## ESI

## Bimetallic phosphide decorated Mo-BiVO<sub>4</sub> for significantly improved photoelectrochemical activity and stability

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**Table S1.** The dissolved amount of V and Bi in the used electrolyte after stability testing for three kinds of films.

Samples	The dissolved amount of Bi (mg/L)	The dissolved amount of V (mg/L)
BiVO <sub>4</sub>	0.36996	0.67617
Mo-BiVO <sub>4</sub>	0.33365	0.62050
NiCoP/Mo-BiVO <sub>4</sub>	0.24561	0.24907



**Fig. S1.** J-V curves recorded under AM 1.5G illumination (a), EIS in Nyquist plots measured at 0.9 V *vs.* RHE under AM 1.5G illumination (b) and IPCE spectra measured at 1.23 V *vs.* RHE (c) for optimizing the amount of NiCoP decorated on Mo-BiVO<sub>4</sub>. The sample of 2 mg/mL NiCoP shows the best PEC activity among all samples. Therefore, it is chosen as the optimal decoration amount (corresponding to ca. 2% NiCoP decorated on Mo-BiVO<sub>4</sub>).



**Fig. S2.** J-V curves measured without (a) and with (b) AM 1.5G illumination for sulfite oxidation (with 0.1 M Na<sub>2</sub>SO<sub>3</sub>) of pure BiVO<sub>4</sub>, Mo-BiVO<sub>4</sub> and NiCoP/Mo-BiVO<sub>4</sub> photoanodes. (c) Charge separation efficiency and charge injection efficiency (d).

To exclude the influence of the sulfite oxidation kinetics on the surface of different samples, J-V measurements for sulfite oxidation without light illumination for the prepared photoanodes are carried out, and the results shows that there is no obvious distinction of the onset potential among pure BiVO<sub>4</sub>, Mo-BiVO<sub>4</sub> and NiCoP/Mo-BiVO<sub>4</sub> samples, revealing that all photoanodes present very slow sulfite oxidation kinetics. Under AM 1.5G illumination, the photocurrent density of pure BiVO<sub>4</sub> is 3.11 mA/cm<sup>2</sup>, while Mo-BiVO<sub>4</sub> and NiCoP/Mo-BiVO<sub>4</sub> photoanode display the photocurrent density of 4.30 mA/cm<sup>2</sup> and 4.55 mA/cm<sup>2</sup>, respectively.

The calculation of surface charge injection and separation efficiency was according to the following equation:

$$\eta_{\rm inj} = J_{H_2O} / J_{Na_2SO_3}$$

$$\eta_{\rm sep} = J_{Na_2SO_3}/J_{abs}$$

where  $\eta_{inj}$  is the surface charge injection efficiency of the semiconductor,  $\eta_{sep}$  is the charge separation efficiency,  $J_{H_2O}$  is the photocurrent density for water oxidation acquired in Na<sub>2</sub>SO<sub>4</sub> solution,  $J_{Na_2SO_3}$  is the photocurrent density for sulfite oxidation acquired with the presence of 0.1 M Na<sub>2</sub>SO<sub>3</sub> in the Na<sub>2</sub>SO<sub>4</sub> solution, and  $J_{abs}$  is the theoretical photocurrent density assuming that the absorbed irradiation was completely converted.



**Fig. S3.** XRD patterns (a) before and after PEC stability test of NiCoP/Mo-BiVO<sub>4</sub> and SEM images (b) of NiCoP/Mo-BiVO<sub>4</sub> after PEC stability test.