

Electronic Supplementary Information

Vanadium carbide: an efficient, robust, and versatile cocatalyst for photocatalytic hydrogen evolution under visible light

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1. Experimental section

1.1 Chemicals and materials

All chemicals were of analytical grade and used as received without further purification. VC powder were purchased from Hefei Zhonghang Nanometer Technology Development Co., Ltd. CdS and Zn_{0.5}Cd_{0.5}S were synthesized according to our previous reports.^{1,2} All solutions used throughout the experiments were prepared with ultrapure water (18.2 MΩ).

1.2 Characterization

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were taken with a Tecnai-G²-F30 field emission transmission electron microscope. X-ray diffraction (XRD) patterns were investigated with a Rigaku smartlab diffractometer with a nickel filtrated Cu K α radiation. X-ray photoelectron spectroscopy (XPS) measurements of the samples were performed on a Thermo Scientific Escalab-250Xi electron spectrometer using an Al K α X-ray source. Binding energies were referenced to the C 1s peak (set at 284.8 eV) of the sp² hybridized (C=C) carbon from the sample. UV-vis diffuse reflectance spectra were recorded on a PerkinElmer Lambda-750 UV-vis-near-IR spectrometer equipped with an integrating sphere and BaSO₄ powders were used as a reflectance standard. UV-vis absorption spectra were taken with a Thermo Scientific-Evolution 220 spectrophotometer. Photoluminescence spectra were determined by a Horiba Scientific FluoroMax-4 spectrofluorometer spectrometer.

1.3 Photocatalytic hydrogen evolution experiments

The photocatalytic hydrogen evolution experiments were performed in a sealed Pyrex reactor with a top flat quartz window for light irradiation and a silicone rubber septum was fixed on its side for sampling produced H₂ in the headspace of reaction cell. In a typical procedure, ErB and VC powder were added to a solution containing 100 mL of 15 vol.% TEOA aqueous solution under vigorous stirring. The pH values of the reaction solution were adjusted by addition of hydrochloric acid or sodium hydroxide. For testing the versatility of VC as a H₂ evolution cocatalyst of semiconductor-based photocatalysts such as CdS and Zn_{0.5}Cd_{0.5}S, a 300-W Xe lamp equipped with an optical

cut-off filter ($\lambda \geq 420$ nm) was used as a light source. The reaction mixture solution was prepared by directly mixing CdS or $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ (44 mg) and VC (5 mg) powder in reaction cell containing 100 mL of 10 vol.% lactic acid under vigorous stirring. Then, the reaction solution was thoroughly degassed by repeated evacuation- N_2 filling, and finally refilled with N_2 to reach ambient pressure. After that, the reaction solution was irradiated by a 30-W LED lamp equipped with an optical cut-off filter ($\lambda \geq 420$ nm). During the reaction, the mixture solution was continuously stirred. The amount of H_2 produced was manually taken out by a gas-tight syringe (Agilent, 1.0 mL) and analyzed at given time intervals with a precalibrated gas chromatography (Tech comp; GC-7900) with a thermal conductivity detector, a 5 Å molecular sieve column (4 mm \times 5 m), and with N_2 as carrying gas.

1.4 Electrocatalytic hydrogen evolution reactions

The electrochemical measurements were carried out in a standard three-electrode electrochemical set-up using a CHI660E potentiostat. The saturated Ag/AgCl and graphite rod were used as reference electrode and counter electrode, respectively. The working electrodes were prepared by drop-casting ethanol/water solution containing VC powder (5 mg mL⁻¹) onto the carbon paper (HESEN, HCP030P, thickness, 0.3 mm). The loading amount of VC on carbon paper was controlled to be 0.8 mg cm⁻². The electrocatalytic activity of VC towards H_2 evolution was examined by obtaining polarization curves using linear sweep voltammetry (LSV) at a scan rate of 5 mV s⁻¹ in a 0.5 M Na_2SO_4 solution containing TEOA (15 vol.%, pH 9). All the applied potentials are reported as reversible hydrogen electrode potential scale using E (vs. RHE) = E (vs. Ag/AgCl) + 0.2142 V after IR correction. Potentiostatic EIS was used to determine the uncompensated solution resistance (R_s).

2. Additional figures

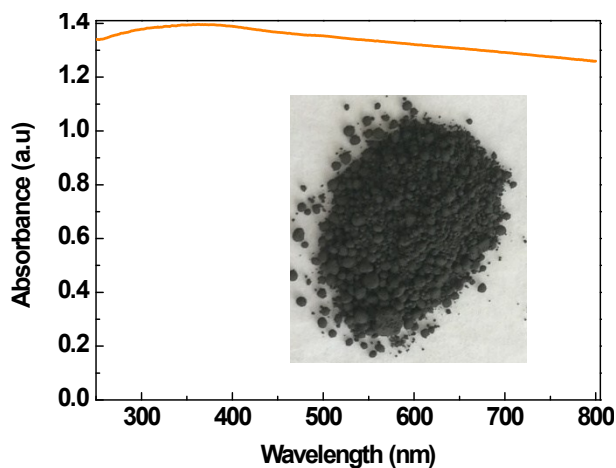


Fig. S1 UV-vis absorption spectrum along with the color of VC catalyst.

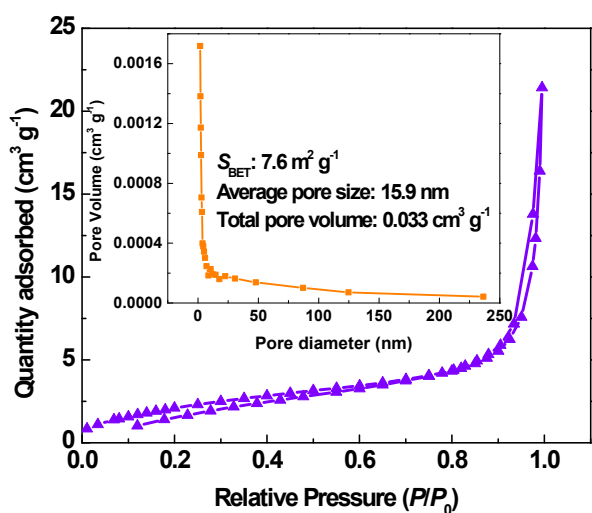


Fig. S2 N₂ adsorption-desorption isotherm and pore size distribution (inset) of VC.

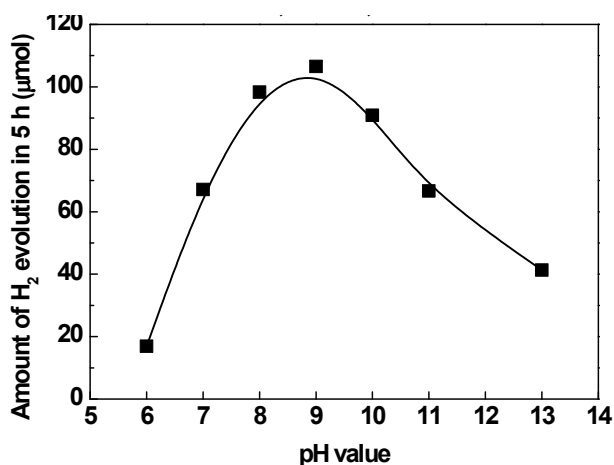


Fig. S3 H₂ evolution from TEOA (15 vol.%, 100 mL) solution containing VC (1 mM) and ErB (0.5 mM) at different pH values. Light source, white LED lamp (30 W), $\lambda \geq 420$ nm.

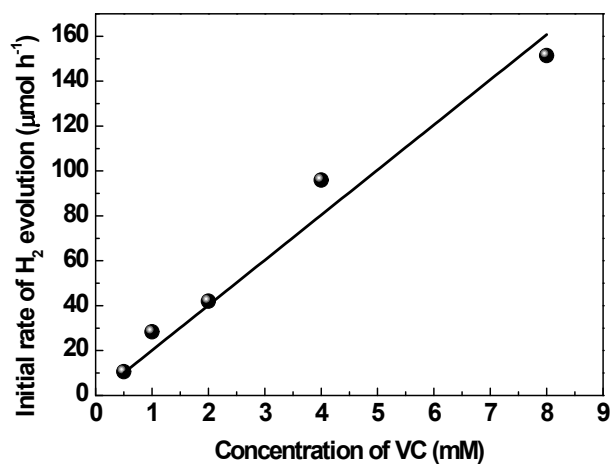


Fig. S4 Initial rate of H₂ evolution from TEOA solution (15 vol.%, 100 mL, pH 9) containing ErB (0.5 mM) and different concentrations of VC catalyst. Light source, white LED lamp (30 W), $\lambda \geq 420$ nm.

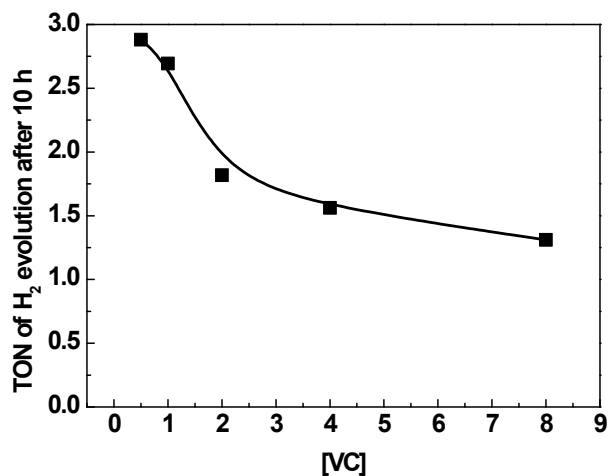


Fig. S5 TON of H₂ evolution from TEOA solution (15 vol.%, 100 mL, pH 9) containing ErB (0.5 mM) and different concentrations of VC catalyst. Light source, white LED lamp (30 W), $\lambda \geq 420$ nm.

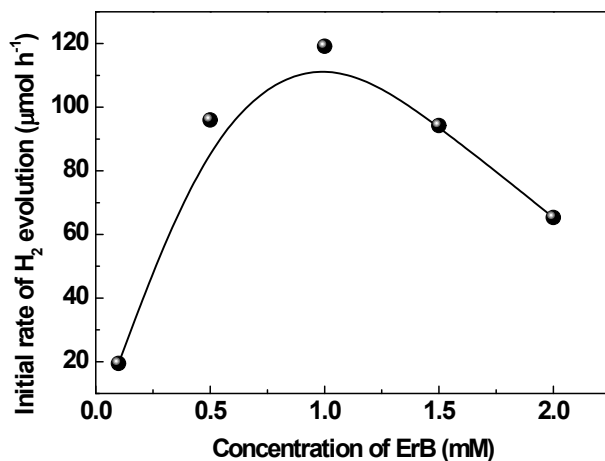


Fig. S6 Initial rate of H₂ evolution from TEOA solution (15 vol.%, 100 mL, pH 9)

containing VC (4 mM) and different concentrations of ErB. Light source, white LED lamp (30 W), $\lambda \geq 420$ nm.

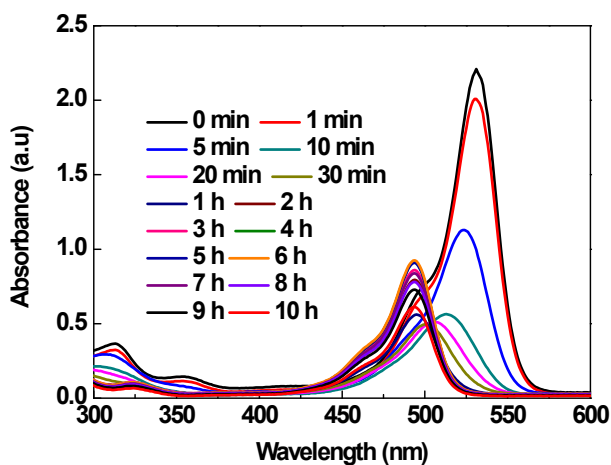


Fig. S7 Absorption spectra of systems containing ErB (0.5 mM) and VC (4.0 mM) in TEOA solution (15 vol.%, 100 mL, pH 9) upon irradiation. Light source, white LED lamp (30 W), $\lambda \geq 420$ nm.

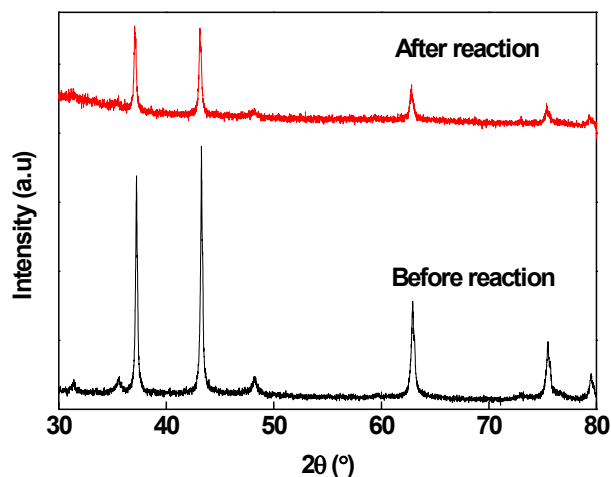


Fig. S8 XRD patterns of VC catalyst before and after reactions.

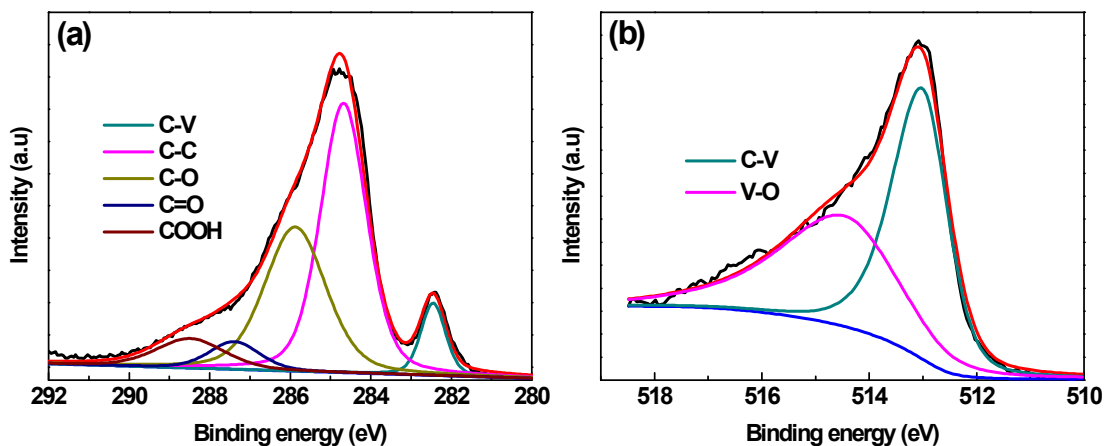


Fig. S9 (a) C 1s and (b) V 2p XPS spectra of VC catalyst after H₂ evolution reaction.

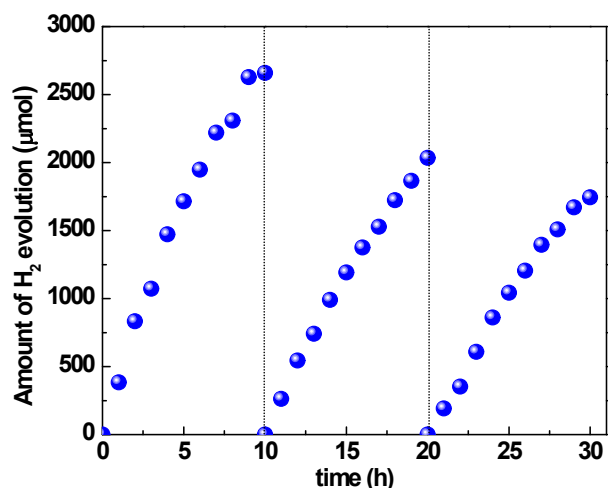


Fig. S10 Stability test of photocatalytic H₂ evolution for CdS/VC.

Table S1 Comparison of catalytic H₂ evolution activity of VC with other carbides.

Photocatalyst	Reaction conditions	Light source	H ₂ evolution rate (mmol h ⁻¹ g _{carbide} ⁻¹)	Ref.
CdS/WC	Lactic acid (10 vol.%), 100 mL	300 W Xe lamp, >420 nm	111.0	3
g-C ₃ N ₄ /Mo ₂ C	Triethanolamine (10 vol.%), 100 mL	300 W Xe lamp, >420 nm	50.7	4
CdS/Ti ₃ C ₂	Lactic acid (25 vol.%), 80 mL	300 W Xe lamp, >420 nm	573.7	5
Ni ₃ C/CdS	Na ₂ S-Na ₂ SO ₃ (0.25 M), 80 mL	350 W Xe lamp, >420 nm	1428.0	6
	Lactic acid (10 vol.%), 80 mL		1802.0	
CdS/VC	Lactic acid (10 vol.%), 100 mL	300 W Xe lamp, >420 nm	38.8	This work
ErB/VC	triethanolamine (15 vol.%), 100 mL	30 W white LED lamp, >420 nm	3.8	This work

References

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