAuCl$_4$·4H$_2$O were dissolved into 10 mL OLA in a three-neck round bottom flask under magnetic stirring and heated at 100 °C for 30 min under the N$_2$ atmosphere. The resulting product was collected by centrifugation and washed with hexane and ethanol for several times and finally freeze-dried for 3 days. The obtained sample was labeled as Au$_z$Cd$_{0.3}$Zn$_{0.7}$G$_2$, where $z$ means the mass of HAuCl$_4$·4H$_2$O applied.

**Characterization:** X-ray diffraction (XRD) patterns were obtained from an X-ray powder diffractometer (Bruker D8 Advance, Germany) with monochromatic Cu K$_\alpha$ as a radiation source. FESEM images were collected on a GeminiSEM 500 scanning electron microscope. Transmission electron microscopy (TEM) images were acquired by TEM (JEM-1011) at an accelerating voltage of 100 kV. TEM, HRTEM, HAADF-STEM, and EDX mappings were collected on on FEI Talos F200X TEM at 200 kV. Raman spectra were recorded on a JY LABRAM-HR confocal laser micro-Raman spectrometer with a 514.5 nm wavelength at room temperature. UV-Vis absorption spectra were recorded in the range of 250–900 nm at room temperature using a Shimadzu UV-2450 spectrometer. The steady-state photoluminescence (PL) spectra were using F-4500 (Hitachi Analytical Instruments). The electrochemical impedance spectroscopy (EIS) were measured on a electrochemical workstation (CHI 760E, Shanghai Chenhua, China) by using a conventional three-electrode quartz cell in which platinum sheet used as counter electrode and a saturated calomel electrode used as reference electrode, an 0.5 M K$_2$SO$_4$ aqueous solution was used as the electrolyte. The EIS Nyquist plots was obtained with a frequency range varied from 0.05 Hz to 100 kHz and the amplitude was set at 10 mV.

**Photocatalytic hydrogen production activity:** The photocatalytic H$_2$ production test was conducted in a 250ml round-bottom flask with 100ml aqueous solution containing 0.35 M Na$_2$S and 0.25 M Na$_2$SO$_3$. 10 mg of various as-prepared photocatalysts was added. A 300 W Xenon lamp equipped with a 420 nm UV cut-off filter was used to provide the visible light, which was positioned about 20 cm away from the flask reactor with the irradiation area and mean intensity of 24 cm$^2$ and ~140
mW cm$^{-2}$ measured by PL-MW2000 spectroradiometer (Perfect Light, China). Before irradiation, the solution with photocatalyst was bubbled for 30 min with high-purity nitrogen to ensure oxygen-free condition and then stirred for several minutes to obtain homogenous mixture. The reaction was kept magnetic stirring at 15 °C. The amount of H$_2$ produced was determined using a gas chromatography (GC-7806) equipped with TCD detector (N$_2$ as carrier gas).
Figure S1. FESEM images and EDX spectra of intermediates for synthesis of $\text{C}_{0.5}\text{Z}_{0.5}\text{G}_{2}$ collected at 180 °C (A) 0 h, (B) 0.5 h, (C) 1 h, (D) 1.5 h, (E) 6 h, (F) 12 h. Scale bars: 200 nm for all panels.
Figure S2. TEM images of (A, B) self-standing CdS and (C, D) $\text{Cd}_{0.3}\text{Zn}_{0.7}$ without the addition of graphene during the synthesis.
Figure S3. FESEM images of pure CdS on graphene prepared without DETA.

Note: In order to shed light on the growth process of CdS/ZnS-RGO, some control experiments were applied. Figure S2 shows TEM images of self-standing CdS and Cd$_{0.3}$Zn$_{0.7}$ prepared under the similar experimental process to Cd$_{x}$Zn$_{1-x}$G$_{2}$ just without the application of graphene. CdS product is consisting of nanorods stacking tightly and Cd$_{0.3}$Zn$_{0.7}$ resembles with the addition of some nanoparticles attached around the nanorod stem. It’s obviously that samples prepared are also nanorod assemblages, much bigger than their respective counterparts prepared in presence of graphene. In case of no DETA, it was found that only big-sized CdS aggregates were obtained on graphene sheets instead of nanorod bundles (see Figure S3). Hence, the presence of DETA plays a vital role in mediating the growth of 1D nanorod. With graphene as substrate, the formation of CdS/ZnS heterostructures was controlled by heterogeneous nucleation, in conjunction with DETA serving as structural direction agent to dominate the formation of 1D CdS nanorods. The time-dependent intermediates are also detected by SEM-EDX characterization to give information with Cd$_{0.5}$Zn$_{0.5}$G$_{2}$ as a sampling example. As the electric oven heated
from room temperature to 180 °C and the reaction immediately quenched, the sample was harvested for SEM testing. From Figure S1A, solid nanoparticles has already been anchored and EDX result justifies the absorption of Zn and Cd ions on RGO sheets. At 0.5 and 1.0 h of the reaction, it’s obvious that CdS nanorod bunches are growing bigger. Zn content sharply decreases from EDX spectrum in Figure S1B-C due to the rapid growth of CdS crystals. Till 1.5 h, Zn content in EDX result begins to increase in Figure S1D, suggesting the formation of few ZnS nuclei. At 6 h, it can be clearly observed that some nanoparticles are capping on CdS nanorods and the relative atomic ratio of Zn to Cd also notably becomes larger, as proved by EDX result in Figure S1E. As the reaction extends to 12 h, ZnS particle aggregates grow bigger (see Figure S1F). As a result, the formation mechanism was proposed as follows. Ions of Cd and Zn are anchored on RGO sheets relying on the electrostatic interaction. By reaction with thiourea, CdS nuclei formed from solution readily depending on the heterogeneous nucleation. The crystal growth of CdS was dominated by DETA into hexagonal nanorods by combination with the inherent nature of hexagonal CdS, followed by heterogeneous growth of cubic ZnS phase greatly depending on the low lattice mismatching of h-CdS and c-ZnS.
Figure S4. TEM and FESEM images of (A-C) Cd$_{1.0}$Zn$_{0}$G$_{2}$, (D-F) Cd$_{0.7}$Zn$_{0.3}$G$_{2}$, (G-I) Cd$_{0.5}$Zn$_{0.5}$G$_{2}$. scale bar: (A,B) 300 nm, (C,H,G) 200 nm, (D,E) 100 nm, (F,I) 50 nm.
Figure S5. TEM and FESEM images of (A-C) Cd$_{0.3}$Zn$_{0.7}$G$_2$, (D-F) Cd$_{0.2}$Zn$_{0.8}$G$_2$, (G-I) Cd$_{0}$Zn$_{1.0}$G$_2$. Scale bar: (A,D) 1 μm, (B,E,F,I) 100 nm, (C) 50 nm, (G,H) 200 nm.
Figure S6. XRD patterns of Cd$_x$Zn$_{1-x}$G$_2$ samples with different Cd : Zn molar ratio.
Figure S7. The EDX spectra of Cd$_{1.0}$Zn$_{0.0}$G$_{2}$, Cd$_{0.5}$Zn$_{0.5}$G$_{2}$ and Cd$_{0}$Zn$_{1.0}$G$_{2}$. 
Figure S8. XRD patterns of $\text{Au}_z\text{Cd}_{0.5}\text{Zn}_{0.5}\text{G}_2$ with different $z$ values.

Figure S9. EDX spectrum of the as-prepared $\text{Au}_2\text{Cd}_{0.5}\text{Zn}_{0.5}\text{G}_2$ composite.
**Figure S10.** HRTEM image of a typical nanorod of $\text{Au}_2\text{Cd}_{0.5}\text{Zn}_{0.5}\text{G}_2$. (The circle marked is Au nanoparticle domain).
Figure S11. XPS spectra of (A) survey, (B) Au 4f, (C) Zn 2p, (D) Cd 3d, (E) S 2p, (F) C 1s and (G) N 1s.

Note: XPS technique was implied to detect the chemical state of elements in Cd$_{0.3}$Zn$_{0.7}$G$_2$-Au$_2$, whose survey spectrum (Figure S11A) displayed the chemical composition. The photoelectron spectrum of Au 4f in Figure S11B can be assigned to 4f$_{7/2}$ and 4f$_{5/2}$ located at 84.3 eV and 87.9 eV with a peak at 88.9 eV corresponding to Zn 3p$_{3/2}$ orbit. In Figure S11C, Zn 2p$_{3/2}$ and 2p$_{1/2}$ peaks are located at 1022.2 and 1045.3 eV, displaying the valence of +2 for Zn. Cd 3d spectrum in Figure S 11D can be clearly identified as bands of 3d$_{5/2}$ and 3d$_{3/2}$ at 405.6 eV and 412.4 eV, respectively. As shown in Figure S11E, S 2p$_{3/2}$ and 2p$_{1/2}$ peaks center are located at...
162.2 eV and 163.4 eV. High-resolution C 1s spectrum in Figure 11F includes C-C/C=C, C-N, C-O, C=O and O-C=O peaks located at 284.6 eV, 285.2 eV, 286.0 eV, 287.0 eV, and 288.8 eV, respectively. N 1s spectrum in Figure S11G can be deconvoluted into three peaks resulting from pyridinic N, pyrrolic N and amino N with center as 398.8 eV, 399.9 eV and 401.2 eV, respectively.
Figure S12. \( \text{H}_2 \) production rate under visible light irradiation of \( \text{Cd}_x\text{Zn}_{1-x}\text{G}_2 \) with different \( x \) value for 1 h (inset scale bar: 100 nm).

**Note:** The change in \( \text{H}_2 \) production rate of \( \text{Cd}_x\text{Zn}_{1-x}\text{G}_2 \) with different \( x \) value have a great relationship with the morphology features they evolved. Initially, the bare \( \text{CdS} \) nanorod bunches formed and then with the \( \text{Zn/Cd ratio} \) increasing the tip of \( \text{CdS} \) nanorod covered \( \text{ZnS} \) nanocrystals gradually, the first peak of \( \text{H}_2 \) production appeared as the tip of the nanorods covered entirely \((1.0 \geq x \geq 0.8)\). Increasing the \( \text{Zn/Cd ratio} \) continuously the \( \text{H}_2 \) production going down, due to the \( \text{ZnS} \) nanocrystals on the tip is only grew bigger without increasing the contact area of heterojunction \((0.8 \geq x \geq 0.6)\). The contact area of \( \text{ZnS/CdS} \) increasing with \( \text{ZnS} \) grow on both tip and side of the \( \text{CdS} \) nanorods, lead to the second peak of hydrogen production \((0.6 \geq x \geq 0.3)\), excess \( \text{ZnS} \) caused another drop in the end \((0.3 \geq x \geq 0)\).
Figure S13. H₂ production rate under visible light irradiation of (A) Cd₀.₃Zn₀.₇Gₓ with different y value for 1 h, (B) Auₓ⁻Cd₀.₃Zn₀.₇G₂ with different z value for 1 h. The H₂ production rate in the initial 3 h of (C) Cd₀.₃Zn₀.₇ and Cd₀.₃Zn₀.₇G₂ as well as (D) Cd₁.₀Zn₀ and Cd₁.₀Zn₀G₂.

Note: Au₁⁻Cd₀.₃Zn₀.₇G₂ showed improved H₂ production rate, i.e. 6.68 mmol h⁻¹ g⁻¹, compared with Cd₀.₃Zn₀.₇G₂. As increasing Au content, H₂ production rate of Auₓ⁻Cd₀.₃Zn₀.₇G₂ was augmented to 9.96 mmol h⁻¹ g⁻¹, 2.2 times that of Cd₀.₃Zn₀.₇G₂. Continual addition of Au rendered the declination of production rate over Au₅⁻Cd₀.₃Zn₀.₇G₂.
Figure S14. Raman spectra of GO, Cd₀.₃Zn₀.₇G₂ before and after 30 h catalytic H₂ production.
Figure S15. EIS Nyquist plots of Cd$_{0.3}$Zn$_{0.7}$, Cd$_{0.3}$Zn$_{0.7}$G$_2$, and Au$_2$-Cd$_{0.3}$Zn$_{0.7}$G$_2$ (Figure S15B is the part marked in Figure S15A).
### Table S1. Comparative data of phototalytic H$_2$ production properties of CdS-related photocatalysts.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Incident light (nm)</th>
<th>Aqueous reaction solution</th>
<th>H$_2$ evolution rate (µmol h$^{-1}$ g$^{-1}$)</th>
<th>Stability (h)</th>
<th>Year (Ref.)</th>
</tr>
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<tbody>
<tr>
<td>Au$<em>2$Cd$</em>{0.3}$Zn$_{0.7}$S$_2$</td>
<td>≥420</td>
<td>0.35 M Na$_2$S and 0.25 M Na$_2$SO$_3$</td>
<td>9960</td>
<td>30</td>
<td>This work</td>
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<tr>
<td>Cd$<em>{0.3}$Zn$</em>{0.7}$S$_2$</td>
<td>≥420</td>
<td>0.35 M Na$_2$S and 0.25 M Na$_2$SO$_3$</td>
<td>4500</td>
<td>30</td>
<td>This work</td>
</tr>
<tr>
<td>CdS/ZnS</td>
<td>≥400</td>
<td>0.1 M Na$_2$S and 0.1 M Na$_2$SO$_3$</td>
<td>792</td>
<td>60</td>
<td>(2014)$^9$</td>
</tr>
<tr>
<td>CdS/Zn$_{1-x}$Cd$_x$S</td>
<td>&gt; 400</td>
<td>0.1 M Na$_2$S and 0.04 M Na$_2$SO$_3$</td>
<td>2128</td>
<td>N/A</td>
<td>(2010)$^7$</td>
</tr>
<tr>
<td>CdS/ZnS</td>
<td>≥380</td>
<td>0.1 M Na$_2$S</td>
<td>N/A</td>
<td>N/A</td>
<td>(2013)$^3$</td>
</tr>
<tr>
<td>Cd$<em>{0.3}$Zn$</em>{0.7}$S</td>
<td>≥420</td>
<td>0.5 M Na$_2$S and 0.5 M Na$_2$SO$_3$</td>
<td>1667</td>
<td>15</td>
<td>(2012)$^6$</td>
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<td>Zn$<em>{0.3}$Cd$</em>{0.7}$S-RGO</td>
<td>≥420</td>
<td>0.35 M Na$_2$S and 0.25 M Na$_2$SO$_3$</td>
<td>1824</td>
<td>12</td>
<td>(2012)$^6$</td>
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<tr>
<td>CdS/CNT/Plt</td>
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<td>819</td>
<td>4</td>
<td>(2011)$^9$</td>
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<tr>
<td>CdS/Pl/WO$_3$</td>
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<td>lactic acid</td>
<td>2900</td>
<td>9</td>
<td>(2014)$^7$</td>
</tr>
<tr>
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<td>≥420</td>
<td>EtOH/H$_2$O = 1:1, v/v</td>
<td>8528</td>
<td>20</td>
<td>(2016)$^9$</td>
</tr>
<tr>
<td>WS$_2$-CdS</td>
<td>&gt; 420</td>
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<td>1984</td>
<td>16</td>
<td>(2015)$^9$</td>
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<tr>
<td>MoS$_2$/RGO-CdS</td>
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<td>g-C$_3$N$_4$/CdSNS</td>
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<td>triethanolamine</td>
<td>2563</td>
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<td>NiS/Zn$<em>{0.3}$Cd$</em>{0.7}$S-RGO</td>
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<td>0.35 M Na$_2$S and 0.25 M Na$_2$SO$_3$</td>
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<td>675</td>
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<td>Cu$<em>{0.5}$S-Zn$</em>{1-x}$Cd$_x$S</td>
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<td>0.1 M Na$_2$S and 0.1 M Na$_2$SO$_3$</td>
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<td>25</td>
<td>(2017)$^{17}$</td>
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Improving multiple*: the ratio of H$_2$-production rate for the optimal catalyst to pure CdS.

**References**


