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Supplementary Information

Enhanced Photoelectrochemical Water Oxidation on a $BiVO_4$ Photoanode Modified with Multi-Functional Layered Double Hydroxide Nanowalls

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EXPERIMENTAL SECTION

Chemicals

$Bi(NO_3)_3·5H_2O$, $Co(NO_3)_3·6H_2O$, $Al(NO_3)_3·9H_2O$, urea, NH_4F were purchased from Sinopharm Chemical Reagent (Beijing Co. Ltd.) All reagents were of analytical grade and were used without further purification. Deionized water was used throughout the experiments. FTO substrates (F: SnO_2, 15 $m\Omega·cm^{-2}$) were received from Nippon Sheet Glass Co., Ltd.

Preparation of $BiVO_4$ photoanodes

The $BiVO_4$ photoanode was prepared by a modified method from a Bi metal precursor reported previously.[1] In a typical synthesis, a Bi metal film was first electrodeposited in an undivided cell on the electrochemical workstation (CHI 660C, CH Instrument Co. USA). The FTO conductive glass substrate was used as a working electrode. An Ag/AgCl electrode and Pt wire were used as the reference and counter electrodes, respectively. The electrolyte was prepared by dissolving $Bi(NO_3)_3·5H_2O$ (1 mmol) into a solution containing H_2O (100 mL) and absolute ethanol (50 mL). The deposition was carried out by passing 8.35×10^{-2} $C·cm^{-2}$ at E = -0.6 V vs. Ag/AgCl. After electrodeposition, the Bi metal film was washed with ethanol and dried by blowing air.

Then the Bi metal film was converted into $BiVO_4$ by a chemical-thermol process. 200 μL of 0.2 $mol·L^{-1}$ $VO(acac)_2$ dimethylsulfoxide (DMSO) solution were dipped onto the surface of the Bi metal film (geometric area = 2 cm^2). The film was then heated at 450 ^oC for 2 hours in air. After calcination, the film was placed in a 1 $mol·L^{-1}$ NaOH solution for 30 min while stirring gentally to remove the residual V_2O_5. Finally, after soaking in the NaOH solution, the resulting $BiVO_4$ photoanode was obtained by washing with water thoroughly, and dried at 70 ^oC for 1 h.

Preparation of LDH@$BiVO_4$ composite photoanodes

The CoAl-LDH was grown on $BiVO_4$ photoanodes by a hydrothermal method. In a typical run, $Co(NO_3)_3\cdot 6H_2O$ (15 mmol·L^{-1}), $Al(NO_3)_3\cdot 9H_2O$ (5 mmol·L^{-1}), urea (50 mmol·L^{-1}), and NH_4F (20 mmol·L^{-1}) were dissolved in deionized water to form a solution. This solution was transferred into a Teflon-lined stainless-steel autoclave and then one piece of $BiVO_4$ photoanode was placed at an angle against the wall of the Teflon liner with the conducting side facing down. Hydrothermal progress was conducted at 100 °C for 4 h in an electric oven. Finally, the resulting CoAl-LDH@$BiVO_4$ composite photoanodes were washed with water thoroughly, and dried at 50 °C for 1 h. The sample prepared by the same procedure without adding $Al(NO_3)_3\cdot 9H_2O$ is named $Co(OH)_2$@$BiVO_4$ and the one prepared by using a FTO substrate instead of $BiVO_4$ photoanode is named CoAl-LDH/FTO.

Characterizations

Powder X-ray diffraction (XRD) patterns of all the samples were carried out using a graphite-filtered Cu Kα radiation operating at 40 kV and 30 mA, λ= 0.15418 nm (Shimadzu XRD-6000 diffractometer).

X-ray photoelectron spectrometry (XPS) was recorded using Al Kα radiation (Thermo VG ESCALAB MK II). The positions of all BEs were calibrated by using the C 1s line at 284.8 eV.

Scanning electron microscopy with an accelerating voltage of 20 kV (SEM, Zeiss SUPRA 55) was applied for detailed morphology analyses.

Solid-state UV-Vis absorption spectra were measured at room temperature by using a spectrometer equipped with an integrating sphere attachment (Shimadzu UV-3000) by using $BaSO_4$ as a background sample. The signal from the FTO conductive glass was subtracted.

Photoluminescence (PL) measurements were conducted by using a laser with an excitation of 325 nm at room temperature (Hitachi F-7000 spectrofluorometer).

TEM and EDS mappings were taken using microscopy (JEOL JEM-2010F) combined with an EDX (OxFord X-Max^{N} 80-TLE) spectroscopy. For TEM observations, the samples were scraped from the FTO substrate and ultrasonically dispersed in ethanol and then a drop of the suspension was deposited onto a carbon coated Cu grid followed by the evaporation of solvent in air.

Electrochemical and PEC tests

All electrochemical and PEC measurements were carried out in an undivided cell on the electrochemical workstation (CHI 660C, CH Instrument Co. USA). The photoanodes were used as working electrodes. An Ag/AgCl electrode and Pt wire were used as the reference and counter electrodes, respectively. The electrolyte was $0.1\cdot\text{mol}\cdot\text{L}^{-1}$ phosphate buffer solution (pH=7), unless otherwise stated. The scan rate in all the current-voltage curve measurement was $10\ \text{mV}\cdot\text{s}^{-1}$. All potentials mentioned in this work were converted into that versus RHE (in V) according to equation (S1):

$$E_{RHE} = E_{Ag/AgCl} + E_{Ag/AgCl\ vs.\ NHE} + 0.059pH \qquad (S1)$$

unless otherwise noted. The $E_{Ag/AgCl\ vs\ NHE}$ in equation (S1) is 0.197 V at 20 °C. The light source used in the PEC experiments was a 300 W xenon lamp equipped with a AM 1.5G filter (illumination intensity: $100\ \text{mW}\cdot\text{cm}^{-2}$) and the light illuminated from the back side. The illumination area of all tested photoanodes was $2\ \text{cm}^2$.

Electrochemical Impedance Spectroscopy (EIS) was performed on the electrochemical workstation mentioned above at 1.23 V vs. RHE under illumination with a 0.1 V amplitude perturbation between 100000 and 0.1 Hz. The impedance data measured were fitted to an appropriate equivalent circuit by using ZView software (version 3.2c) to derive the resistance values.

PEC measurements with H_2O_2 as a hole scavenger were recorded in $0.1\ \text{mol}\cdot\text{L}^{-1}$ phosphate buffer solution electrolyte (pH=7) with the addition of $0.1\ \text{mol}\cdot\text{L}^{-1}$ H_2O_2. The efficiency of substrate oxidation (ϕ_{ox}) by surface-reaching holes was calculated by equation (S2):

$$\phi_{ox} = J^{H2O}/J^{H2O2} \qquad (S2)$$

In which J^{H2O} is the photocurrent density obtained in the PEC water oxidation experiment, while the J^{H2O2} is the photocurrent density obtained in the PEC measurements with H_2O_2 as a hole scavenger (Fig. S6).[2]

Incident photon-to -current efficiency (IPCE) at each wavelength was measured using a 300 W Xe arc lamp motioned above. Monochromatic light was generated by using Oriel Cornerstone 130 monochromator and the output was measured with a photodiode detector. IPCE was measured at 1.23 V vs. RHE and obtained using equation (S3):

$$\text{IPCE} = (1240\text{I})/(\lambda\text{P}_{\text{light}}) \qquad \text{(S3)}$$

where I is the photocurrent density ($\text{mA}\cdot\text{cm}^{-2}$); λ is the incident light wavelength (nm), and P_{light} ($\text{mW}\cdot\text{cm}^{-2}$) is the power density of monochromatic light at a specific wavelength.

The absorbed photon-to-current efficiency (APCE) was obtained by dividing the IPCE by the light harvesting efficiency (LHE) using equation (S4) and (S5):

$$\text{APCE} = \text{IPCE}/\text{LHE} \qquad \text{(S4)}$$

$$\text{LHE} = 1\text{-}10^{-A(\lambda)} \text{ (A}(\lambda)\text{ is the absorbance at wavelength } \lambda\text{)} \qquad \text{(S5)}$$

Figure Captions

Figure S1 XRD pattern of $Co(OH)_2@BiVO_4$ photoanodes

Figure S2 Optical bandgap energy of $BiVO_4$.

Figure S3 XPS core level spectra of $Co(OH)_2@BiVO_4$ photoanode, (A) O1s and (B) Co2p

Figure S4 XPS core level spectra of CoAl-LDH@$BiVO_4$ and $BiVO_4$ photoanodes (A) Bi4f and (B) V2p

Figure S5 SEM images of CoAl-LDH/FTO electrode, (A) Top-view and (B) Cross-sectional observation

Figure S6 SEM images of $Co(OH)_2@BiVO_4$ photoanode

Figure S7 Enlarged image of current-voltage curves (in Fig. 3A) of the photoanodes $BiVO_4$ (black), CoAl-LDH@$BiVO_4$ (red) and $Co(OH)_2@BiVO_4$ (green) under illumination (solid line)

Figure S8 Current-voltage curves of CoAl-LDH grown directly on FTO under illumination (solid line) and in the dark (dash line)

Figure S9 Current-voltage curves of $BiVO_4$ under illumination in the presence of 0.1 M H_2O_2 as a hole scavenger in 0.1 M PBS electrolyte

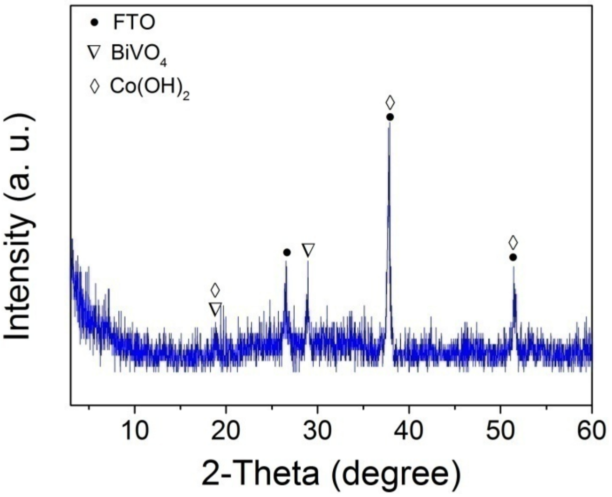

Fig. S1 XRD pattern of Co(OH)$_2$@BiVO$_4$ photoanodes

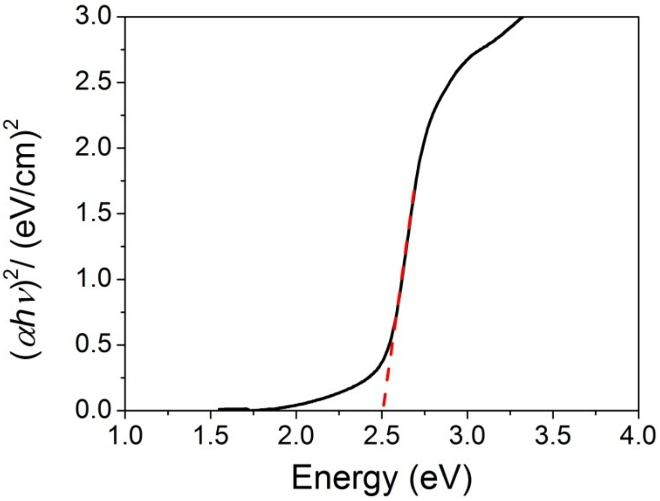

Fig. S2 Optical bandgap energy of $BiVO_4$

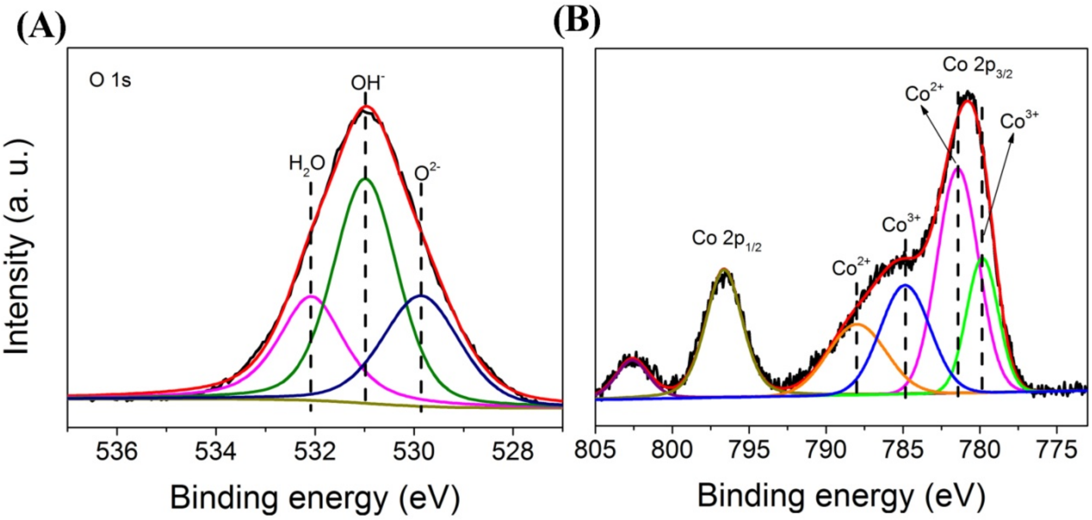

Fig. S3 XPS core level spectra of $Co(OH)_2$@$BiVO_4$ photoanode, (A) O1s and (B) Co2p.

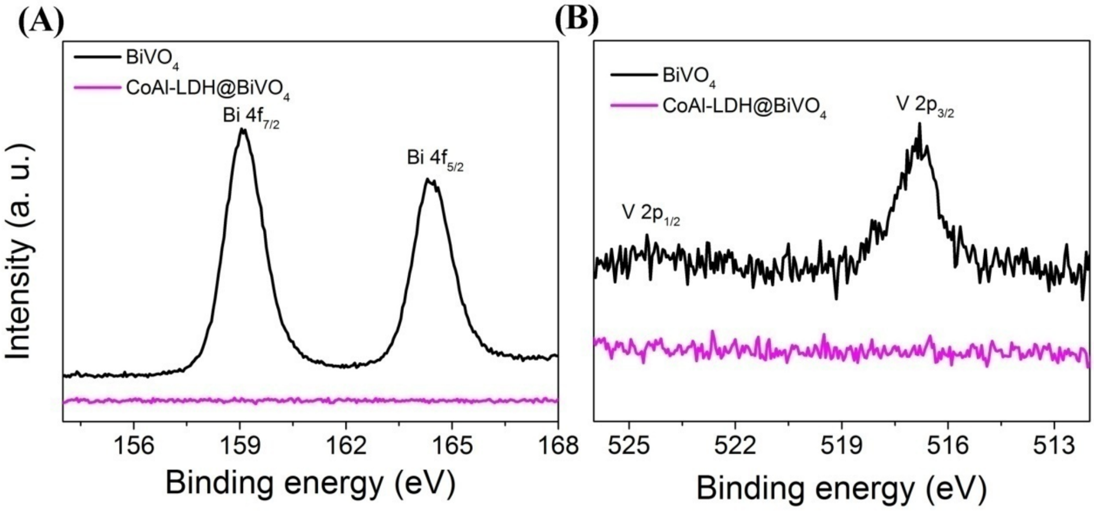

Fig. S4 XPS core level spectra of CoAl-LDH@$BiVO_4$ and $BiVO_4$ photoanodes (A) Bi4f and (B) V2p

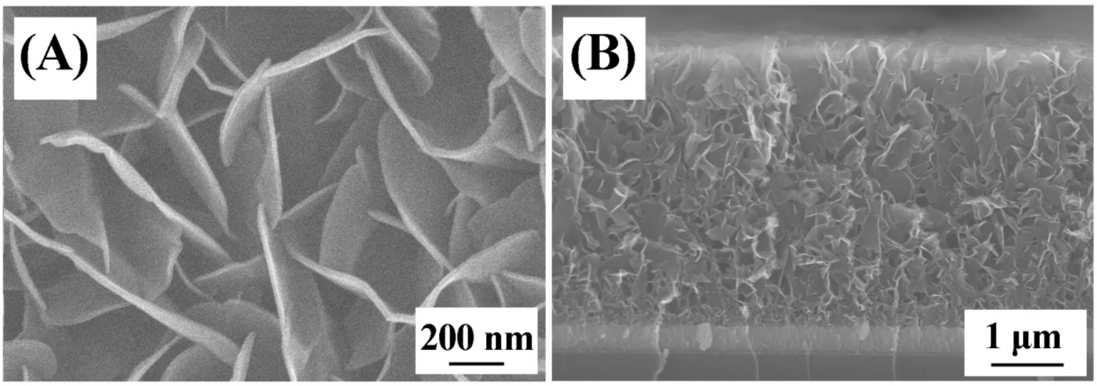

Fig. S5 SEM images of CoAl-LDH/FTO electrode, (A) Top-view and (B) Cross-sectional observation.

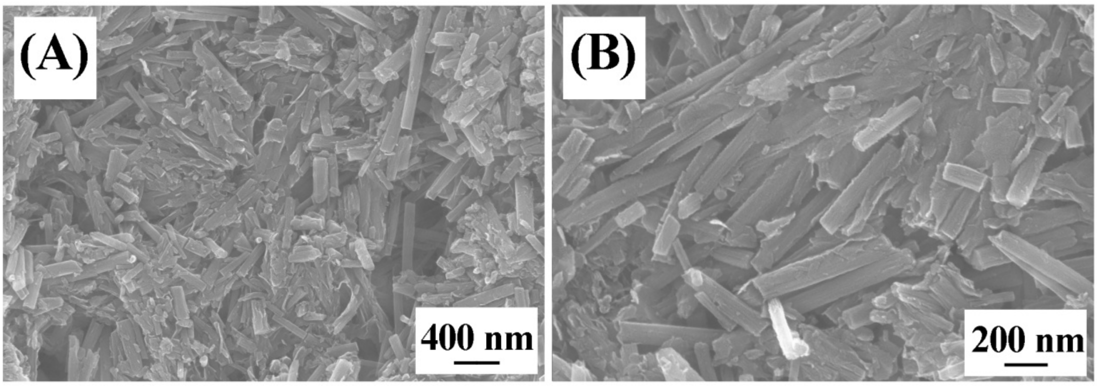

Fig. S6 SEM images of $Co(OH)_2@BiVO_4$ photoanode

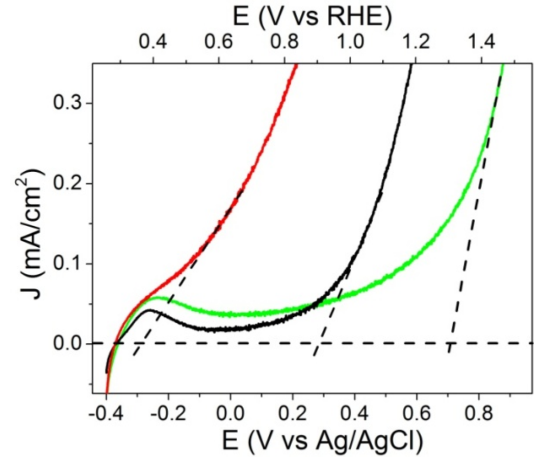

Figure S7 Enlarged image of current-voltage curves (in Fig. 3A) of the photoanodes $BiVO_4$ (black), CoAl-LDH@$BiVO_4$ (red) and $Co(OH)_2$@$BiVO_4$ (green) under illumination (solid line)

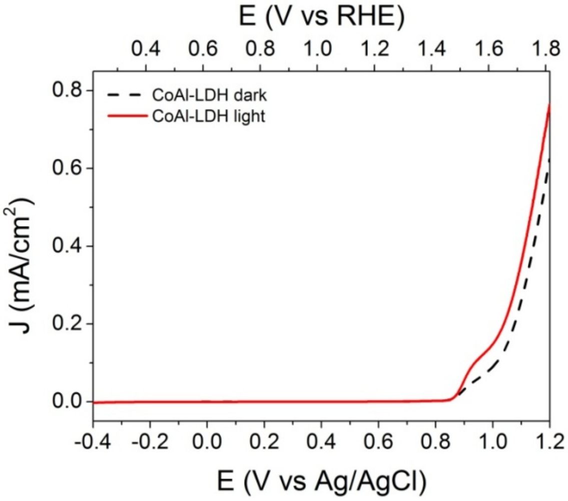

Fig. S8 Current-voltage curves of CoAl-LDH grown directly on FTO under illumination (solid line) and in the dark (dash line).

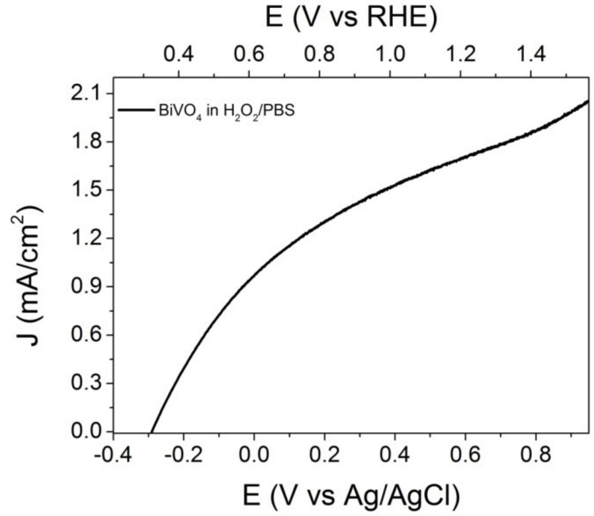

Fig. S9 Current-voltage curves of $BiVO_4$ under illumination in the presence of 0.1 M H_2O_2 as a hole scavenger in 0.1 M PBS electrolyte.

References

1. D. Kang, Y. Park, J. C. Hill and K.-S. Choi, *The Journal of Physical Chemistry Letters*, 2014, **5**, 2994-2999.
2. W. He, Y. Yang, L. Wang, J. Yang, X. Xiang, D. Yan and F. Li, *ChemSusChem*, 2015, **8**, 1568-1576.