

## Supporting information

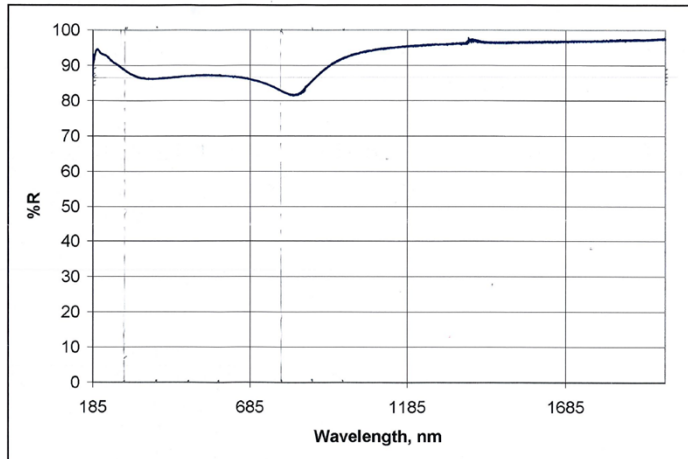
# Improving BiVO<sub>4</sub> photoanodes for solar water splitting through surface passivation

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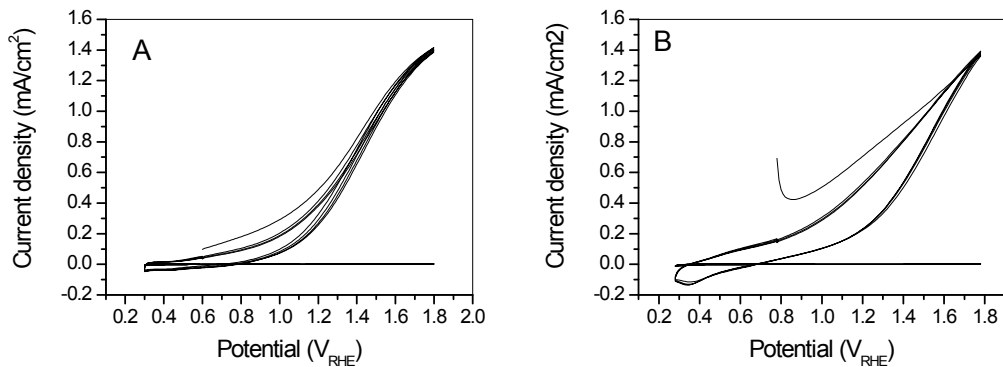
**1. The mirror will only cause a distortion (enriching of the NIR part) of the simulated sunlight spectrum.**



**Figure S1.** The reflection spectrum of the UV-enhanced mirror, which is used for flipping the simulated sunlight. (model PAUV-PM-5010M-C, provided by Melles Griot)

Compared with the AM1.5 sunlight, the actual light hitting  $\text{BiVO}_4$  is slightly enriched by the NIR photons due to the high reflectance in NIR region for the mirror. The net result is ~10% less photons (wavelength between 300 nm and 600 nm) will be available. Since  $\text{BiVO}_4$  can not absorb the NIR light (>800nm), a slightly smaller photocurrent for  $\text{BiVO}_4$  photoelectrodes than that under a real AM1.5 sunlight.

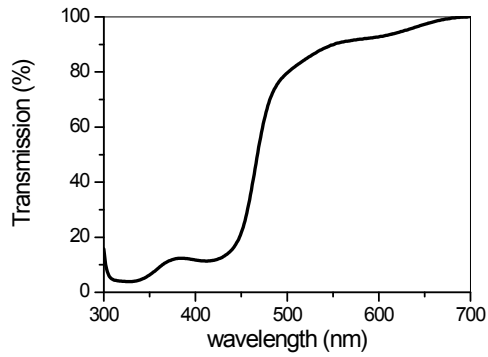
**2. Without loading the NiO<sub>x</sub>, the characterization of BiVO<sub>4</sub> films either in phosphate or in borate electrolyte does not passivate the electrode.**



**Figure S2.** (A) CVs of an as-prepared BiVO<sub>4</sub> film electrode in 0.2M NaPi. (B) CVs of an the same BiVO<sub>4</sub> film electrode in 0.2M NaBi. Bothe the dark current and photocurrent under white light illumination are shown.

Figure S2 shows that exposure of BiVO<sub>4</sub> to the phosphate electrolyte or borate electrolyte will give very repeatable *low* photocurrent during 4 cycles of electrochemical sweeping between 0.3V<sub>RHE</sub> and 1.8V<sub>RHE</sub>. The anomalies in current during the 1<sup>st</sup> CV cycle are due to the fact that the starting potential is not from the open circuit potential.

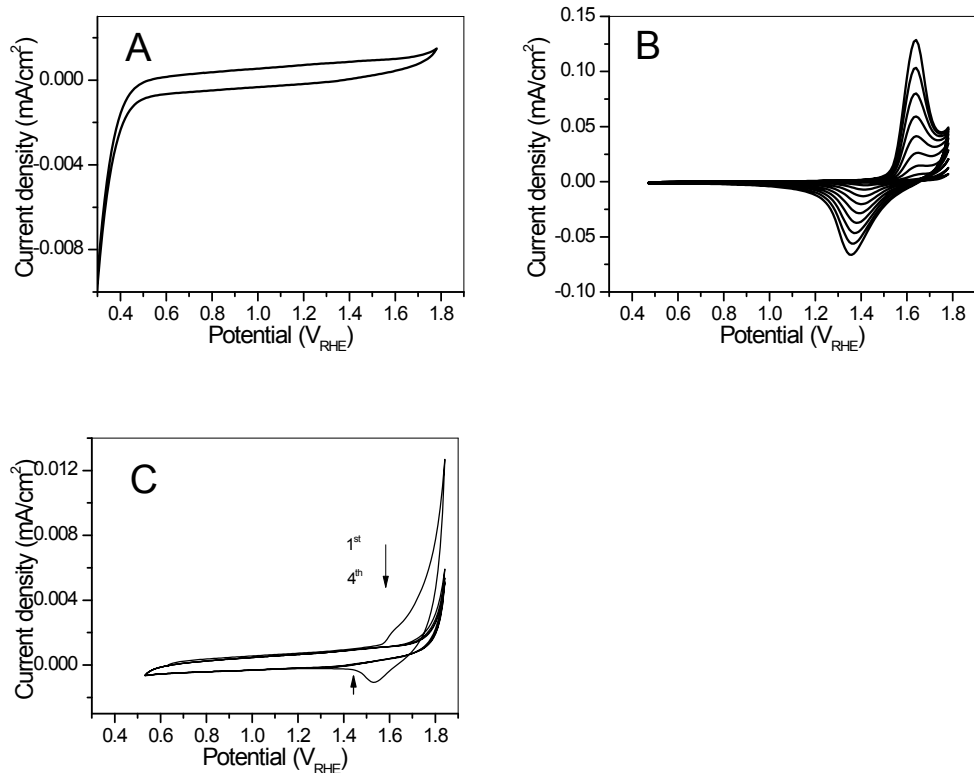
**3. The  $\text{BiVO}_4$  film only absorbs ~90% of the photons of wavelength from 300 nm to 600 nm.**



**Figure S3.** The light absorption spectrum of the  $\text{BiVO}_4$  film electrode.

The  $\text{BiVO}_4$  film only absorbs ~90% of the photons at the plateau of the UV-vis absorption spectrum. This will cause the measured photocurrent lower than the value if all the photons can be absorbed by the film electrodes.

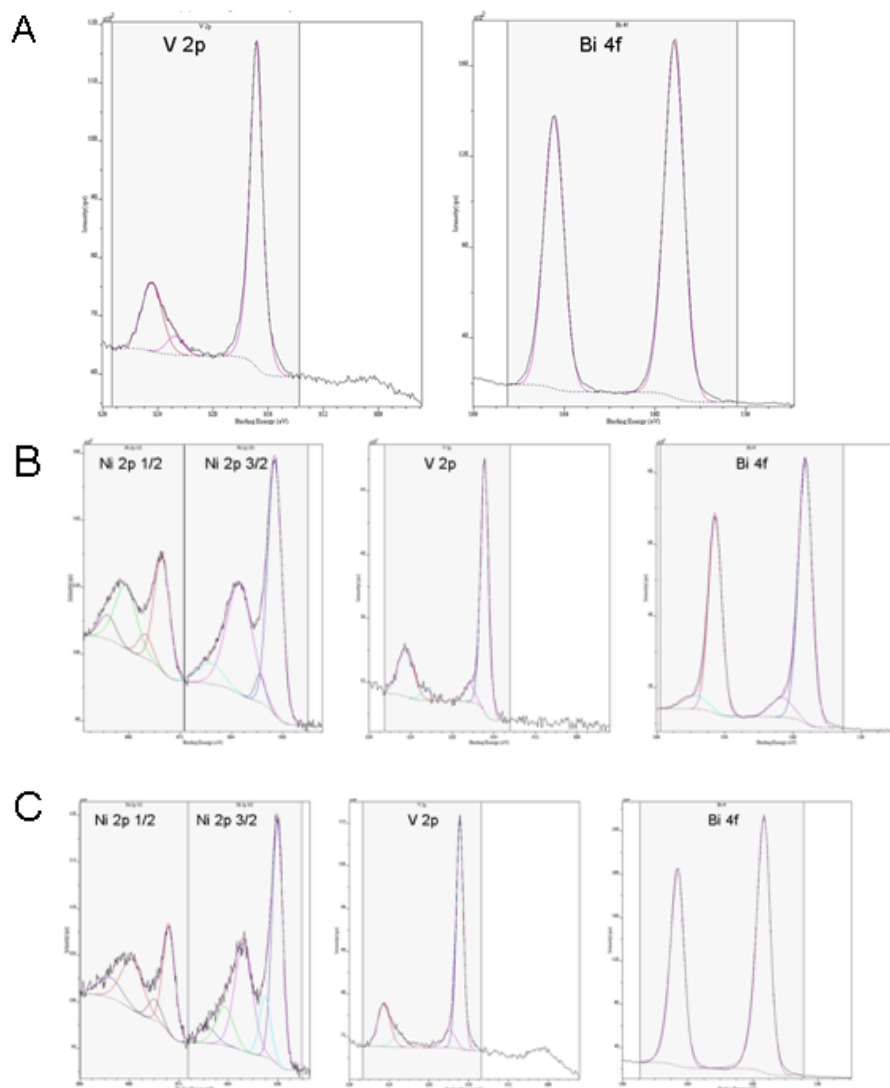
**4. The control experiments demonstrate that the NiO<sub>x</sub> films on FTO can be removed in phosphate electrolyte.**



**Figure S4.** (A) CV of blank FTO substrate in NaB<sub>7</sub> electrolyte. (B) the CV for loading of NiO<sub>x</sub> onto FTO substrate in Ni<sup>2+</sup> containing NaB<sub>7</sub> electrolyte. (C) CV for the removal of NiO<sub>x</sub> from FTO substrate in NaP<sub>7</sub> electrolyte

From Figure S4, it can be clearly seen that NiO<sub>x</sub> can be loaded in borate buffered electrolyte, and can be removed in phosphate containing electrolyte.

## 5. XPS spectra for composition analysis of the elements on the surface



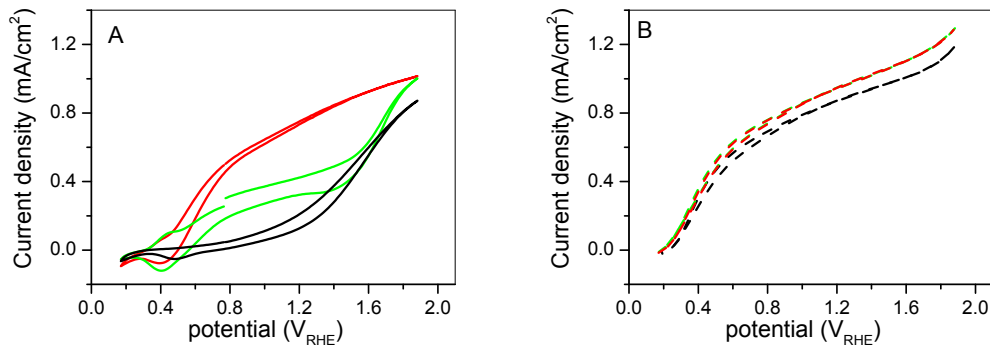
**Figure S5.** (A) XPS spectra of the Bi V for as-prepared  $\text{BiVO}_4$  electrode, (B) XPS spectra of Ni, Bi and V for the  $\text{BiVO}_4$  film right after  $\text{NiO}_x$  loading, (C) XPS spectra of Ni, Bi and V for the  $\text{BiVO}_4$  film right after treating  $\text{NiO}_x$ -loaded film in phosphate electrolyte. The spectra are fitted and the composition is quantified and summarized in Table 1 in the main text.

## 6. The photocurrent from BiVO<sub>4</sub> is not due to the photoetching of BiVO<sub>4</sub>

For a BiVO<sub>4</sub> film (100nm thick) working at ~1 mA/cm<sup>2</sup> for 20min, a rough estimation shows that the electrons pass through will be ~8.1 time the amount of Oxygen from BiVO<sub>4</sub>. This safely excludes the possibility that the photocurrent (~1.5 mA/cm<sup>2</sup> for ~1h) shown in the maintext can be due to the photoetching of BiVO<sub>4</sub>.

$$\frac{N_{electron}}{N_{oxygen} \times 2} = \frac{\frac{1mA/cm^2 * 1200seconds}{96485}}{\frac{100 * 10^{-7} cm * 6.2g/cm^2}{209 + 50.9 + 64} \times 4 \times 2} = 8.1$$

## 7. sulfite adding significantly increases the photocurrents by increasing the hole transfer rate, and makes the passivation effect less-observable for BiVO<sub>4</sub> photoelectrode



**Figure S7.** CVs under the AM 1.5 illumination for another BiVO<sub>4</sub> electrode treated at different stages, (black) as-prepared BiVO<sub>4</sub> film, (green) BiVO<sub>4</sub> film after electrochemical loading of NiO<sub>x</sub>, and (red) BiVO<sub>4</sub> film after removal of NiO<sub>x</sub> OER center. (A) in 0.2M NaBi, (B) in 0.1M NaBi + 0.05M Na<sub>2</sub>SO<sub>3</sub>.

After adding sulfite, there is only a minor change after NiO<sub>x</sub> loading and no observable change when NiO<sub>x</sub> OER center is removed (Figure S7B). It can be clearly seen that sulfite adding significantly increases the photocurrent, which is a result of the increased hole transfer rate. The hole transfer process get so much facilitated for sulfite containing electrolyte that the effect resulted from passivation (after removal of NiO<sub>x</sub> OER center) is almost not observable.