

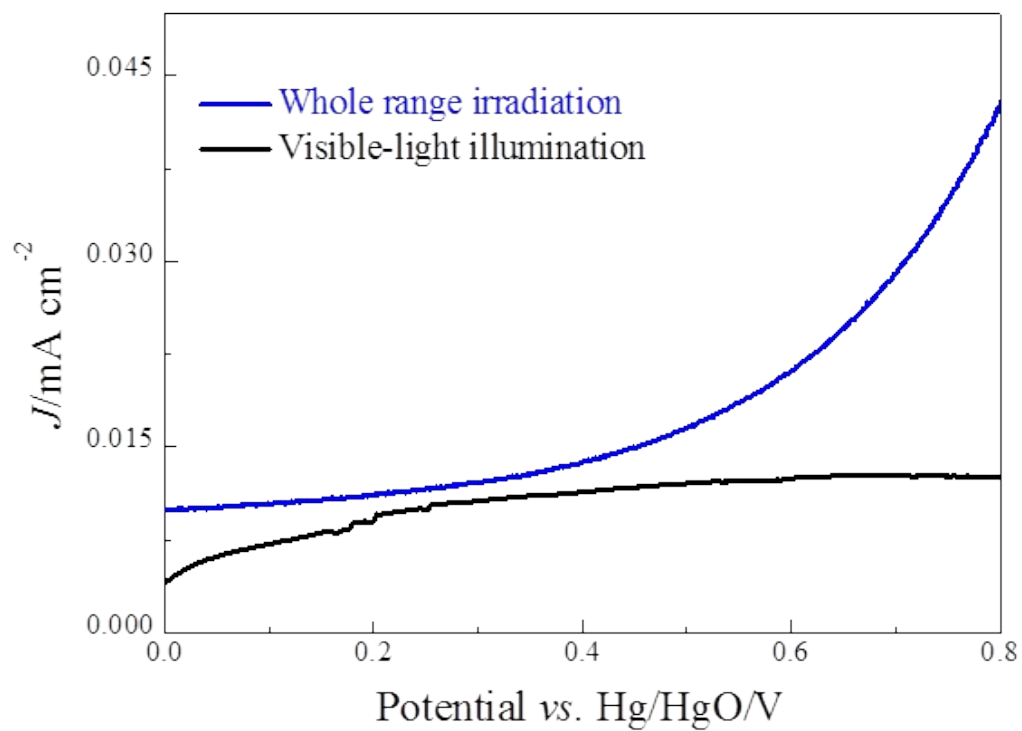
## *Supporting Information*

# **Removal of SO<sub>2</sub> on a Nanoporous Photoelectrode with Simultaneous H<sub>2</sub> Production**

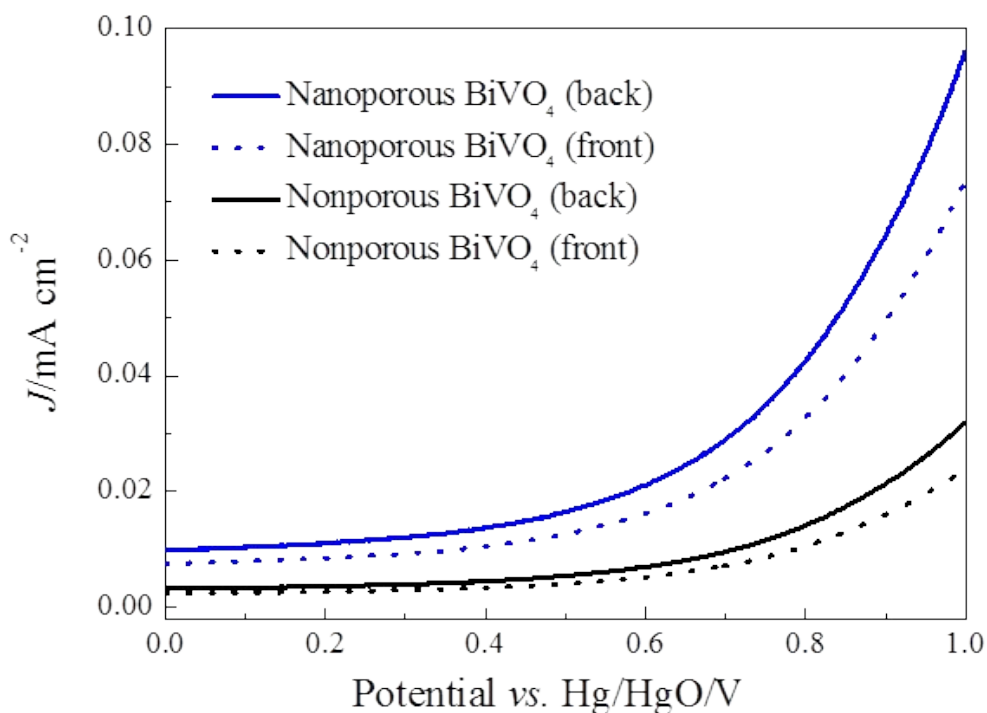
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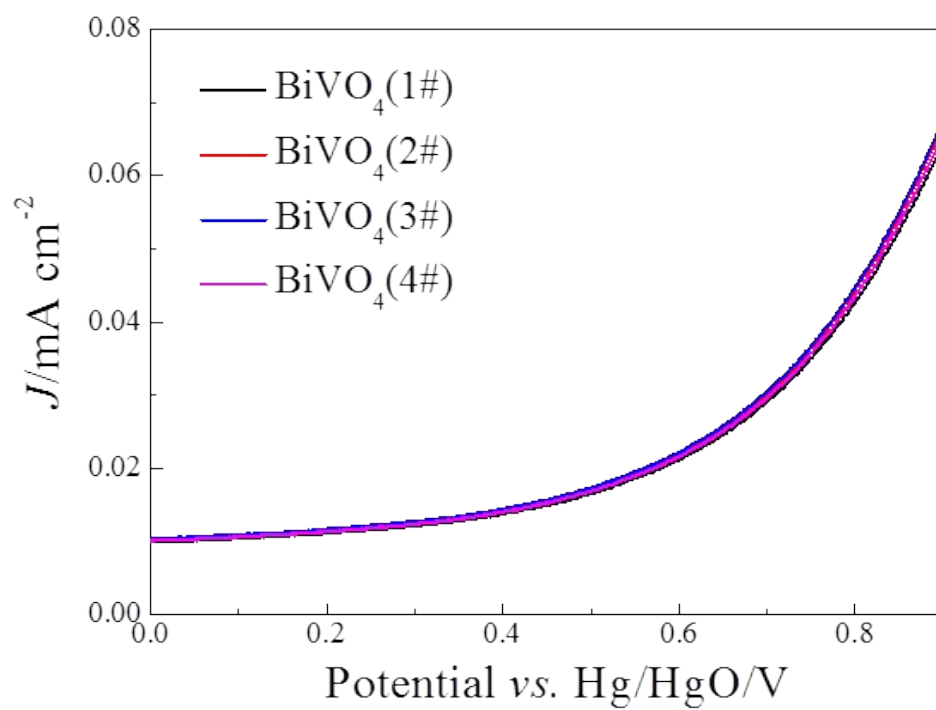


**Fig. S1**  $J$ - $V$  curves of porous  $\text{BiVO}_4$  in  $\text{NaOH}$  (aq) under visible-light illumination and whole range irradiation.

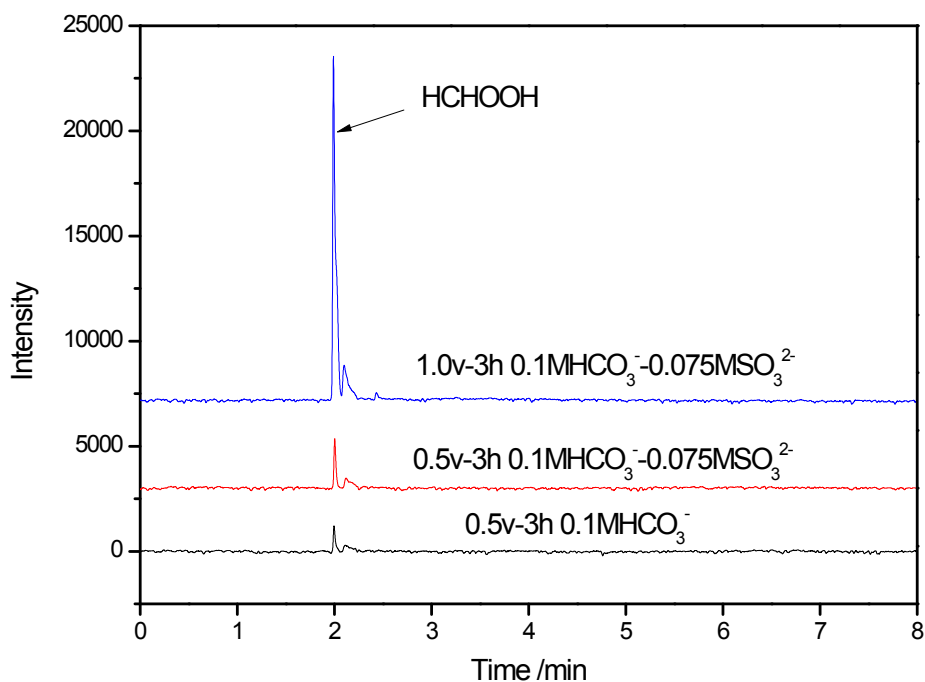


**Fig. S2**  $J$ - $V$  curves of porous BiVO<sub>4</sub> and nonporous one from back side and film side separately in NaOH(aq).

As shown in Fig. S2, for all these electrodes, back-side illumination produces higher photocurrent than front-side illumination, which has been reported to be related to the poor electron transport in BiVO<sub>4</sub> (J. Phys. Chem. C 115, 17594 - 17598 (2011)). In BiVO<sub>4</sub>, the BiVO<sub>4</sub> crystal is composed of non-interconnecting VO<sub>4</sub> tetrahedra. The conduction band of BiVO<sub>4</sub> consists mainly of V 3d orbitals, consequently, the photogenerated electrons have to hop between VO<sub>4</sub> tetrahedra in BiVO<sub>4</sub>. In the PEC cell, the photogenerated electrons need to travel from the place generated to the FTO conductive substrate. Under backside illumination most electrons are generated close to the FTO substrate, the required diffuse length is thus shorter than for front side illumination.



**Fig. S3**  $J$ - $V$  curves of porous BiVO<sub>4</sub> in NaOH(aq) (4 different samples prepared under same condition).



**Fig. S4** The liquid phase analysis of the product by GC.

It is shown that CO<sub>2</sub> is reduced to HCHOOH, if there is a high amount of CO<sub>2</sub> in the flue gas. However, the SO<sub>2</sub> removal rate is still higher than 97%. Only the H<sub>2</sub> production is decreased due to the consumption of electrons for CO<sub>2</sub> reduction. This result also shows that the current PEC process may also be promising for a simultaneous removal of SO<sub>2</sub> and CO<sub>2</sub>. Another research work on simultaneous removal of SO<sub>2</sub> and reduction of CO<sub>2</sub> is underway in our lab, which is not the research focus in this work.