Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Solar Water Oxidation Using Nickel-Borate Coupled $BiVO_4$ Photoelectrodes

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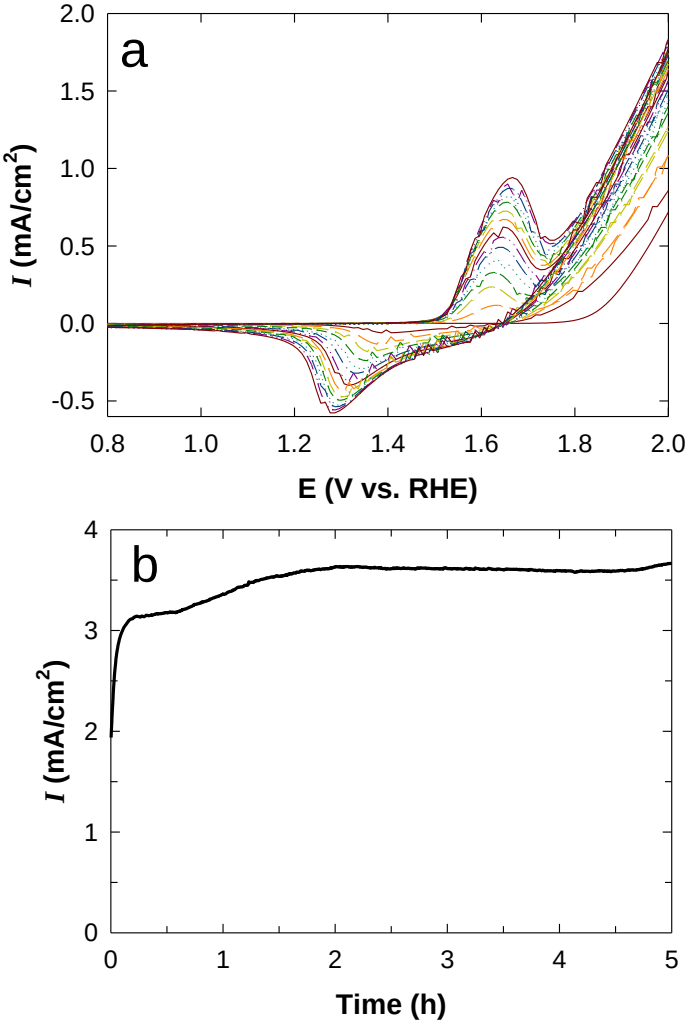

Figure S1. Electrodeposition processes of Ni-Bi on FTO by (a) cyclic potential sweep and (b) constant current techniques (at 1.984 V vs. RHE).

For the electrodeposition of Ni-Bi, we applied 1.2 V_{SCE} (1.984 V_{RHE}) to either FTO glass or FTO/$BiVO_4$. As long as substrates are conductive enough at this potential, Ni-Bi can be electrodeposited on them. For example, the (dark) anodic currents of FTO and FTO/$BiVO_4$ electrodes flow from at ~1.8 V_{RHE} (Fig. S1 and 1, respectively), enabling Ni-Bi deposition. Ni-Bi can be deposited directly on the FTO surface of FTO/$BiVO_4$ because $BiVO_4$ is rather porous (Fig. 4b). However, $BiVO_4$ is quite thick (~ 550 nm; yet conductive) and Ni-Bi is located only on the $BiVO_4$ top layer (Fig. 4c & e). It is of note that Ni-Bi deposition proceeds quickly (within a few seconds) while diffusion of Ni^{2+} and borate into the pores between $BiVO_4$ particles may take longer time. If a sufficient diffusion time is given, Ni-Bi can be formed on the FTO surface of FTO/$BiVO_4$ (through pinholes).

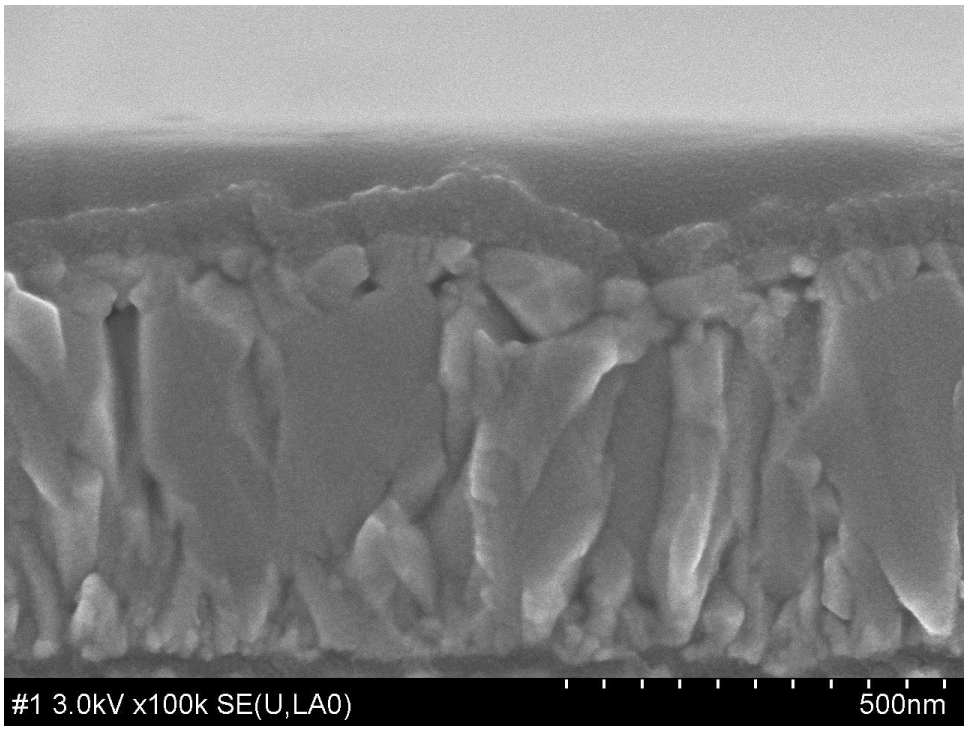

Figure S2. FE-SEM image of $BiVO_4$/Ni-Bi (PD-1 h) film. It is apparent that Ni-Bi is ~ 60 nm thick.

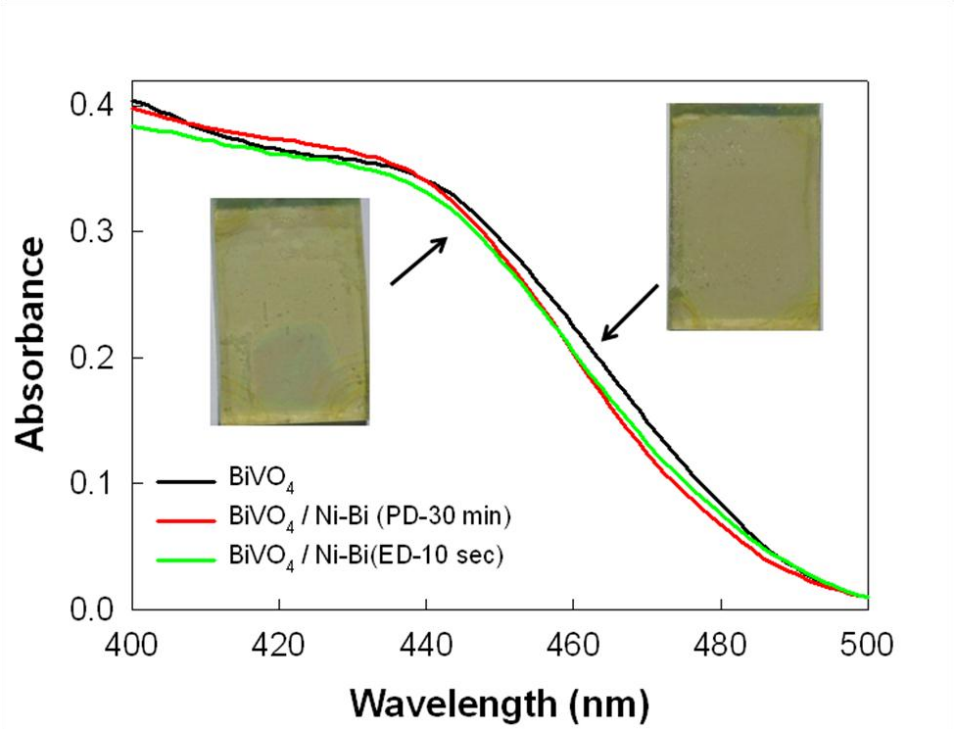

Figure S3. UV-Vis absorption spectra of bare $BiVO_4$, Ni-Bi photodeposited $BiVO_4$ electrode for 30 min (PD-30 min), and electrodeposited $BiVO_4$ electrode for 10 sec (ED-10 sec). Inset: photograph of $BiVO_4$ and $BiVO_4$/Ni-Bi (PD-30 min).

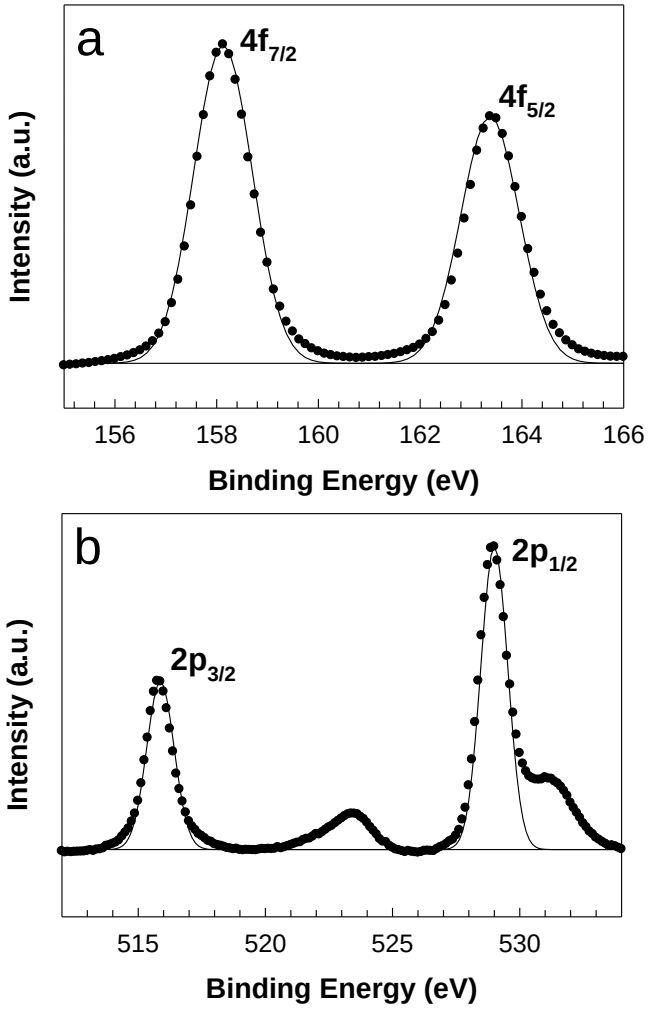

Figure S4. XPS spectra of (a) Bi 4f and (b) V 2p for $BiVO_4$.

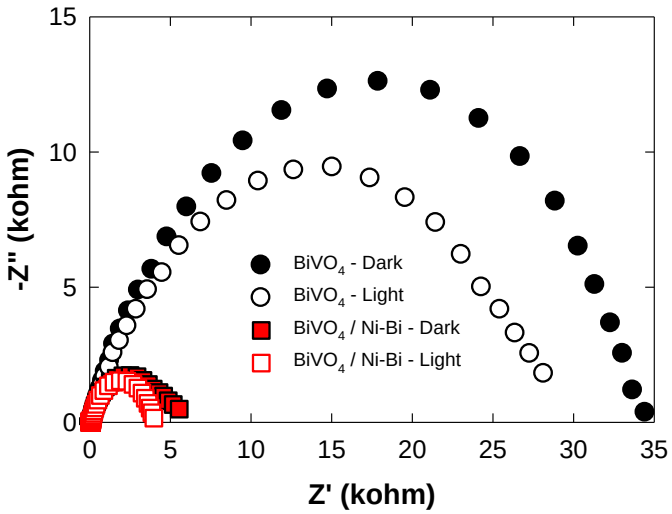

Figure S5. Impedance analysis (Nyquist plots) for $BiVO_4$ and $BiVO_4$/Ni-Bi (PD-30 min) electrodes in 0.1 M borate solution (pH 9.2) in the dark and under AM 1.5-irradiation.

For the impedance analysis (Nyquist plots), alternating current (AC) impedance measurements were carried out through application of a bias potential of + 0.484 V vs. RHE in 0.1 M borate solution with a frequency range of 10 MHz to 0.01 Hz and an AC voltage of 10 mV rms (Garmy Instruments) in the dark and under an AM 1.5-light.

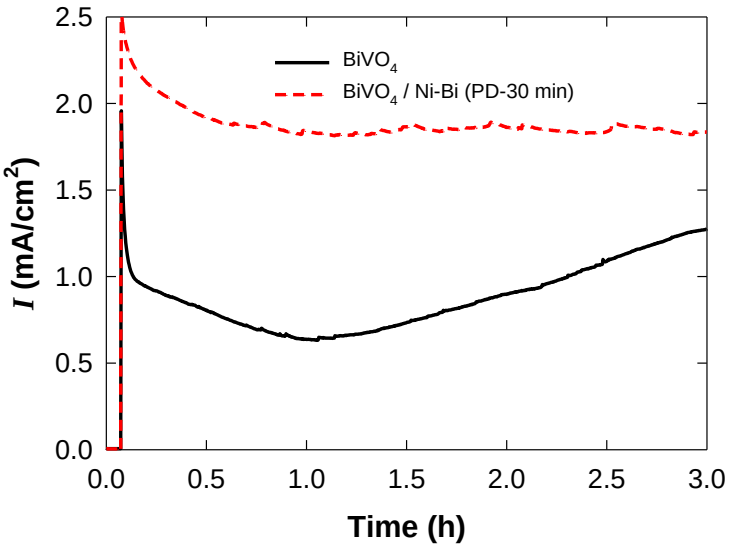

Figure S6. Time-profiled photocurrent flows generated during oxygen evolution tests. AM 1.5-light of 400 mW/cm^2 (4 Sun) was irradiated to bare and Ni-Bi deposited $BiVO_4$ electrodes at 1.23 V vs. RHE in 0.1 M borate electrolyte (pH 9.2).

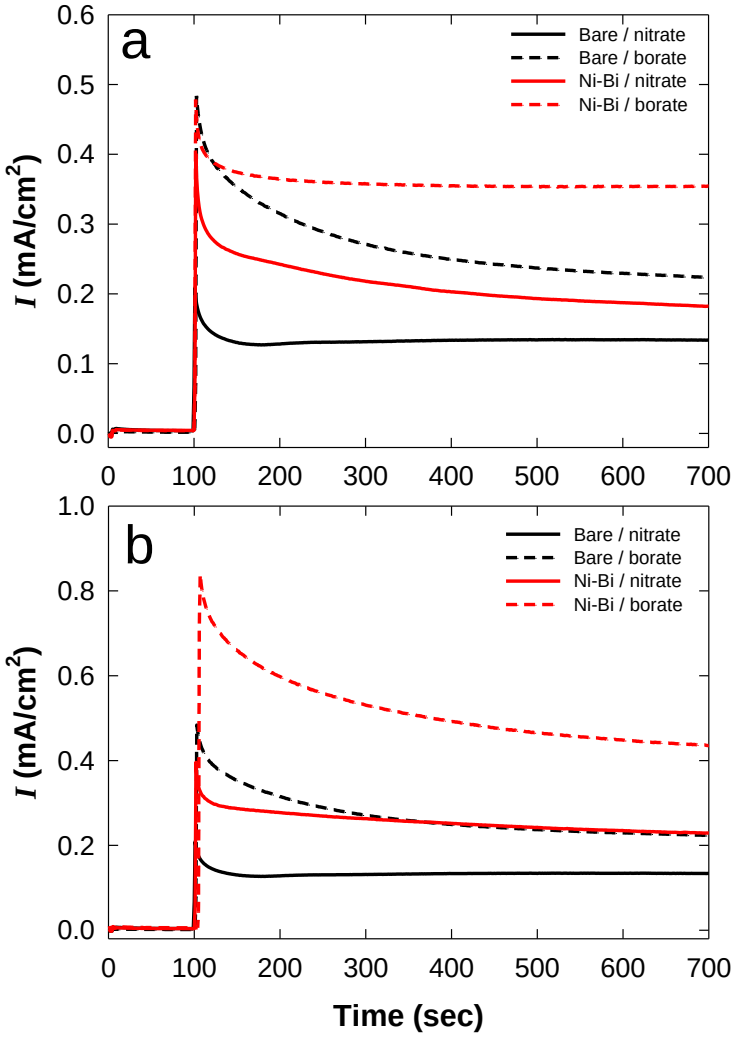

Figure S7. Time-profiled photocurrent flows generated at (a) $BiVO_4$/Ni-Bi (ED-10 sec) and (b) $BiVO_4$/Ni-Bi (PD-30 min) in 0.1 M nitrate (pH 9.2) or 0.1 M borate electrolytes (pH 9.2). E = 1.23 V vs. RHE; AM 1.5-light (100 mW/cm^2).