Freestanding nano-photoelectrode as highly efficient and visible-light-driven photocatalyst for water-splitting

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Figure S1. (a) SEM image of pristine WS$_2$. (b) SEM image, (c) TEM image and SAED patterns (Insert) and (d) high magnification of TEM image of ZnO seeds/WS$_2$ sample.

Compared to bulk WS$_2$ (Figure S1a), WS$_2$ is exfoliated to be nanosheets after being ultrasonicated in ethanol in the presence of Zn(OAc)$_2$·2H$_2$O and LiOH (Figure S1b). The exfoliated nanosheets are also observed in the TEM image (Figure S1c). Two sets of diffraction spots are observed in corresponding SAED pattern (inset in Figure S1c), which are assigned to the WS$_2$ phase (JCPDS No. 08-0237) and ZnO phase (JCPDS No. 36-1451), suggesting the co-existence of ZnO and WS$_2$. ZnO nanoseeds with diameters around 5 nm were anchored on WS$_2$ nanosheets when observed in a high magnification TEM image (Figure S1d).
Figure S2. SEM image of C(0.6)/Z/W(10). Nanorod arrays grown on a 2D substrate are clearly distinguished.
Figure S3. XRD pattern of C(0.6)/Z/W(10). The peaks are well indexed to CdS (JCPDS NO. 77-2306), ZnO (JCPDS NO. 36-1451) and WS$_2$ (JCPDS NO. 08-0237).
Figure S4. (a) TEM image of C(0.6)/Z/W(10) and its EDX spectrum. Zn, O, Cd, S and W are detected, suggesting the existence of WS$_2$ in the structure.
Figure S5. HAADF images of C(0.6)/Z/W(10). Nanoarrays with hollow heads are clearly observed in the HAADF images.
Figure S6. EDX line scan profiles of Zn and Cd (b) along the line marked in (a).
**Figure S7.** HRTEM image of the solid core corresponding to Figure 2h. The fringes distance with 0.52 nm corresponds to the [001] direction of ZnO.
Figure S8. (a) TEM image of P(1.0)/C(0.6)/Z/W(10). (b) Raman spectra of PEDOT:PSS (blue), P(1.0)/C(0.6)/Z/W(10) (magenta) and C(0.6)/Z/W(10) (cyan).
Figure S9. Photocatalytic hydrogen evolution performance over samples with different amount of (a) CdS in C(\(\chi\))/Z, (b) WS\(_2\) in C(0.6)/Z/W(y) and (c) PEDOT:PSS in P(z)/C(0.6)/Z/W(10).
Figure S10. FT-IR spectrum of P(z)/C(0.6)/Z/W(10) after 60h long time test photocatalytic H₂ evolution test.
Figure S11. TRPL spectra of samples with different amount of (a) CdS in C(x)/Z, (b) WS₂ in C(0.6)/Z/W(y) and (c) PEDOT:PSS in P(z)/C(0.6)/Z/W(10).
Figure S12. UV-vis spectra of samples with different amount of (a) CdS in C(\(\chi\))/Z, (b) CdS in C(\(\chi\))/Z/WS\(_2\)(10), (c) WS\(_2\) in C(0.6)/Z/W(\(\gamma\)) and (d) PEDOT:PSS in P(z)/C(0.6)/Z/W(10).
Figure S13. Linear sweep voltammagrams of (a) ZnO, (b) C(0.6)/Z, (c) C(0.6)/Z/W(10) and (d) P(1.0)/C(0.6)/Z/W(10)
Figure S14. (a) UV-vis spectrum and (b) Tauc plot of WS$_2$. 
Figure S15. UV-vis spectrum of PEDOT:PSS.
Figure S16. Photocurrent density of samples under (a) $\lambda = 500$ nm, (b) $\lambda = 550$ nm, (c) $\lambda = 600$ nm and (d) $\lambda = 700$ nm.
Figure S17. Photocurrent density of WS$_2$ under $\lambda$ = 500 nm (black), $\lambda$=550 nm (red), $\lambda$=600 nm (blue) and $\lambda$ = 700 nm (magenta).
Figure S18. Spectra of the long wavelength light and their intensity. (a) $\lambda = 500$ nm, (b) $\lambda = 550$ nm, (c) $\lambda = 600$ nm and (d) $\lambda = 700$ nm.
Table S1 Comparison of reported CdS/ZnO based photocatalysts and the samples from this work.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Reaction conditions</th>
<th>H$_2$ evolution rate</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS/ZnO (Pt)</td>
<td>0.1 M Na$_2$S and 0.1 M Na$_2$SO$_3$, 300 W Xe lamp.</td>
<td>3870</td>
<td>1</td>
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<tr>
<td>CdS/Au/ZnO</td>
<td>0.1 M Na$_2$SO$_3$ and 0.1 M Na$_2$S, 300 W Xe lamp.</td>
<td>608</td>
<td>2</td>
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<tr>
<td>ZnO–CdS/RGO (Pt)</td>
<td>0.1 M Na$_2$S and 0.1 M Na$_2$SO$_3$, 300 W Xe lamp.</td>
<td>11000</td>
<td>3</td>
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<tr>
<td>CdS/ZnO</td>
<td>0.5 M Na$_2$S and 0.5 M Na$_2$SO$_3$, 500 W Xe, λ $&gt;$ 400 nm</td>
<td>851</td>
<td>4</td>
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<tr>
<td>ZnO/Pt/CdS</td>
<td>0.1 M Na$_2$S and 0.1 M Na$_2$SO$_3$, 450 W Xe arc lamp (working at 400 W) fitted with water filter</td>
<td>31600</td>
<td>5</td>
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<tr>
<td>CdS/ZnO</td>
<td>0.1 M Na2S and 0.04 M Na$_2$SO$_3$, 500W Xe lamp, λ $&gt;$ 420 nm</td>
<td>~360</td>
<td>6</td>
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<tr>
<td>CdS/ZnO/WS$_2$</td>
<td>0.2 M Na$_2$S and 0.3 M Na$_2$SO$_3$, 300 W Xe lamp equipped with an AM 1.5G filter (100 mW·cm$^{-2}$).</td>
<td>33733</td>
<td>Present work</td>
</tr>
<tr>
<td>PEDOT:PSS/CdS/ZnO/WS$_2$</td>
<td>0.2 M Na$_2$S and 0.3 M Na$_2$SO$_3$, 300 W Xe lamp equipped with an AM 1.5G filter (100 mW·cm$^{-2}$).</td>
<td>68533</td>
<td>Present work</td>
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Table S2. Fitting parameters of the ESI plots in Figure 3f.

<table>
<thead>
<tr>
<th></th>
<th>ZnO</th>
<th>C(0.6)/Z</th>
<th>C(0.6)/Z/W(10)</th>
<th>P(1.0)/C(0.6)/Z/W(10)</th>
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<tbody>
<tr>
<td>$R_s$ (Ω)</td>
<td>14.7</td>
<td>14.3</td>
<td>14.9</td>
<td>14.5</td>
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<td>$R_{ct}$ (Ω)</td>
<td>1742</td>
<td>938.7</td>
<td>704.2</td>
<td>532.9</td>
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References