

Supporting Information

Boosting photocatalytic hydrogen production of CdS/BiVO₄ nanoplates by transferring in-plane plasmon resonant energy of gold nanoparticles

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Experimental Section

Chemicals. Sodium sulfite (Na₂SO₃, Wako), Sodium sulfide nonahydrate (Na₂S·9H₂O, 95%, Kanto), cadmium acetate dihydrate ((CH₃COO)₂Cd·2H₂O, 99.9%, Wako), bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O, 99.99%, Wako), ammonium vanadate(V) (NH₄VO₃, 99.9%, Wako), nitric acid (HNO₃, 67%, TCI), oleic acid (OA, tech. grade 90%, Sigma-Aldrich), oleylamine (OLAM, 90%, Sigma-Aldrich), 1-octadecene (ODE, 90%, Aldrich), (3-Aminopropyl)trimethoxysilane (APTMS, 97%, Sigma-Aldrich), and 3-mercaptopropionic acid (MPA, 99.0%, Sigma-Aldrich) were used as received without further purification.

Preparation of BiVO₄ Nanoplates. Bismuth vanadate (BiVO₄) nanoplates were prepared according to the previous literature [1] with slight modification. 0.5 mmol of Bi(NO₃)₃·5H₂O was added to 12 mL of ODE solution containing 1 mL of OLAM and 1 mL of OA in a 100 mL three-neck flask, followed by degassing at 110 °C for 15 min. Next, the solution was heated up and kept stirring at 170 °C for 5 min for complete dissolution, followed by cooling down to 140 °C naturally. Subsequently, 1 mmol of NH₄VO₃ in 12 mL of 11% HNO₃ aqueous solution was freshly prepared and injected to the above solution. The temperature of solution was kept at 100 °C for 20 min. The resulting BiVO₄ nanoplates were washed and purified with 1:1 hexane/ethanol solution by centrifugation for further use and characterization.

Preparation of Water Dispersible BiVO₄ Nanoplates. The OLAM/OA molecules on BiVO₄ nanoplates were replaced by water-soluble MPA molecules under alkaline condition via ligand exchange method. Briefly, the collected BiVO₄ nanoplates were dispersed in 2 mL of 1:1 hexane/CHCl₃, followed by the addition of 1 mL of MPA solution and 1 mL of 0.1 M NaOH solution. The solution was under vigorous stirring for 30 min. The nanoplates were then collected and washed several time with ethanol/acetone by centrifugation. The obtained nanoparticles were dried in a vacuum for further photocatalytic reaction.

Preparation of Au-decorated Nanoplates (Au on BiVO₄). Gold nanoparticles were deposited on the basal planes of BiVO₄ nanoparticles through photo-deposition. 300 μ L of 1 wt% HAuCl₄ solution was added dropwise to a solution with pH=10 containing a certain amount of water dispersible BiVO₄ sample. Subsequently, the solution was exposed to the illumination by 300 W Xe lamp with 390 nm long-pass filter for 10 min. The resulting Au-deposited BiVO₄ nanoparticles were washed with water/ethanol and collected by centrifugation.

CdS Deposition. Cadmium sulfide (CdS) nanoparticles were deposited on BiVO₄ nanoplates through chemical bath deposition. [2] CdS deposition solution was freshly prepared by dissolving 0.03 mmol of cadmium acetate dihydrate in 3 mL solution containing 0.06 mmol of thiourea, followed by steady stirring for 90 min at room temperature. Subsequently, the solution was added dropwise to 100 mL alkaline solution with pH=10 containing a certain amount of water dispersible BiVO₄ sample and the reaction was incubated at 90 °C for 4.5 h. The resulting nanoparticles were washed with water/ethanol and collected by centrifugation for further use.

Thin Silica Coating. A certain amount of water-dispersible Au on BiVO₄ nanoplates was dispersed into 30 mL of a basic solution with pH value equal to ca. 9-10. After that, 200 μ L of fresh 1% APTMS in ethanol solution was added dropwise to the above solution for 1 h of reaction at room temperature under steady stirring, followed by thermal treatment at 60 °C for 1 h. The obtained SiO₂-capped Au on BiVO₄ nanoplates were washed with a mixture of deionized water and ethanol by centrifugation for further use.

Photocatalytic Hydrogen Evolution. Photocatalytic experiments were performed with a Pyrex glass reactor (wavelength of transmitted light > 300 nm) coupled with a closed-circulation system. ca. 3 mg of CdS/BiVO₄ photocatalysts was dispersed in 80 mL of solution containing 0.8 mmole of Na₂SO₃, 0.8 mmole of Na₂S and 60 μL of 5 mM H₂PtCl₆ solution (ca. 2 wt% relative to photocatalysts). A 300 W Xe lamp (R300-3J, Cermax, Excelitas Technology) was used as the irradiation light source. The reactor temperature was controlled at around 20 °C through flowing water inside an aluminium jacket, followed by side illumination. The evolution of hydrogen gas was analyzed by using a gas chromatograph (Agilent Tech. 7890A) equipped with a thermal conductivity detector.

Characterization. The crystal structure of each sample was investigated using X-ray powder diffraction (Rigaku SmartLab 9kW AMK) with Cu K α radiation ($\lambda = 1.54186$ Å) under 200 mA and 45 kV. Lattice fringes of nanoparticles were examined using scanning transmission electron microscope equipped with energy-dispersive X-ray spectroscopy (EDS) operating at 200 kV (JEOL, JEM-ARM200F). Morphology, size and elemental analysis of nanoparticles were examined using scanning electron microscope equipped with energy-dispersive X-ray spectroscopy (Hitachi, SU8000 and JEOL, JSM-7900F). Diffuse reflectance spectroscopy (DRS) measurements were carried out on UV-Vis-NIR spectrometer (Shimadzu, UV-3600). Photoluminescence (PL) spectra of photocatalysts were measured on fluorescence spectrometer at an excitation wavelength of 280 nm. (Shimadzu, RF-5300PC). Time-resolved photoluminescence (TRPL) measurement for each photocatalyst was carried out on a C11367-02 HAMAMATSU Quantaaurus-Tau at an excitation wavelength of 280 nm. The PL decay fitting of TRPL spectra were carried out with a bi-exponential function, i.e., $F(t)=A_0+A_1\exp\left(\frac{-t}{\tau_1}\right)+A_2\exp\left(\frac{-t}{\tau_2}\right)$.

References

- [1] Dong, C.; Lu, S.; Yao, S.; Ge, R.; Wang, Z.; Wang, Z.; An, P.; Liu, Y.; Yang, B.; Zhang, H., Colloidal Synthesis of Ultrathin Monoclinic BiVO₄ Nanosheets for Z-Scheme Overall Water Splitting under Visible Light. *ACS Catal.* **2018**, *8*, 8649-8658.

- [2] Yu, Z. B.; Xie, Y. P.; Liu, G.; Lu, G. Q.; Ma, X. L.; Cheng, H.-M., Self-assembled CdS/Au/ZnO Heterostructure Induced by Surface Polar Charges for Efficient Photocatalytic Hydrogen Evolution. *J. Mater. Chem. A* **2013**, *1*, 2773-2776.

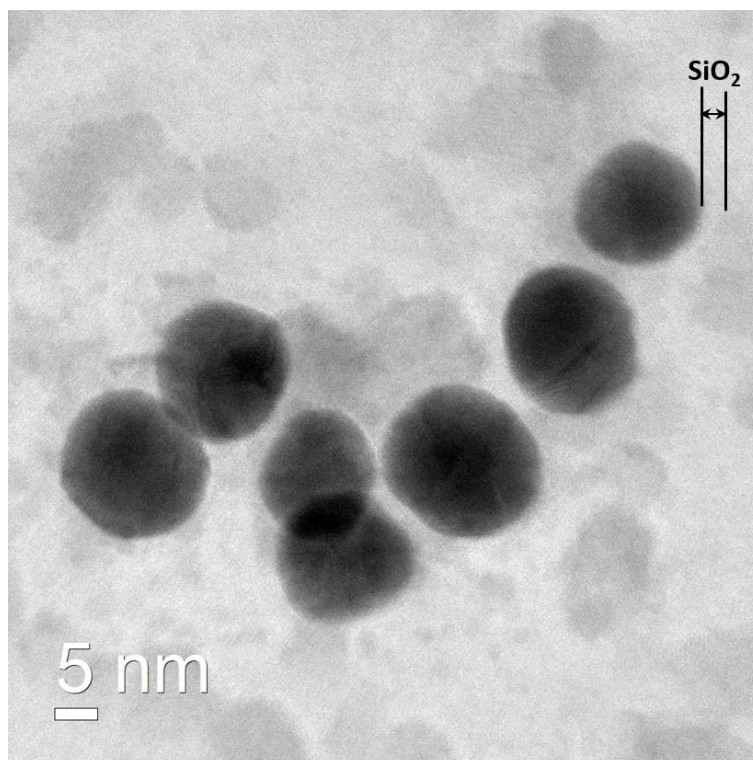
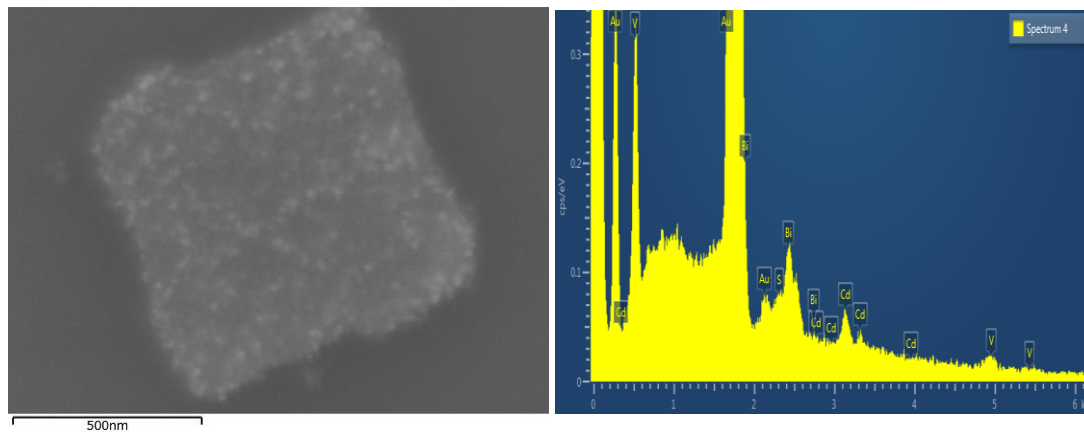


Fig. S1 TEM image of CdS/SiO₂-capped Au on BiVO₄ photocatalyst. (The label inside indicates the location and thickness of SiO₂ modification with MPTMS molecules.)



Element	Line Type	Wt%	Wt% Sigma	Atomic %	Standard Label	Factory Standard
S	K series	5.01	1.05	16.87	FeS2	Yes
V	K series	14.21	2.67	30.10	V	Yes
Cd	L series	24.27	2.52	23.30	Cd	Yes
Au	M series	17.01	2.52	9.32	Au	Yes
Bi	M series	39.50	3.47	20.40	Bi	Yes
Total:		100.00		100.00		

Fig. S2 Chemical composition analysis over single CdS/Au on BiVO₄ photocatalyst using by SEM equipped with energy dispersive x-ray spectrometer. The loading amounts of CdS and Au over BiVO₄ nanoplate are ca. 22 wt% and 10 wt%, respectively. Atomic percentage of V and Cd elements are used for the calculation of BiVO₄ and CdS amounts, respectively.