Electronic Supplementary Information

Layered metallic vanadium diboride as an active cocatalyst for efficient dye-sensitized photocatalytic hydrogen evolution

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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. V$_2$O$_5$ was obtained from Beijing Chemical Works, VB$_2$, VN, VC, WB, and Mo$_2$B$_5$ powders were purchased from Hefei Zhonghang Nanometer Technology Development Co., Ltd., triethanolamine (TEOA, 99.8%) was purchased from Xilong scientific, TiO$_2$ nanoparticles (P25, 20% rutile and 80% anatase) were purchased from Degussa, and organic dyes including Erythrosin B (ErB), Eosin Y (EY), Rose Bengal (RB), Fluorescein sodium (FS), and Rhodamine B were obtained from Tianjin Guangfu Fine Chemical Research Institute. All solutions used throughout the experiments were prepared with ultrapure water (18.2 MΩ). Ru(bpy)$_3$Cl$_2$ was synthetized by a reported procedure.$^1$ VS$_2$ was synthesized by a one-step hydrothermal reaction of ammonia (1.9 mL), NH$_4$VO$_3$ (4.02 mmol), and thioacetamide (TAA, 40.2 mmol) in the presence of polyvinylpyrrolidone (PVP, 297 mmol) in 60 mL water at 180 °C for 20 h. After that, the product was collected by centrifugation, washed with deionized water and ethanol, and dried in a vacuum oven at 60 °C for 12 h. Finally, the obtained powders were calcined at 300 °C for 2 h under N$_2$ atmosphere with a heating rate of 2 °C min$^{-1}$. CdS nanoparticles were synthesized according to a reported procedure.$^2$

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 Kα radiation. X-ray photoelectron spectroscopy (XPS) measurements of the samples were performed on a Thermo Scientific Escalab-250Xi electron spectrometer using an Al Kα X-ray source. Binding energies were referenced to the C 1s peak (set at 284.8 eV) of the sp$^2$ 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 BaSO$_4$ 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 H₂ evolution experiments

Photocatalytic H₂ evolution experiments were performed with a PCX50C Discover multichannel photocatalytic reaction system (Beijing Perfectlight Technology Co. Ltd.) with white-light LED lamps (10 W×9, 380nm≤λ≤780nm, 450 mW/cm²) as the light source. In a typical procedure, ErB and VB₂ powders were added to a quartz reactor (60 mL) containing 25 mL of 10 vol.% TEOA aqueous solution under vigorous stirring. The pH values of the reaction solution were adjusted by addition of hydrochloric acid or sodium hydroxide. Then, the reaction solution was thoroughly degassed by repeated evacuation-N₂ filling, and finally refilled with N₂ to reach ambient pressure. After that, the reaction solution was irradiated under continuous stirring. The amount of H₂ 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×5 m), and with N₂ as carrying gas.

Ru(bpy)₃Cl₂ was also used as the photosensitizer and the photocatalytic H₂ evolution reaction catalyzed by VB₂ was performed as follows: Ru(bpy)₃Cl₂ (1 mM) and VB₂ powders (6 mM) were added to a reaction cell (250 mL) containing 100 mL of 0.1 M ascorbic acid aqueous solution under vigorous stirring. Then, the reaction solution was thoroughly degassed by repeated evacuation-N₂ filling, and finally refilled with N₂ to reach ambient pressure. After that, the reaction solution was irradiated by a 300-W Xe lamp (CEL-HXF300) with a cut-off filter (λ≥420 nm) under continuous stirring. The temperature of the reaction solution was controlled by a flow of cooling water. The amount of H₂ produced was analyzed by a gas chromatography (Tech comp; GC-7900) with a thermal conductivity detector, a 5 Å molecular sieve column (4 mm×5 m), and with N₂ as carrying gas.

To verify the versatility of VB₂ as a H₂ evolution catalyst in semiconductor-based photocatalytic systems, 44 mg of CdS or TiO₂ was mixed with 5 mg of VB₂ in a reaction cell (250 mL) containing 100 mL of 10 vol.% lactic acid aqueous solution under vigorous stirring. The reaction solution was then thoroughly degassed by repeated evacuation-N₂
filling, and finally refilled with N\textsubscript{2} to reach ambient pressure. Afterward, the reaction solution was irradiated under continuous stirring. A 300-W Xe lamp (CEL-HXF300) was used as a light source equipped with a cut-off filter of 420 nm for CdS-based and without a filter for TiO\textsubscript{2}-based photocatalytic systems. The temperature of the reaction solution was controlled by a flow of cooling water. The amount of H\textsubscript{2} produced was analyzed by a gas chromatography (Tech comp; GC-7900) with a thermal conductivity detector, a 5 Å molecular sieve column (4 mm×5 m), and with N\textsubscript{2} as carrying gas.

**Electrocatalytic hydrogen evolution reactions**

The electrochemical measurements were carried out in a standard three-electrode electrochemical set-up using a CHI760E potentiostat. The saturated Ag/AgCl and graphite rod were used as reference electrode and counter electrode, respectively. For the fabrication of working electrode, the catalyst suspension was prepared by dispersing 25 mg of catalysts into 5 mL of ethanol/H\textsubscript{2}O (4/1, v/v) mixed solution containing 100 \textmu L of 0.5 wt% Nafion solution by ultrasonication for 30 min. Afterward, the as-prepared catalyst suspension was loaded onto carbon paper (HESEN, HCP030P, thickness, 0.3 mm). The loading amount of VB\textsubscript{2} on carbon paper was controlled to be 0.8 mg cm\textsuperscript{-2}. The electrocatalytic activity of VB\textsubscript{2} towards H\textsubscript{2} evolution was examined by obtaining polarization curves using linear sweep voltammetry (LSV) at a scan rate of 10 mV s\textsuperscript{-1} in a 0.5 M Na\textsubscript{2}SO\textsubscript{4} solution containing TEOA (10 vol\%, pH 11). All the applied potentials are reported as reversible hydrogen electrode potential scale using E (vs. RHE)=E (vs. Ag/AgCl)+0.2142 V after \textit{iR}\textsubscript{s} correction. Potentiostatic electrochemical impedance spectroscopy (EIS) was used to determine the uncompensated solution resistance (\textit{R}\textsubscript{s}). EIS measurements were carried out at a forward bias of -0.05 V vs. Ag/AgCl with an AC amplitude of 5 mV in the frequency range of 10 mHz to 100 kHz.

2. **Additional data**
Fig. S1 HRTEM image of VB$_2$. 

Fig.S2 N$_2$ adsorption-desorption isotherm and corresponding pore size distribution curve (inset) of VB$_2$. 

S5
**Fig. S3** UV-vis-DRS of VB$_2$. Inset shows the digital photos of VB$_2$ powders.

**Fig. S4** Survey XPS spectrum of VB$_2$.

**Fig. S5** H$_2$ evolution from TEOA (10 vol%, 25 mL) solution containing ErB (0.5 mM) and VB$_2$ (4.0 mM) at different pH values. Reaction conditions: light source, white LED lamp (380nm$\leq \lambda \leq$780nm).
Table S1 A comparison of catalytic activity of VB$_2$ with recently reported transition metal-based catalysts for H$_2$ evolution.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Photosensitizer</th>
<th>Reaction conditions</th>
<th>Light source</th>
<th>H$_2$ evolution rate (mmol h$^{-1}$ g cocatalyst$^{-1}$)</th>
<th>Ref.</th>
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<tr>
<td>NiS$_x$/G</td>
<td>EY</td>
<td>Triethanolamine (10 vol.%), 100 mL</td>
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<td>CoS$_x$/G)</td>
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<td>Triethanolamine (10 vol.%), 80 mL</td>
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<td>VC</td>
<td>ErB</td>
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<td>VC/CdS</td>
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<td>Triethanolamine (15 vol.%), 100 mL</td>
<td>300 W Xe lamp, ≥420 nm</td>
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<td>Mo$_2$C</td>
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<td>300 W Xe lamp, ≥420 nm</td>
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<td>Mo$_2$C/CdS</td>
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<td>Na$_2$S-Na$_2$SO$_3$ (1 M), 100 mL</td>
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<td>Mo$_2$N/CdS</td>
<td>CdS</td>
<td>Na$_2$S-Na$_2$SO$_3$ (1 M), 200 mL</td>
<td>300 W Xe lamp, ≥420 nm</td>
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<td>Co$<em>3$N/Zn$</em>{0.5}$Cd$_{0.5}$S</td>
<td>Zn$<em>{0.5}$Cd$</em>{0.5}$S</td>
<td>Na$_2$S(1.05M)-Na$_2$SO$_3$ (0.75 M), 200 mL</td>
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<td>Ni$_3$N/CdS</td>
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<td>Ni$_2$P/g-C$_3$N$_4$</td>
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<td>VS$_2$/g-C$_3$N$_4$</td>
<td>g-C$_3$N$_4$</td>
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<td>solar simulator AM 1.5</td>
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<td>VB$_2$/CdS</td>
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<td>VB$_2$</td>
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</table>

This Work
**Fig. S6** Time course of H$_2$ evolution catalyzed by VB$_2$ using Ru(bpy)$_3$Cl$_2$ as a photosensitizer in 100 mL of 0.1 M ascorbic acid aqueous solution under visible light irradiation. Reaction conditions: Ru(bpy)$_3$Cl$_2$, 1 mM; catalyst, 6 mM; light source, 300-W Xe lamp with a cut-off filter of 420 nm.

**Fig. S7** (a) Photocatalytic H$_2$ evolution on pristine CdS and CdS/VB$_2$. (b) Photocatalytic H$_2$ evolution on pristine TiO$_2$ and TiO$_2$/VB$_2$. Reaction conditions: CdS or TiO$_2$, 44 mg; VB$_2$, 5 mg; 10 vol.% lactic acid, 100 mL; light sources, 300-W Xe lamp with a cut-off filter of 420 nm for CdS-based systems and without filter for TiO$_2$-based systems.
Fig. S8 (a) XRD patterns of V$_2$O$_5$, VS$_2$, VN, VC, and VB$_2$.

Fig. S9 (a) XRD patterns of as-received WB and Mo$_2$B$_5$. (b) Comparison of H$_2$ evolution
activity of VB$_2$ with WB and Mo$_2$B$_5$ in ErB-TEOA (10 vol%, 25 mL, pH 11) system under visible light irradiation. Reaction conditions: ErB, 1 mM; catalyst, 6 mM; light source, white LED lamp (380nm$\leq\lambda\leq$780nm).

**Fig. S10** TON of H$_2$ evolution from ErB/VB$_2$ system in TEOA (10 vol%, 25 mL, pH 11) solution. Reaction conditions: VB$_2$, 4.0 mM; light source, white LED lamp (380nm$\leq\lambda\leq$780nm).
Fig. S11 (a) Initial rate and (b) TON of H₂ evolution from ErB/VB₂ system in TEOA (10 vol%, 25 mL, pH 11). Reaction conditions: ErB, 1.0 mM; light source, white LED lamp (380nm≤λ≤780nm).

Fig. S12 Absorption spectra of ErB (1.0 mM) in TEOA solution (10 vol%, 25 mL, pH 11) during the photocatalytic H₂ evolution catalyzed by VB₂ (6.0 mM). Reaction conditions: light source, white LED lamp (380nm≤λ≤780nm). The VB₂ was removed prior to measurement and the solution was diluted by 10 times.
**Fig. S13** XRD patterns of VB$_2$ before and after H$_2$ evolution stability test.

**Fig. S14** High resolution XPS spectra of (a) V 2p and (b) B 1s of VB$_2$ after H$_2$ evolution stability test.
**Fig. S15** (a) TEM and (b) HRTEM images of VB$_2$ after H$_2$ evolution stability test and corresponding SAED pattern (inset in panel (a)). (c) HAADF-STEM image of VB$_2$ after H$_2$ evolution stability test and corresponding EDX elemental maps (V, B, and O).
Fig. S16 (a) XRD patterns of air-annealed VB$_2$. (b) Catalytic activity of air-annealed VB$_2$ toward H$_2$ evolution in ErB-TEOA (10 vol%, 25 mL, pH 11) system. The air-annealing of VB$_2$ was carried out in air at different temperatures for 3 h, and the obtained samples were denoted as a-VB$_2$-x, where x represents the annealing temperature. Reaction conditions: ErB, 1.0 mM; catalyst, 6 mM; light source, white LED lamp (380nm$\leq$$\lambda$$\leq$780nm).

References