

Vanadium tetrasulfide as an earth-abundant and noble-metal-free cocatalyst for solar-to-hydrogen conversion reaction

Rama Krishna Chava*, Taeseong Kim, Youngsoo Kim*, and Misook Kang*

Department of Chemistry, College of Natural Sciences, Yeungnam University,
280 Daehak-Ro, Gyeongsan, Gyeongbuk-38541, Republic of Korea.

Corresponding Author's Address:

Dr. Rama Krishna Chava (Email: drcrkphysics@hotmail.com, rama@ynu.ac.kr)

Prof. Youngsoo Kim (kimys6553@yu.ac.kr)

Prof. Misook Kang (Email: mksang@ynu.ac.kr);

Department of Chemistry, College of Natural Sciences, Yeungnam University, 280 Daehak-Ro, Gyeongsan-38541, Gyeongbuk, Republic of Korea.

1. Experimental section

1.1. Synthesis of CdS NRs: All chemicals were used directly without further purification. Typically, 1.92 g of cadmium nitrate and 1.42 g of thiourea were dissolved in 50 mL ethylenediamine at room temperature with the aid of magnetic stirring. The mixture was stirred for 30 min. The solution was then transferred to an autoclave and treated at 180 °C for 18 h. The yellow precipitate of CdS obtained after centrifugation at 4000 rpm for 15 min and washed sequentially with ethanol and distilled water five times. The resulting CdS nanorods were dried at 70 °C for overnight.

1.2. Synthesis of CdS/VS₄ HSs: CdS/VS₄ heterostructures were prepared using a solvothermal reaction. First, the CdS NRs (20 mg) were dispersed in 30 mL of ethanol and mixed well via magnetic stirring and sonication. Subsequently, 10 mM thiourea was added to the above solution, which was then stirred for 30 min. Next, 2 mM NH₃VO₃ was added, and the mixture was stirred for another 30 min. The resulting solution was transferred to a Teflon liner and placed in a stainless-steel autoclave. The autoclave was then heated in an electric oven at 180 °C for 12 h. Finally, the product was obtained after centrifugation and washing sequentially three times with distilled water and ethanol. The obtained CdS/VS₄ composite was vacuum dried at 60 °C for 10 h and stored for further characterization. The obtained CdS/VS₄ heterostructured composite with 2 mM vanadium precursor and 10 mM thiourea was denoted as CV-1. Other composites with different vanadium contents were prepared similarly. The other CdS/VS₄ heterostructured composite samples had NH₃VO₃:thiourea concentration ratios of 3:15 and 5:25 and were denoted as CV-2 and CV-3, respectively. For comparison, VS₄ was prepared under identical conditions, without the addition of CdS.

1.3. Characterization details: The crystal structures of the prepared photocatalyst samples were investigated using powder X-ray diffraction (XRD) with Cu-K α radiation (PANalytical XPert diffractometer) at an operating voltage and current of 40 kV and 30 mA, respectively.

The morphologies of the samples were analyzed via transmission electron microscopy (TEM) using a Hitachi H-7600 instrument. High-resolution TEM, lattice spacing, selected area electron diffraction (SAED) pattern, and scanning TEM-energy dispersive X-ray spectroscopy (STEM-EDS) mapping analyses were performed using an FEI Titan G2 FE-TEM instrument at an operating voltage of 200 kV. The oxidation states and atomic percentages of individual elements in CdS, VS₄, and CdS/VS₄ and the valence band edge positions of the photocatalyst samples were determined using X-ray photoelectron spectroscopy (XPS; Thermo Scientific K-alpha X-ray photoelectron spectrometer). Brunauer–Emmett–Teller (BET) specific surface areas and the corresponding pore-size distribution curves were acquired using a BELSORP-II mini system. The optical absorption and light-harvesting nature of the obtained samples were investigated via UV–vis diffuse reflectance spectroscopy (DRS) using a Scinco spectrophotometer. Charge carrier recombination studies were conducted on a Scinco spectrofluorometer by recording the transient photoluminescence (PL) spectra at an excitation wavelength of 350 nm. To determine the electron lifetime in the samples, time-resolved PL measurements were performed using a scanning confocal microscope (MicroTime-200, Picoquant, Germany). The work functions of both photocatalyst materials (CdS and VS₄) were determined by measuring the contact potential difference (CPD) values which were obtained from air photoemission spectroscopy (APS) instrument (KP Technology Ltd.) with a Kelvin probe measurement system. The measurements were conducted using a 296 nm UV light excitation light source, and the work function of the Au tip was used as the standard reference.

1.4. Visible photocatalytic H₂ evolution reaction studies: The photocatalytic H₂ evolution activity of the obtained samples was tested in a 100 mL reactor. Typically, 5 mg of the photocatalyst sample was suspended in a 50 mL aqueous solution containing 10 vol.% lactic acid. Before visible light irradiation, the reaction vessel was closed with a rubber septum and purged with Ar gas to maintain anaerobic conditions. Next, the reactor was irradiated with a

150 W Xenon light source (Abet Technologies) equipped with a 420 nm cut-off filter. The incident light power density was approximately 0.75 W cm⁻². A magnetic stirrer at the bottom of the reactor maintained the sample in suspension. H₂ gas released during the photocatalytic reactions was analyzed at regular intervals using a gas chromatograph fitted with a thermal conductivity detector (Scinco GC). The reaction conditions for the recycling tests were similar to those described above, except that the reaction time was extended to 24 h. The recycling experiments were performed as follows: The samples were cleaned with DI water and ethanol several times and then dried in a vacuum oven for 12 h. Thereafter, the obtained sample was dispersed in a fresh aqueous solution containing 10 vol.% lactic acid, and a second H₂ evolution activity experiment was conducted. This process was repeated six times to test the recyclability. The apparent quantum yield (AQY) was determined using Equation 1:

$$\begin{aligned} \text{AQY} &= \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 \\ &= \frac{\text{number of evolved Hydrogen molecules} \times 2}{\text{number of incident photons}} \times 100 \quad \text{--- (1)} \end{aligned}$$

The solar-to-hydrogen (STH) conversion efficiency was determined using equation 2:

$$\text{STH} = \frac{R_{\text{H}_2} \times \Delta G_r}{P_{\text{sun}} \times S}$$

$$\text{STH} = [(\text{H}_2 \text{ mmol/s}) * 273 \text{ kJ}] / [\text{intensity (mW/cm}^2) * \text{area cm}^2] \times 100 \quad \text{----- (2)}$$

Where R_{H_2} is the rate of hydrogen generation in mol s⁻¹; ΔG_r is the Gibbs energy change for the reaction (237 kJ mol⁻¹); P_{sun} is the energy flux of the incident light in W m⁻²; and S is the irradiated area.

1.5. Electrochemical measurements: The working electrodes for the transient photocurrent and electrochemical impedance spectroscopy (EIS) measurements were prepared as follows: 5 mg of the prepared photocatalyst powder was added to 1 mL of ethanol and 20 μ L of Nafion

mixed solution via ultrasonication. Subsequently, 500 μL of the solution was dropped onto a $2 \times 2 \text{ cm}^2$ fluorine-doped tin oxide (FTO) glass substrate with an active area of approximately 0.25 cm^2 . The electrodes were then dried in an oven and calcined at $100 \text{ }^\circ\text{C}$ for one hour. Transient photocurrent measurements were performed on an electrochemical analyzer (IVIUM STAT) in a standard three-electrode system using the as-prepared material as the working electrodes, Ag/AgCl (saturated KCl) as the reference electrode, and a Pt wire as the counter electrode. All measurements were obtained in an aqueous electrolyte solution with $0.5 \text{ M Na}_2\text{SO}_4$. A Xe lamp (150 W) with a UV cut-off filter ($\geq 420 \text{ nm}$) was used as the light source. The EIS measurements of the working electrodes in the three-electrode system were also performed using the same instrument over a frequency range of $0.01\text{--}100 \text{ kHz}$ with an AC amplitude of 5 mV .

Table S1: Comparison of H₂ evolution activities of 1D CdS based heterostructures.

Catalyst	Light source	H ₂ evolution rate ($\mu\text{mol.g}^{-1}.\text{h}^{-1}$)	Quantum Efficiency	Ref.
CdS/Ni ₂ P	300 W Xe lamp $\lambda > 420$ nm	1200	41%	(1)
CdS/Ti ₃ C ₂ T _x	300 W Xe lamp $\lambda > 420$ nm	15400	--	(2)
CdS/MoS ₂	300 W Xe lamp $\lambda > 420$ nm	2320	65.8%	(3)
CdS/CoS ₂	300 W Xe lamp $\lambda \geq 400$ nm	58000	39.6%	(4)
FeS/FeS ₂	300 W Xe lamp $\lambda \geq 400$ nm	2071	--	(5)
CuS/Mn _{0.3} Cd _{0.7} S	500 W Hg-Xe arc $\lambda = 420$ nm	106840	18.32%	(6)
g-C ₃ N ₄ /NiS	300 W Xe lamp $\lambda \geq 400$ nm	4042	--	(7)
CdS/SnS ₂	150 W Xe lamp $\lambda > 420$ nm	35650	18.45%	(8)
CdS/WS ₂	$\lambda > 420$ nm	14100	--	(9)
Graphene/VS ₄	500 W Xe lamp $\lambda > 420$ nm	700	--	(10)
CdS/Bi doped C QDs	300 W Xe lamp $\lambda \geq 420$ nm	1770	1.94	(11)
CdS/Pt	150 W Xe lamp $\lambda > 420$ nm	2598	--	This work
CdS/MoS₂	150 W Xe lamp $\lambda > 420$ nm	2982	--	This work
CdS/VS₄	150 W Xe lamp $\lambda > 420$ nm	5846	16.1%	This work

References

- (1) Z. J. Sun, H. F. Zheng, J. S. Li, P. W. Du, *Energy Environ. Sci.*, 2015, **8**, 2668-2676.
- (2) J. -Y. Li, Y. -H. Li, F. Zhang, Z. -R. Tang, Y. -J. Xu, *Appl. Catal. B.*, 2020, **269**, 118783.
- (3) M. M. Liu, F. Y. Li, Z. X. Sun, L. F. Ma, L. Xu, Y. H. Wang, *Chem. Commun.*, 2014, **50**, 11004-11007.
- (4) J. Tang, B. Gao, J. B. Pan, L. Chen, Z. H. Zhao, S. Shen, J. -K. Guo, C. -T. Au, S. -F. Yin, *Appl. Catal. A.*, 2019, **588**, 117281.
- (5) J. Jia, Q. Q. Zhang, Z. Li, X. Y. Hu, W. H. Liu, J. Fan, *J. Mater. Chem. A*, 2019, **7**, 3828–3841.
- (6) Y. L. Han, X. F. Dong, Z. B. Liang, *Catal. Sci. Technol.*, 2019, **9**, 1427–1436.
- (7) H. Zhao, H. Z. Zhang, G. W. Cui, Y. M. Dong, G. L. Wang, P. P. Jiang, X. M. Wu, N. Zhao, *Appl. Catal. B.*, 2018, **225**, 284–290.
- (8) R. K. Chava, J. Y. Do, M. S. Kang, *J. Mater. Chem. A*, 2019, **7**, 13614-13628.
- (9) K. Zhang, M. Fujitsuka, Y. K. Du, T. Majima, *ACS Appl. Mater. Interfaces*, 2018, **10**, 20458–20466.
- (10) W. W. Guo, D. F. Wu, *Int. J. Hydrogen Energy*, 2014, **39**, 16832-16840.
- (11) Y. J. Wang, J. Chen, L. M. Liu, X. X. Xi, Y. M. Li, Z. L. Geng, G. Y. Jiang, Z. Zhao, *Nanoscale*, 2019, **11**, 1618–1625.