Electronic Supplementary Information

Multidirectional-charge-transfer urchin-type Mo-doped W18O49 nanostructures on CdS nanorods for enhanced photocatalytic hydrogen evolution

P. Bhavani, D. Praveen Kumar, Seonghyun Jeong, Eun Hwa Kim, Hanbit Park, Sangyeob Hong, Madhusudana Gopannagari, D. Amaranatha Reddy, Jae Kyu Song and Tae Kyu Kim

*a Department of Chemistry and Chemical Institute for Functional Materials, Pusan National University, Busan 46241, Republic of Korea

b Department of Chemistry, Kyung Hee University, Seoul 17104, Republic of Korea

*Corresponding authors. E-mail) tkim@pusan.ac.kr (T.K.K.) and jaeksong@khu.ac.kr (J.K.S.)
Experimental Details

Photocatalytic \( \text{H}_2 \) production: The photocatalytic \( \text{H}_2 \) production reactions were evaluated in a 135 mL quartz reactor at ambient conditions. Typically, 1.0 mg of the photo catalyst was dispersed in 15 mL of aqueous solution containing 20\% lactic acid (LA), and it act as a sacrificial reagent. Then, the reactor was closed with a gas-tight rubber septum. Prior to irradiation, the suspension was evacuated and outgassing with Argon (Ar) gas for 30 min to remove air. A solar simulator equipped with an AM 1.5 G filter and 150 W Xenon lamp (Abet Technologies) was used as the irradiation source. The output light intensity was adjusted to 1 sun (100 W/m\(^2\)) using 15151 low-cost calibrated Si reference cell (ABET technologie). The experiments were repeated in three times to check reproducibility. Every test was carried out as described above for 3 h under irradiation source. The \( \text{H}_2 \) gas production was analyzed using an off-line gas chromatograph (GC, Young Lin Autochro-3000, model 4900) equipped with a thermal conductivity detector (TCD) and a 5 Å molecular sieve column. The generated \( \text{H}_2 \) gas (100 \( \mu \text{L} \)) was collected at the headspace of quartz reactor, and purged into the GC, and evaluated by a calibration plot to 5 \% standard gas of \( \text{H}_2 \).

The apparent quantum efficiency (QE) was calculated by the following equation.

\[
\text{QE} = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 \%
\]

\[
= \frac{(\text{number of evolved H}_2 \text{ molecules}) \times 2}{\text{number of incident photons}} \times 100 \%
\]

Here the QE was measured under the same photocatalytic hydrogen evolution experimental conditions except the irradiation source, here 150 W Xe lamp with 425 nm band pass filter having 7 optical density greater than 4 in the rejection band and slope factor less than 1 \%, were used as
light sources, instead of the solar stimulator. The output light intensity was measured using 15151 low-cost calibrated Si reference cell (ABET technologies). The liquid level is ~16 cm far from the window of lamp and the illuminated area is 21.24 cm².

**Photo-electrochemical measurements:** Photo-electrochemical studies were obtained in a three-electrode system by 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 low cost calibrated Si reference cell (ABET technologies). The reference and counter electrodes were Ag/AgCl and platinum wire, respectively, and 0.5 M Na₂SO₄ aqueous solution served as the electrolyte. The measured pH value is 6.72. To prepare the working electrode, the as-synthesized 10 mg of CdS and MWO/CdS nanocomposites were first dispersed into ethanol (450 μL) and 50 μL of Nafion mixtures under soft ultrasonic stirring to get 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 80 °C for 3 h. Photoresponses were measured at 0.0 V during on-off cycling of the solar simulator. Electrochemical impedance spectroscopy (EIS) was carried out at open-circuit potential over the frequency range of 10⁵ and 10⁻¹ Hz with an AC voltage magnitude of 5 mV. Moreover, to evaluate the flat-band potential (VFB) of the CdS and MWO/CdS 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 \( E_{\text{NHE}} = E_{\text{Ag/AgCl}} + 0.197 \). The cyclicvoltammograms (CV) were measured with as scanning rate of 10 mV/s using whereas the electrolyte was consisting of 0.1M Na₂SO₄ aqueous solution with 1mM K₃[Fe(CN)₆].¹
Supporting Figures

Figure S1. XRD patterns of MWOE, MWOP and MWOB nanocomposites.

Figure S2. SEM image of CdS nanorods.
Figure S3. FESEM images and EDS elemental mapping analyses of MWOE/CdS.
**Figure S4.** Time-resolved photoluminescence spectra of CdS and MWOE/CdS at 560 nm.
Figure S5. ESR spectra of CdS, MWOE and MWOE/CdS.
Figure S6. N₂ adsorption/desorption isotherms of CdS and MWOE/CdS and the pore-size distribution of MWOE/CdS nanocomposite.

Figure S7. Electrochemical impedance measurements of CdS and MWOE/CdS nanocomposites.
Figure S8. The solvent effect on photocatalytic \( \text{H}_2 \) production rate.

Figure S9. The Mo dopant concentration effect on photocatalytic \( \text{H}_2 \) production rate.
Figure S10. Recycling study of MWOE/CdS nanocomposite.

Figure S11. The effect of various scavengers on photocatalytic H₂ production rate.
Figure S12. Mott–Schottky plots (Potential vs. $E_{\text{Ag/AgCl}}$) of CdS and MWO in 0.5 M Na$_2$SO$_4$ electrolyte solution.
Table S1. Comparisons of photocatalytic H\textsubscript{2} production rate for representative W and Mo oxides based photocatalysts.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Scavenger</th>
<th>Light source</th>
<th>(\text{H}_2) production rate ((\mu\text{mol} \cdot \text{h}^{-1} \cdot \text{g}^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo-W\textsubscript{18}O\textsubscript{49}/CdS</td>
<td>Lactic acid</td>
<td>150 W Xe lamp ((\lambda \geq 420\ \text{nm}))</td>
<td>40,225</td>
<td>Present work</td>
</tr>
<tr>
<td>W\textsubscript{18}O\textsubscript{49}/g-C\textsubscript{3}N\textsubscript{4}</td>
<td>Triethanolamine</td>
<td>300 W Xe lamp ((\lambda \geq 420\ \text{nm}))</td>
<td>738</td>
<td>2</td>
</tr>
<tr>
<td>(\alpha)-MoO\textsubscript{3}-WO\textsubscript{3}/CdS</td>
<td>Artificial waste water</td>
<td>300 W Xe lamp ((\lambda \geq 420\ \text{nm}))</td>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td>WO\textsubscript{3}/TiO\textsubscript{2}</td>
<td>Ethanol</td>
<td>Hg lamp ((\lambda = 254\ \text{nm}))</td>
<td>9,560</td>
<td>4</td>
</tr>
<tr>
<td>Cs/WO\textsubscript{3}</td>
<td>WO\textsubscript{3}:PEG at 1:1 for thin film</td>
<td>250 W Hg lamp ((\lambda = 365-550\ \text{nm}))</td>
<td>3,500</td>
<td>5</td>
</tr>
<tr>
<td>WC-CdS</td>
<td>Na\textsubscript{2}S/Na\textsubscript{2}SO\textsubscript{3}</td>
<td>300 W Xe lamp ((\lambda \geq 420\ \text{nm}))</td>
<td>1,370</td>
<td>6</td>
</tr>
<tr>
<td>MoO\textsubscript{3}-Polymer</td>
<td>Methanol</td>
<td>300 W Hg lamp ((\lambda = 420\ \text{nm}))</td>
<td>350</td>
<td>7</td>
</tr>
<tr>
<td>Pt-IrO\textsubscript{2}/WO\textsubscript{3}</td>
<td>KI solution</td>
<td>Visible light ((\lambda = 400-800\ \text{nm}))</td>
<td>15</td>
<td>8</td>
</tr>
<tr>
<td>CsTaWO\textsubscript{6}/Rh</td>
<td>Methanol</td>
<td>150 W solar ((1\ \text{sun irradiation}))</td>
<td>39</td>
<td>9</td>
</tr>
<tr>
<td>Pt/WO\textsubscript{3}/CdS/TiO\textsubscript{2}</td>
<td>Formic acid</td>
<td>500 W Xe lamp ((\lambda \geq 420\ \text{nm}))</td>
<td>1,059</td>
<td>10</td>
</tr>
<tr>
<td>CdS/WO\textsubscript{3}</td>
<td>Lactic acid</td>
<td>300 W Xe lamp ((\lambda \geq 420\ \text{nm}))</td>
<td>369</td>
<td>11</td>
</tr>
<tr>
<td>CdS/Au/WO\textsubscript{3}</td>
<td>Na\textsubscript{2}S/Na\textsubscript{2}SO\textsubscript{3}</td>
<td>300 W Xe lamp ((\lambda \geq 420\ \text{nm}))</td>
<td>1,500</td>
<td>12</td>
</tr>
<tr>
<td>CdS/Au/U-WO\textsubscript{3}</td>
<td>Na\textsubscript{2}S/Na\textsubscript{2}SO\textsubscript{3}</td>
<td>300 W Xe lamp ((\lambda \geq 420\ \text{nm}))</td>
<td>1,390</td>
<td>13</td>
</tr>
</tbody>
</table>
References


