

Electronic Supplementary Information

Noble Metal-Free Ultrathin MoS₂ Nanosheet-Decorated CdS Nanorods as an Efficient Photocatalyst for Spectacular Hydrogen Evolution under Solar Light Irradiation

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Syntheses and Characterizations

Synthesis of CdS nanorods

The CdS nanorods were synthesized by hydrothermal method.¹ In our synthesis process, 1:1 ratio of cadmium acetate ($(\text{CH}_3\text{CO}_2)_2\text{Cd}\cdot x\text{H}_2\text{O}$) and thiourea ($\text{CH}_4\text{N}_2\text{S}$) were dissolved in 60 mL of ethylene diamine and allowed for stirring 30 min for homogeneous mixing. Resultant solution mixture was transferred into a 100 ml Teflon-lined stainless steel autoclave and placed hot air oven at 160°C for 48 hours. After completion of hydrothermal treatment autoclave cooled normally to become room temperature and obtained yellow colored solid product. This yellow product was washed with de-ionized water and ethanol three times to remove impurities, and then dried at 60 °C for 12 hours

Synthesis of MoS₂ nanosheets

The MoS₂ nanosheets was synthesized by hydrothermal method; 1.2g of Na₂MoO₄·2H₂O and 2.4 g of thioacetamide (C₂H₅NS) were dissolved in 72 ml of deionized water and allowed for stirring 1 hour. The resultant mixture was transferred into a 100 mL Teflon-lined autoclave and maintained at 210 °C for 24 hours. After cooling to room temperature, the obtained black-colored MoS₂ solid product was washed with de-ionized water and ethanol three times to remove impurities, and then dried at 80 °C for 12 hours.

Synthesis of ultrathin MoS₂/CdS

The ultrathin MoS₂/CdS composites were prepared by ultrasonic exfoliation.² First, as synthesized different weight percentages (4%, 6% and 8%) bulk MoS₂ were dispersed in 25 ml DMF and allowed for ultrasonication for 3 hours at room temperature. After sonication, the MoS₂ suspension was dispersed homogeneously, added 250 mg of as-prepared CdS nanorods and the mixture was kept for ultrasonic treatment again for 1 hour followed by 12 hours stirring inducing efficient interaction between exfoliated MoS₂ nanosheets with the CdS nanorods and then removed solvent by vacuum distillation to form ultrathin MoS₂/CdS nanocomposite.

Characterization

Surface morphologies and elemental analyses were evaluated using the HITACHI S-4800 field emission scanning electron microscope (FESEM) equipped with an energy dispersive spectrometer (EDS, Inca 400, Oxford Instruments). The microstructure properties were measured using a JEOL JEM-2100F transmission electron microscope (TEM) with an accelerating voltage of 200 kV. The crystal structures of the samples were determined by X-ray diffraction (XRD) with a Bruker D8 Advanced X-ray diffractometer using Cu K α radiation as the X-ray source. X-ray photoelectron spectroscopy (XPS) measurements were carried out to evaluate the chemical status and elemental composition of the samples with a monochromated Al K α X-ray source (1486.6 eV) at an energy of 15 kV/150 W. Diffuse reflectance spectra (UV-Vis DRS) were recorded with a UV-Vis spectrometer (UV-1800 SHIMADZU, Japan). Photoluminescence (PL) spectra of the photocatalysts were collected at room temperature using a Hitachi F-7000 fluorescence spectrometer.

Photocatalytic activity

Photocatalytic activity was tested in a quartz 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 % 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 natural solar radiation on the roof-terrace of Chemistry Building, Pusan National University, Busan, South Korea with identical experimental procedures those employed in the controlled laboratory. The intensity of solar light is estimated ~ 102.7 mV. 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 5 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 was evacuated, and the reactor was purged with argon. The H₂ gas evolved was

determined using an off-line gas chromatograph (Younglin, Autochro-3000, model 4900) equipped with thermal conductivity detector.

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

$$QE = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 (\%)$$

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

Here the QE was measured under the same photocatalytic hydrogen evolution experimental conditions except the irradiation source: 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 simulator. 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.

Calculation of H₂ production rate in Table 1

We have re-calculated H₂ production rate of previously reported values in the unit of mmol(H₂ produced)·g⁻¹(per amount of catalyst)·h⁻¹(per time of measurement). For example, the rate of H₂ production in Ref 2 is re-calculated as follows:

The rate of H₂ of 1914 μmol·h⁻¹ using 20 mg of photocatalyst

→ The rate of H₂ of 1914 / (2 × 10⁻³) μmol·g⁻¹·h⁻¹ per 1 g of photocatalyst

→ The rate of H₂ of 95.70 mmol·g⁻¹·h⁻¹.

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 BM(bulk

MoS₂/CdS and UM(ultrathin MoS₂)/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 hours. 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 using standard procedures to derive the conduction band flat band potentials. First, the synthesized composites were coated on FTO and considered as a working electrode. Pt served 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 *vs.* Ag/AgCl were converted to the normal hydrogen electrode (NHE) scale by $E_{\text{NHE}} = E_{\text{Ag/AgCl}} + 0.197$.

Supporting Figures

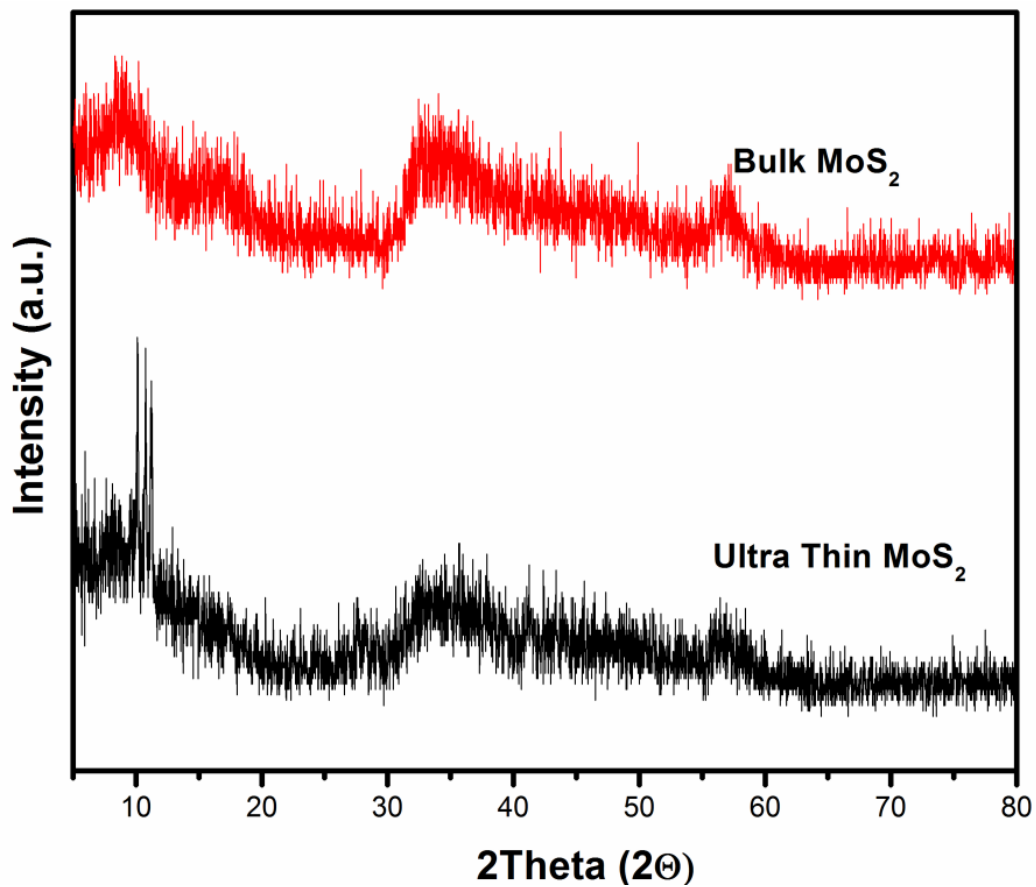


Figure S1. XRD patterns of BM and UM MoS₂ nanosheets.

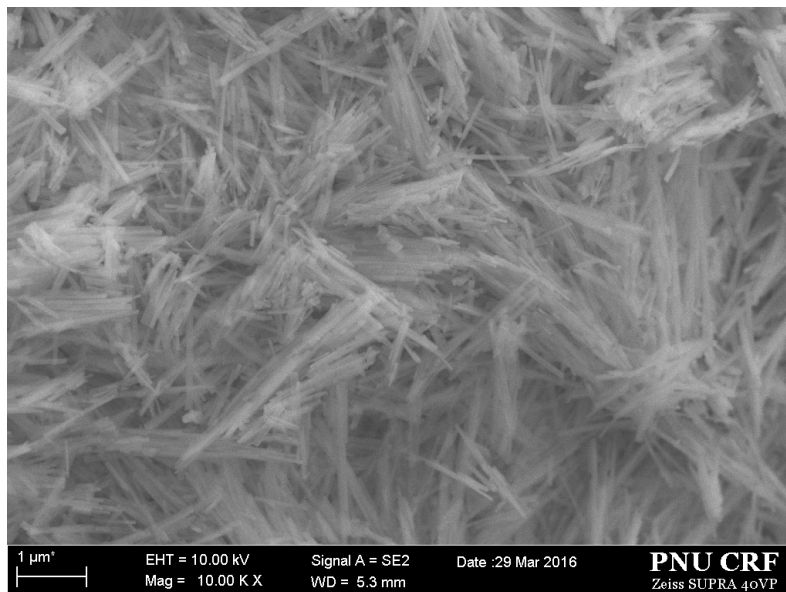


Figure S2. FESEM image of CdS nanorods.

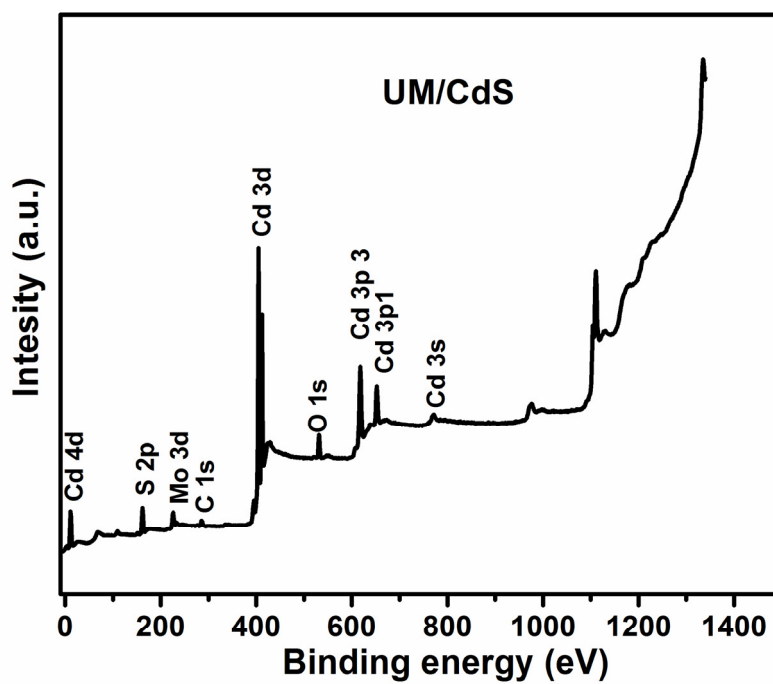


Figure S3. XPS survey spectrum of UM/CdS nanocomposite.

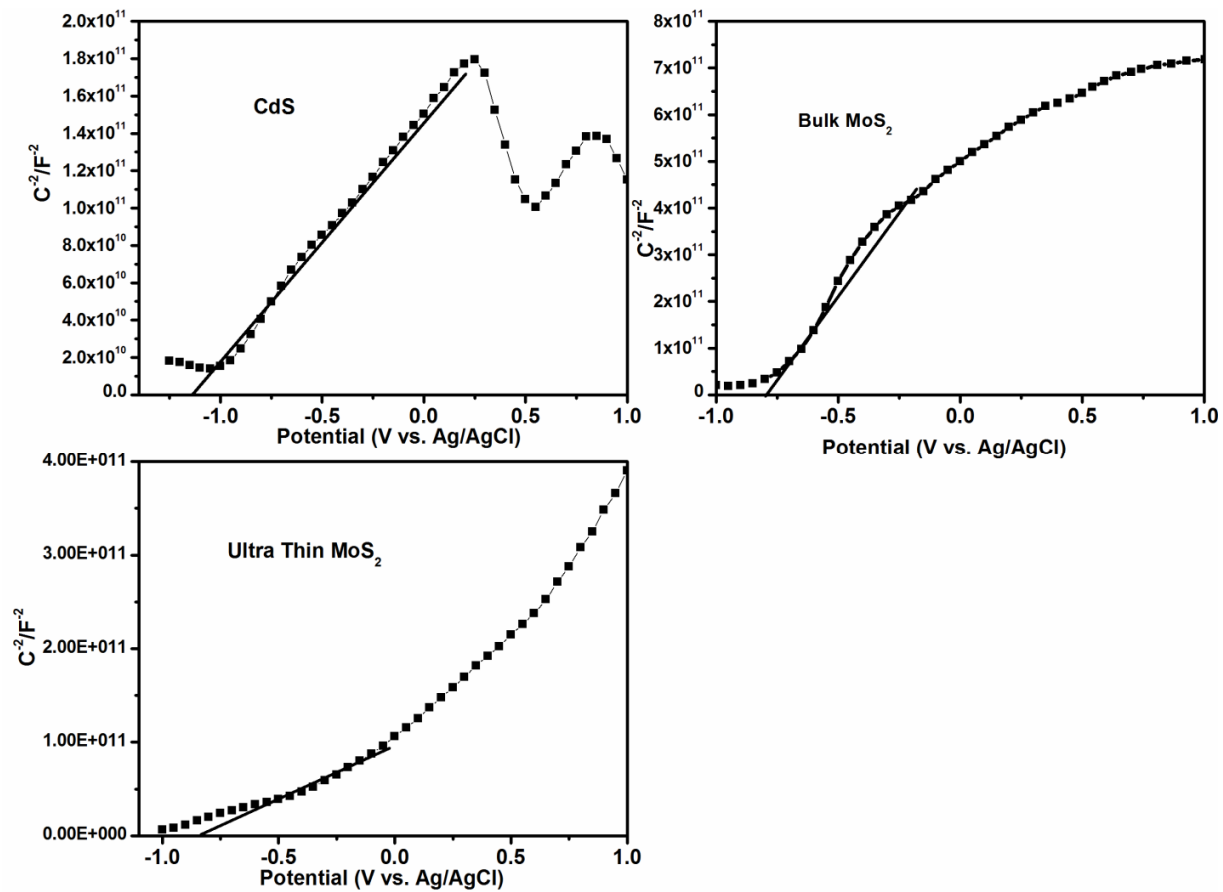


Figure S4. Mott–Schottky plots (Potential vs. Ag/AgCl) of CdS, BM-MoS₂ and UM-MoS₂ in 0.5 M Na₂SO₄ electrolyte solution.

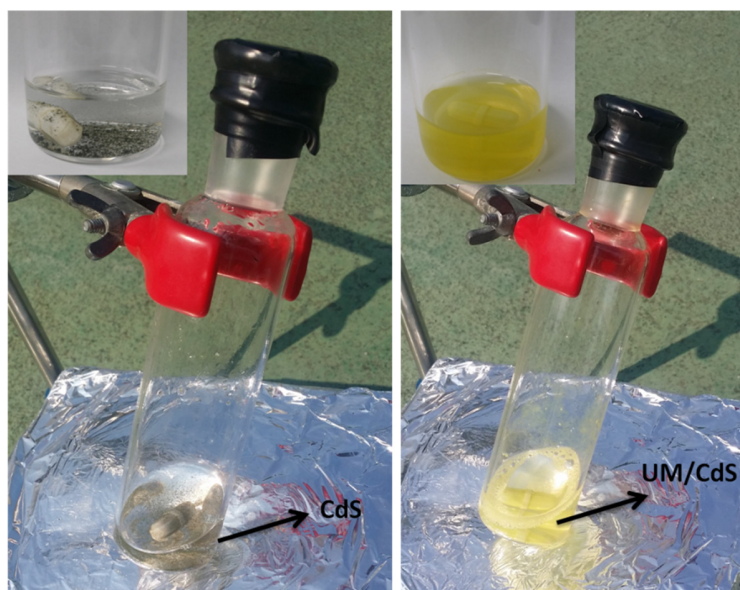


Figure S5. Photographs of photo reactors with CdS and UM/CdS under natural solar light irradiation.

References

- [1] Z. Sun, H. Zheng, J. Li and P. Du, *Energy Environ. Sci.*, 2015, **8**, 2668–2676.
- [2] J. He, L. Chen, F. Wang, Y. Liu, P. Chen, C.-T. Au and S.-F. Yin, *ChemSusChem*, 2016, **9**, 624–630.