Electronic Supplementary Information

Earth abundant transition metal-doped few-layered MoS₂ nanosheets on CdS nanorods for ultra-efficient photocatalytic hydrogen production

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Experimental

Characterization

The crystal structures of the samples were determined by X-ray diffraction (XRD) with a Bruker D8 Advanced X-ray diffractometer using Cu Kα radiation as the X-ray source. Diffuse reflectance spectra (DRS) were recorded with a UV-Vis spectrometer (UV-1800 SHIMADZU, Japan). Surface morphologies and elemental analyses were evaluated using a HITACHI S-4800 field emission scanning electron microscope (FESEM) equipped with an energy dispersive spectrometer (EDS, Inca 400, Oxford Instruments). X-ray photoelectron spectroscopy (XPS) measurements were carried out to evaluate the chemical status and elemental composition of the samples with a monochromated Al Kα X-ray source (hv = 1486.6 eV) at an energy of 15 kV/150 W. Photoluminescence (PL) spectra of the photocatalysts were collected at room temperature using a Hitachi F-7000 fluorescence spectrometer. The N₂ adsorption–desorption isotherm analysis of synthesized materials were carried out at 150 °C using a Tristar 3000 Micromeritics instrument to estimate the surface area of the synthesized nanocomposites.

Photocatalytic activity methodology

Photocatalytic activity was tested in a Pyrex reactor equipped with a top loading port and sealed with a gas-tight rubber septum. The same port was used for outgassing and sampling. Typically, 1 mg of catalyst was dispersed in 15 mL of 20 vol% aqueous lactic acid solution. The gases present in the free space of the quartz reactor and dissolved in the reaction solution were removed by evacuating the reactor followed by purging with argon to obtain an inert atmosphere. Photocatalytic activity experiments were performed under simulated solar radiation. The H₂ gas generated was collected and analyzed using an off-line gas chromatograph (GC). Control and
blank (no catalyst) experiments were carried out under identical conditions. Three sets of experiments were carried out to check reproducibility. The recyclability study also was carried out 3 times to determine the stability of the photocatalyst. Each test was carried out as described above for 5 hours under irradiation. After completion of each test, the gaseous products were evacuated, and the reactor was purged with argon.

**Photo-electrochemical measurements**

Photo-electrochemical measurements were performed in a three-electrode system using a CHI 617B electrochemical workstation. A solar simulator equipped with an AM 1.5G filter and 150 W Xe lamp (Abet Technologies) was used as the irradiation source to produce monochromatic illuminating light. The output light intensity was adjusted to 1 sun (100 W/m²) using 15151 lowcost calibrated Si reference cell (ABET technologies). The reference and counter electrodes were 6 Ag/AgCl and platinum wire, respectively, and Na₂SO₄ aqueous solution served as the electrolyte. To prepare the working electrode, the as-synthesized 10 mg of CdS and Co₄S₃/CdS nanocomposites were first dispersed into ethanol (450 μl) and 50 μl Nafion mixtures using soft ultrasonic stirring to obtain a uniform suspension. The solution containing the catalyst (30 μl) was dropped onto the pretreated indium–tin oxide (ITO) conductor glass substrate, which was then dried in an oven at 100 °C for 3 h. Photo-responses were measured at 0.0 V during on-off cycling of the solar simulator.

**Mott-Schottky experiment**

Mott-Schottky analysis of synthesized materials were performed as follows, first synthesized materials was coated on FTO and considered as a working electrode, Pt as a counter electrode and Na₂SO₄ as electrolyte. Mott–Schottky plots at a frequency of 1 kHz were measured using a
standard potentiostat equipped with an impedance spectra analyzer in the same electrochemical configuration and electrolyte under the dark condition. The measured potentials versus Ag/AgCl were converted to the normal hydrogen electrode (NHE) scale by $E_{\text{NHE}} = E_{\text{Ag/AgCl}} + 0.197$. 
Supporting Figures

**Figure S1.** XRD patterns of bulk MoS$_2$ (BM) and few layered MoS$_2$ (FM)
**Figure S2.** XPS spectra of copper doped MoS$_2$ (CM) showing expanded (a) Cu 2p, (b) Mo 3d and (c) S 2p spectral regions.
Figure S3. XPS spectra of CdS nanorods showing expanded (a) Cd 3d and (b) S 2p regions.
Figure S4. XPS spectra of FM/CdS composite showing expanded (a) Cd 3d, (b) S 2p and (c) Mo 3d regions.
Figure S5. N$_2$ adsorption–desorption isotherms of CdS, FM/CdS and FCM/CdS nanocomposites.
Table S1. Comparison of photocatalytic H₂ evolution rates reported in the literature using MoS₂ and metal-doped MoS₂ as co-catalysts on CdS nanostructures with our present results.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Scavenger</th>
<th>Light Source</th>
<th>H₂ Production in µmol h⁻¹ (catalyst dose)</th>
<th>Ref.</th>
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</thead>
<tbody>
<tr>
<td>MoS₂/CdS</td>
<td>Lactic acid</td>
<td>300 W Xe lamp (λ &gt;420 nm)</td>
<td>31.34 (0.05g)</td>
<td>S1</td>
</tr>
<tr>
<td>MoS₂/CdS</td>
<td>Lactic acid</td>
<td>300 W Xe lamp (λ &gt;420 nm)</td>
<td>540 (0.1g)</td>
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<td>MoS₂/CdS</td>
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<td>300 W Xe lamp (λ &gt;420 nm)</td>
<td>530 (0.1g)</td>
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<tr>
<td>MoS₂/CdS</td>
<td>SO₃²⁻/S²⁻</td>
<td>300 W Xe lamp (λ &gt;420 nm)</td>
<td>381.6 (0.08g)</td>
<td>S4</td>
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<td>MoS₂/CdS</td>
<td>TEOA</td>
<td>300 W Xe lamp (λ &gt;420 nm)</td>
<td>37.1 (0.02g)</td>
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<tr>
<td>MoS₂/CdS</td>
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<td>542.5 (0.05g)</td>
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<td>MoS₂/CdS</td>
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<td>150 W Xe lamp (λ &gt;420 nm)</td>
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<td>MoS₂/CdS</td>
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<td>300 W Xe lamp (λ &gt;420 nm)</td>
<td>9800 (0.2g)</td>
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<tr>
<td>MoS₂/CdS</td>
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<td>300 W Xe lamp (λ &gt;420 nm)</td>
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<td>Co-MoS₂/CdS</td>
<td>SO₃²⁻/S²⁻</td>
<td>300 W Xe lamp (λ =300nm)</td>
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<td>Ni-MoS₂/CdS</td>
<td>SO₃²⁻/S²⁻</td>
<td>300 W Xe lamp (λ =300nm)</td>
<td>480 (0.02g)</td>
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<td>FCM/CdS</td>
<td>Lactic acid</td>
<td>150 W Xe lamp (solar)</td>
<td>196 (0.001g)</td>
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References


