**Supporting Information**

# Accurate modulation of NiS cocatalyst on photoelectron transfer sites of $BiVO_4$ for photocatalytic $H_2O_2$ generation

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**SI-1 Synthesis of $BiVO_4$ photocatalyst**

Typically, $NH_4VO_3$ (0.8422 g) and $Bi(NO_3)_3 \cdot 5H_2O$ (3.4925 g) precursor were respectively dissolved into 30 mL $HNO_3$ solution (2 mol $L^{-1}$) and mixed them homogeneously. Then, ammonia solution (28%) was added into the above solution by dropwise to adjust the pH of the solution (pH = 2.0) under vigorous stirring. After stirring for 0.5 h and aging for 2 h at room temperature, the resultant yellow suspension was carried out hydrothermal treatment in a 100 mL Teflon-lined autoclave at 180 $^oC$ for 24 h. After the reaction system was naturally cooled to room temperature, yellow powder was obtained by washing and drying at 60 $^oC$ overnight.

**SI-2 Characterization**

The morphology and microstructure of photocatalysts were observed by the field emission scanning electronic microscope (SEM) and high-resolution transmission electron microscopy (TEM). The crystal structure was revealed by X-ray diffraction (XRD) patterns using Cu Kα radiation. UV-visible diffuse reflectance spectra (UV-vis DRS) were obtained using a UV-2450 instrument (Shimadzu, Japan). The surface information was obtained using a KRATOA XSAM800 XPS system with Mg Kα source radiation. The adventitious carbon C 1*s* peak was set at 284.8 eV to calibrate all the binding energies. The transient photoluminescence spectra were recorded by a FLS920 fluorescence lifetime spectrophotometer (Edinburgh instruments, UK). The element analysis of the samples was performed by inductively coupled plasma emission spectrometry (ICP-OES, Agilent 730, America). Electron spin resonance (ESR) was measured by ESR spectrometer (A300, Bruker).

**SI-3 Photoelectrochemical measurements**

The photoelectrochemical measurements were carried out on a standard three-electrode configuration (CHI660E): platinum wire and Ag/AgCl are used as the counter and reference electrode, respectively. In addition, a sample-coated FTO conductor glass serves as the working electrode. The $Na_2SO_4$ solution (0.5 mol $L^{-1}$) functions as electrolyte. A 420-nm LED lamp (3 W, 20 mW $cm^{-2}$) was employed as the light source. Meanwhile, the prepared sample (10 mg) was dispersed into a mixing solution of ethanol (2.5 mL) and D-520 Nafion (2.5 mL) with ultrasonic treatment. Then, the obtained slurry was spread on the precleaned FTO glass and then dried at 40 $^oC$ for 24 h. The photocurrent responses (*i–t* curves) can be obtained at a +0.5 V bias potential during the repeated ON/OFF with a set time period of 60 s. Photoelectrochemical impedance spectroscopy (EIS) was measured in the frequency range of 0.001−$10^6$ Hz.

**SI-4 Photocatalytic performance of photodegradation**

Methyl orange (MO) aqueous solution is used as model pollutant molecule to further assess the photocatalytic performance of the synthetic NiS/$BiVO_4$ photocatalysts. Typically, the 80 mg of photocatalyst was dispersed into MO solution (20 mg $L^{-1}$) in a glass bottle. The above suspension was stirred under the dark for 1 h to obtain adsorption-desorption equilibrium. After visible-light irradiation for specific time interval, the supernatant of suspension was centrifuged to measure the concentration of MO by a UV-visible spectrophotometer. The photocatalytic degradation process of MO aqueous solution can be considered as a pseudo-first order reaction. In this case, the kinetic equation is expressed as $\ln(c_0/c) = kt$ ($c_0$ is the initial concentration of MO and

$c$ is the MO concentration after irradiation for $t$ min, $k$ is the apparent rate constant).

**SI-5 The calculation of AQE**

The apparent quantum efficiency (AQE) of the prepared photocatalyst is calculated via the following equation:

$$\mathrm{AQE}(\%) = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\%$$
$$= \frac{\text{number of evolved } H_2O_2 \text{ molecules} \times 2}{\text{number of incident photons}} \times 100\%$$

The power of the visible light (a 420 nm-LED lamp, 3 W) was 20 $mW \cdot cm^{-2}$. Hence, the AQE of the NiS/$BiVO_4$ photocatalyst can be calculated and shown in Table S3.

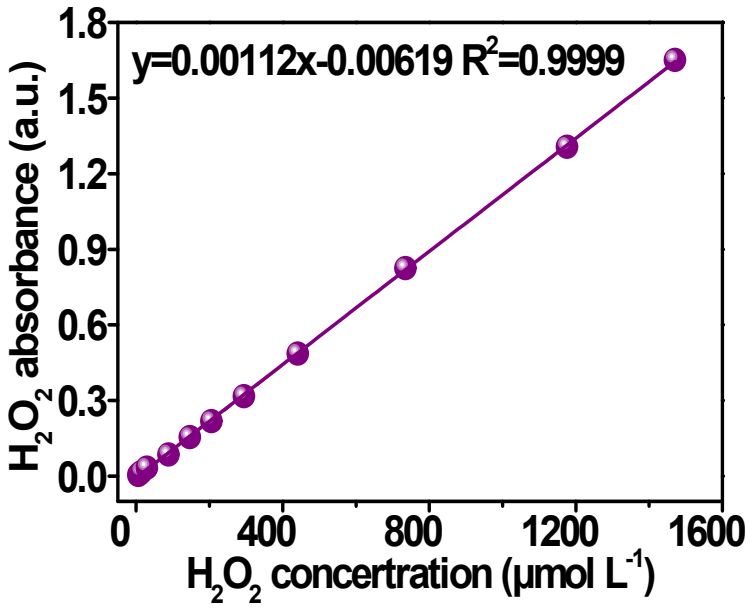


**Fig. S1.** $H_2O_2$ concentration-absorbance standard curve.

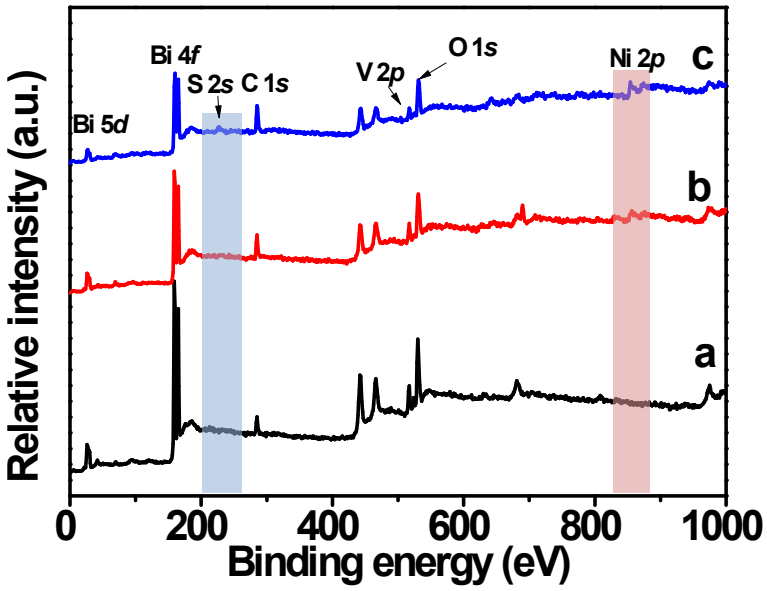


**Fig. S2.** Full-range XPS spectra for various samples: (a) $BiVO_4$, (b) 1 wt% NiS/$BiVO_4$ and (c) 10 wt% NiS/$BiVO_4$.

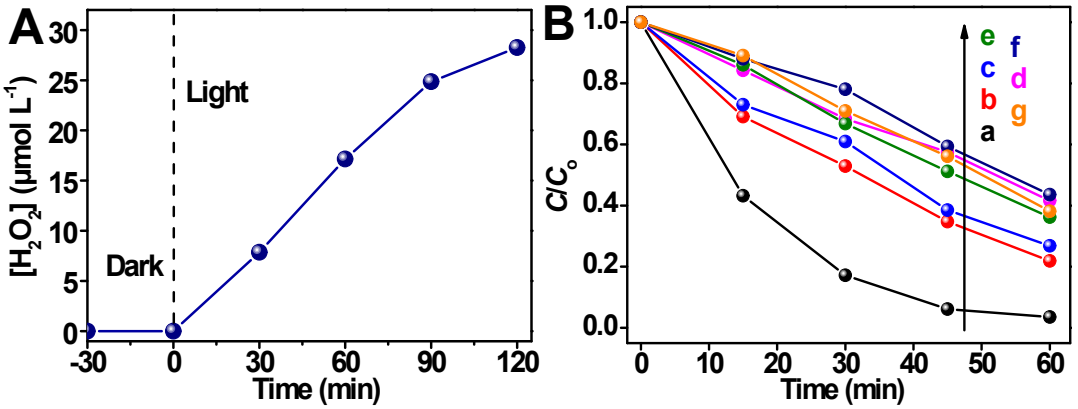


**Fig. S3.** (A) Photocatalytic $H_2O_2$-production activity of 10 wt% NiS/$BiVO_4$ photocatalyst in the pure water; (B) photocatalytic $H_2O_2$ decomposition ($C_0$ = 5 mmol $L^{-1}$): (a) $BiVO_4$, (b) 0.5 wt% NiS/$BiVO_4$, (c) 1 wt% NiS/$BiVO_4$, (d) 3 wt% NiS/$BiVO_4$, (e) 5 wt% NiS/$BiVO_4$, (f) 10 wt% NiS/$BiVO_4$ and (g) 20 wt% NiS/$BiVO_4$.

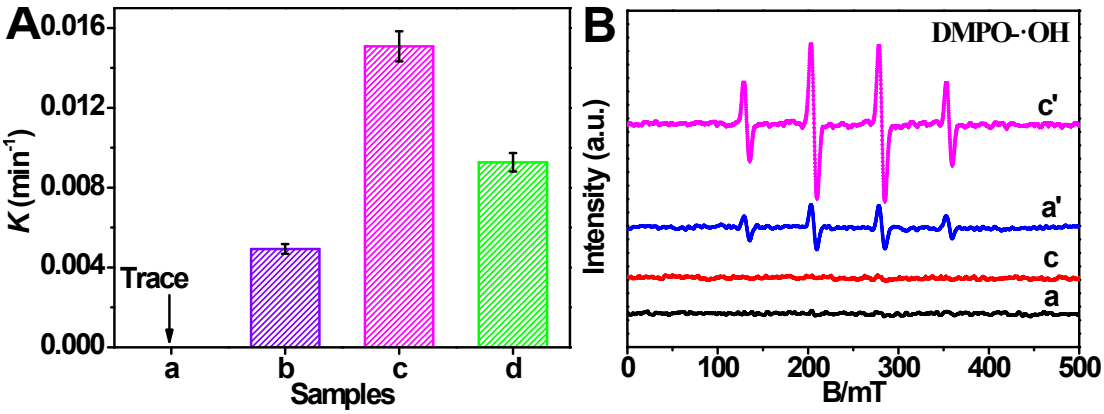


**Fig. S4.** (A) The rate constant (*k*) of MO decomposition and (B) ESR spectra of DMPO trapped ·OH radicals of various photocatalysts: (a) $BiVO_4$, (b) 1 wt% NiS/$BiVO_4$, (c) 10 wt% NiS/$BiVO_4$ and (d) 20 wt% NiS/$BiVO_4$ (a' and c'-light).

**Table S1** Element components (wt%) of various photocatalysts based on the ICP-OES results.

| Samples | Bi | V | O | Ni | S |
|---|---|---|---|---|---|
| $BiVO_4$ | 71.34 | 12.45 | 16.25 | — | — |
| 1 wt% NiS/$BiVO_4$ | 72.07 | 12.56 | 15.22 | 0.1 | 0.05 |
| 5 wt% NiS/$BiVO_4$ | 67.59 | 11.85 | 20.23 | 0.18 | 0.15 |

**Table S2** Element components (atom %) of various photocatalysts based on the XPS results.

| Samples | Bi | V | O | Ni | S |
|---|---|---|---|---|---|
| $BiVO_4$ | 18.08 | 11.94 | 69.98 | 0 | 0 |
| 1 wt% NiS/$BiVO_4$ | 9.52 | 7.35 | 73.39 | 6.89 | 2.85 |
| 10 wt% NiS/$BiVO_4$ | 10.92 | 10.07 | 62.81 | 10.98 | 5.22 |

**Table S3** Comparisons of $H_2O_2$ production for various photocatalysts.

| Photocatalysts | Maximum formed $H_2O_2$ ($\mu mol \cdot L^{-1}$) | AQE (%) | $H_2O_2$ formation rate ($\mu mol \cdot L^{-1} \cdot h^{-1}$) | $k_f$ ($\mu mol \cdot L^{-1} \cdot min^{-1}$) | $k_d$ ($min^{-1}$) |
|---|---|---|---|---|---|
| $BiVO_4$ | 11.25 | 0.055 | 5.63 | 0.2397 | 0.02761 |
| 0.5 wt% NiS/$BiVO_4$ | 41.07 | 0.20 | 20.53 | 0.7226 | 0.0157 |
| 1 wt% NiS/$BiVO_4$ | 60.71 | 0.30 | 30.36 | 1.3043 | 0.013 |
| 3 wt% NiS/$BiVO_4$ | 207.14 | 1.02 | 103.57 | 2.7952 | 0.0095 |
| 5 wt% NiS/$BiVO_4$ | 285.71 | 1.41 | 142.86 | 5.20 | 0.011 |
| 10 wt% NiS/$BiVO_4$ | 975 | 4.8 | 487.5 | 7.5474 | 0.0073 |
| 20 wt% NiS/$BiVO_4$ | 428.57 | 2.11 | 214.28 | 3.30 | 0.009 |

**Table S4** The fitted parameters obtained from decay curves of (a) $BiVO_4$ and (c) 10 wt% $NiS/BiVO_4$.

| Samples | $\tau_1$ (ns) | $A_1$ (%) | $\tau_2$ (ns) | $A_2$ (%) | Average lifetime ($\tau_a$) (ns) | $\chi^2$ |
|---|---|---|---|---|---|---|
| $BiVO_4$ | 0.16 | 72.98 | 2.94 | 27.02 | 2.58 | 2.696 |
| 10 wt% $NiS/BiVO_4$ | 0.16 | 71.49 | 3.09 | 28.51 | 2.75 | 2.564 |

The above fitted parameters are acquired via the following tri-exponential formulas:

$$\tau_a = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$$

where $A_1$ and $A_2$ represent the tri-exponential factors, and $\tau_1$, $\tau_2$ and $\tau_a$ corresponds to the lifetime in various stages (radiation and non-radiation) and average lifetime, respectively. $\chi^2$ is the goodness-of-fit.