Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary information for

Reinforcement of a $BiVO_4$ anode by an Fe_2O_3 underlayer for photoelectrochemical water splitting

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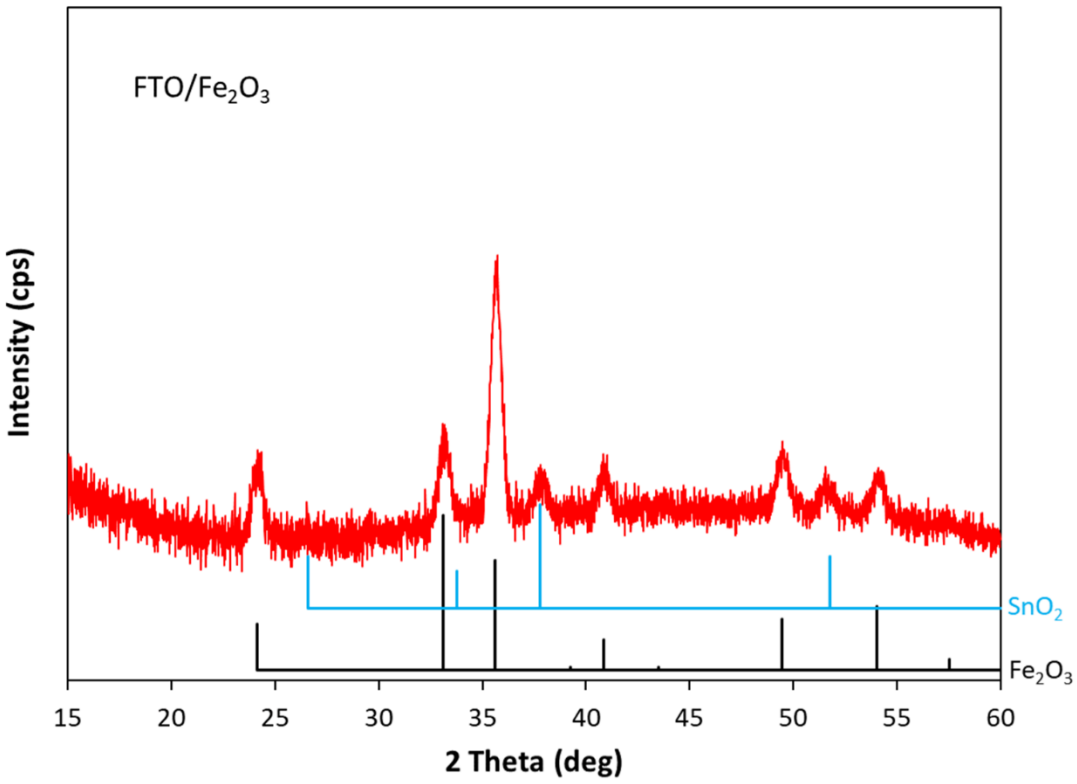


Fig. S1. XRD patterns of FTO/Fe_2O_3, reference α-hematite (JCPDS No. 01-076-8403), and reference tin oxide (JCPDS No. 00-046-1088). Data collected using a Rigaku (SmartLab) X-ray diffractometer. X-ray incident angle at 1° with Cu Kα1 (using 45 kV and 200 mA, λ = 1.540619 Å) radiation.

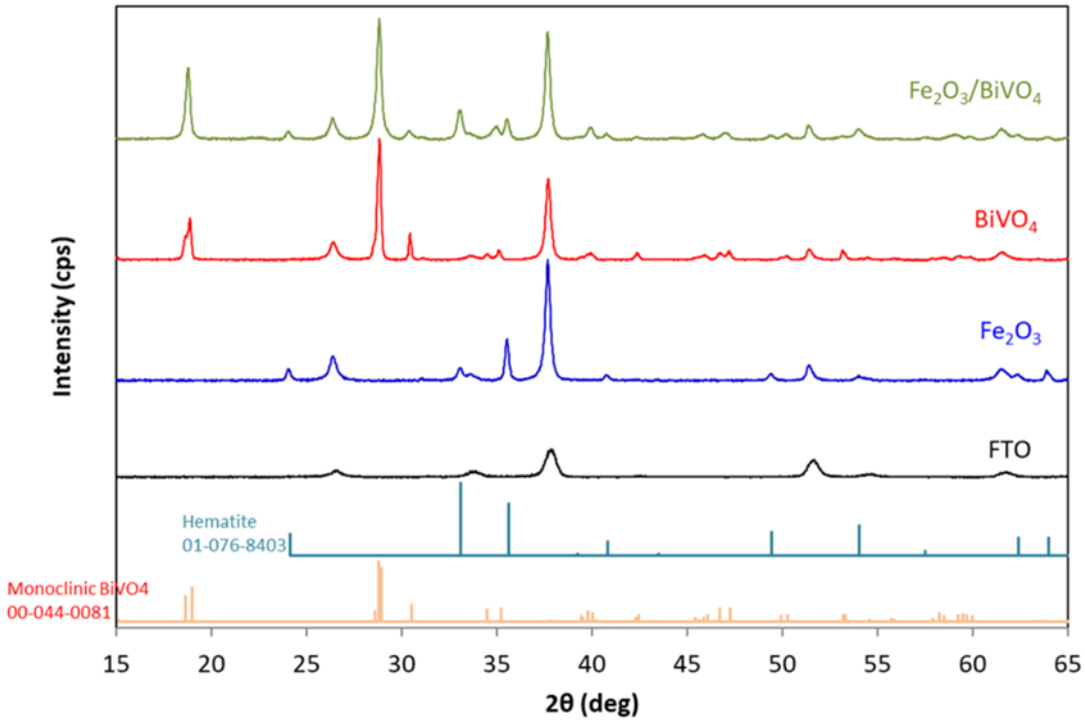


Fig. S2. XRD patterns (from top to bottom) of FTO/Fe_2O_3/$BiVO_4$, FTO/$BiVO_4$, FTO/Fe_2O_3, FTO substrate, reference α-hematite (JCPDS No. 01-076-8403), and reference scheelite-structured monoclinic $BiVO_4$ (JCPDS No. 00-044-0081). Data collected using a Rigaku (MiniFlex 600) X-ray diffractometer.

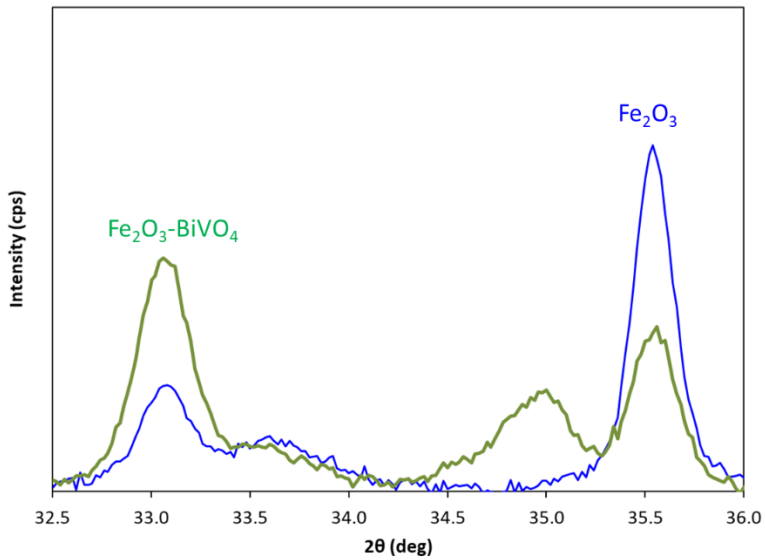
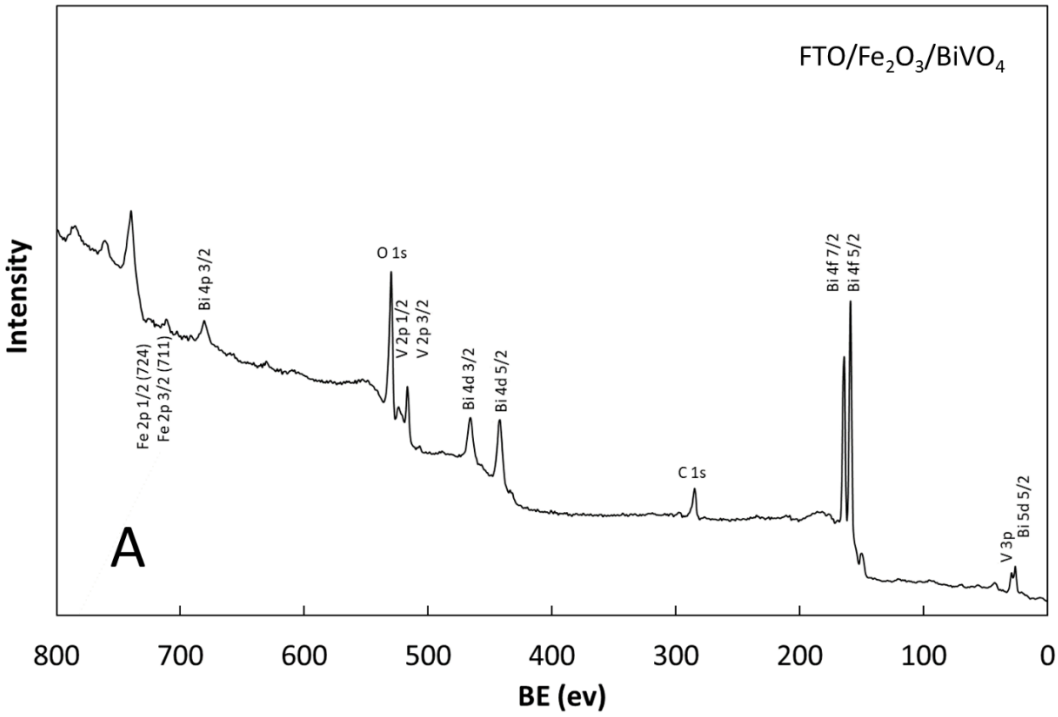
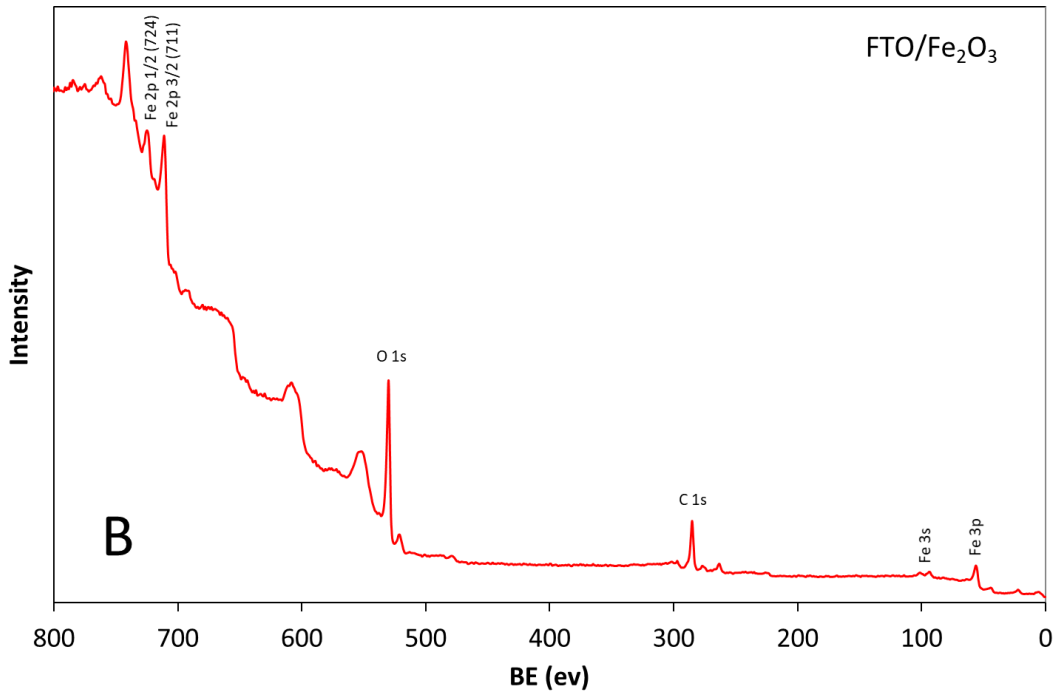


Fig. S3. Partially enlarged XRD patterns of the FTO/Fe_2O_3 film (blue line) and the FTO/Fe_2O_3/$BiVO_4$ film (green line).


FTO/Fe2O3/BiVO4
Intensity
Fe 2p 1/2 (724)
Fe 2p 3/2 (711)
Bi 4p 3/2
O 1s
V 2p 1/2
V 2p 3/2
Bi 4d 3/2
Bi 4d 5/2
C 1s
Bi 4f 7/2
Bi 4f 5/2
V 3p
Bi 5d 5/2
A
800
700
600
500
400
300
200
100
0
BE (ev)


FTO/Fe2O3
Intensity
Fe 2p 1/2 (724)
Fe 2p 3/2 (711)
O 1s
C 1s
Fe 3s
Fe 3p
B
800
700
600
500
400
300
200
100
0
BE (ev)

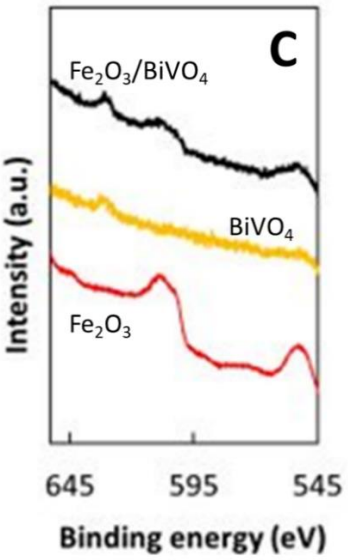


Fig. S4. X-ray photoelectron spectroscopy (XPS) spectra of (A) FTO/Fe_2O_3/$BiVO_4$ film and (B) FTO/Fe_2O_3 film. (C) the figure shows the XPS analysis of the LMM (Mg Kα) peaks of Fe_2O_3. XPS data were collected using a JEOL (JPS-9010MC) X-ray photoelectron spectrometer under ultrahigh vacuum using a monochromatic Mg Kα X-ray source, with 25 scans for each element. The adventitious carbon 1s peak was calibrated to 284.5 eV and used as an internal standard to compensate for any charging effects.

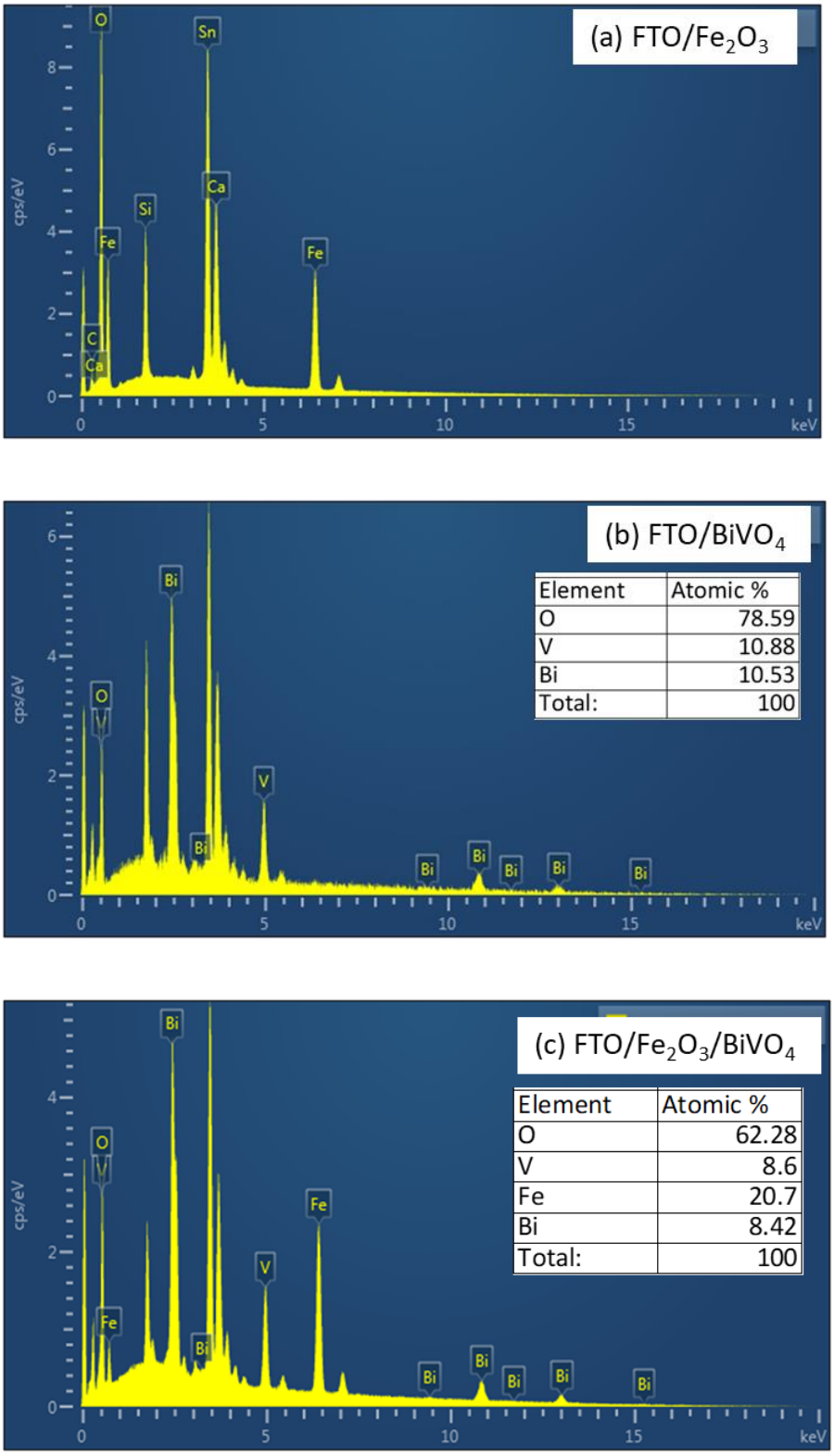


Fig. S5. The energy dispersive X-ray spectroscopy (EDS) elemental spectra of (a) FTO/Fe_2O_3 film, (b) FTO/$BiVO_4$ film, and (c) FTO/Fe_2O_3/$BiVO_4$ film.

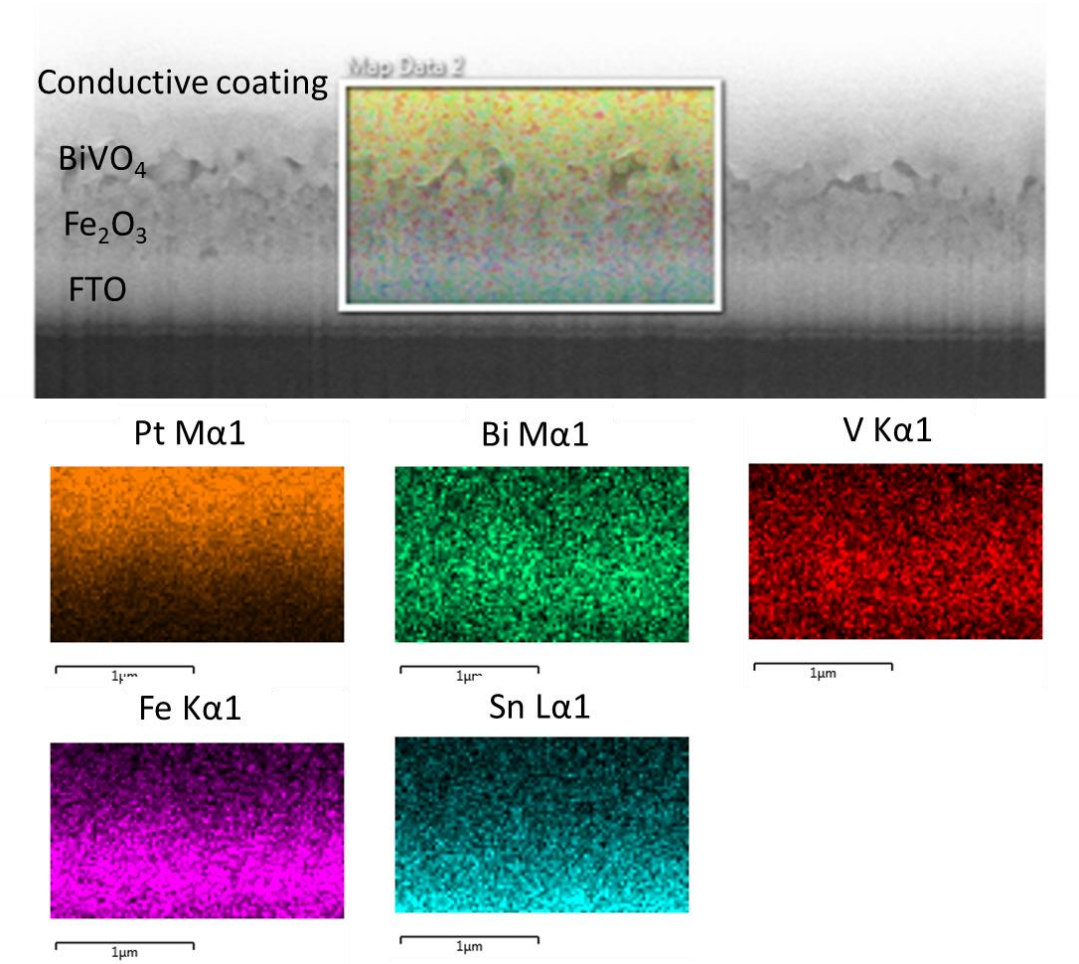


Fig. S6. EDS mapping of cross-sectional image of the $FTO/Fe_2O_3/BiVO_4$ film. EDS elemental analysis using an FIB-SEM. Platinum (Pt) is the conductive coating for the FIB-SEM measurement.

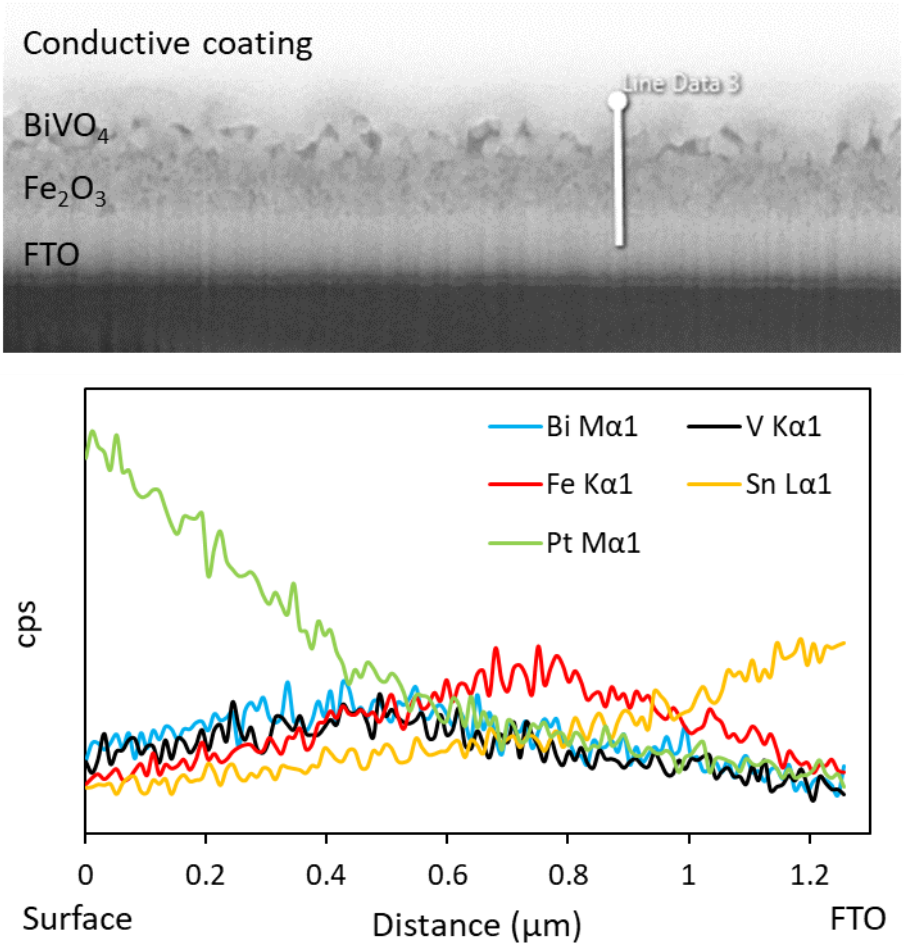


Fig. S7. EDS elemental line analysis of cross-sectional image of the FTO/Fe_2O_3/$BiVO_4$ film.

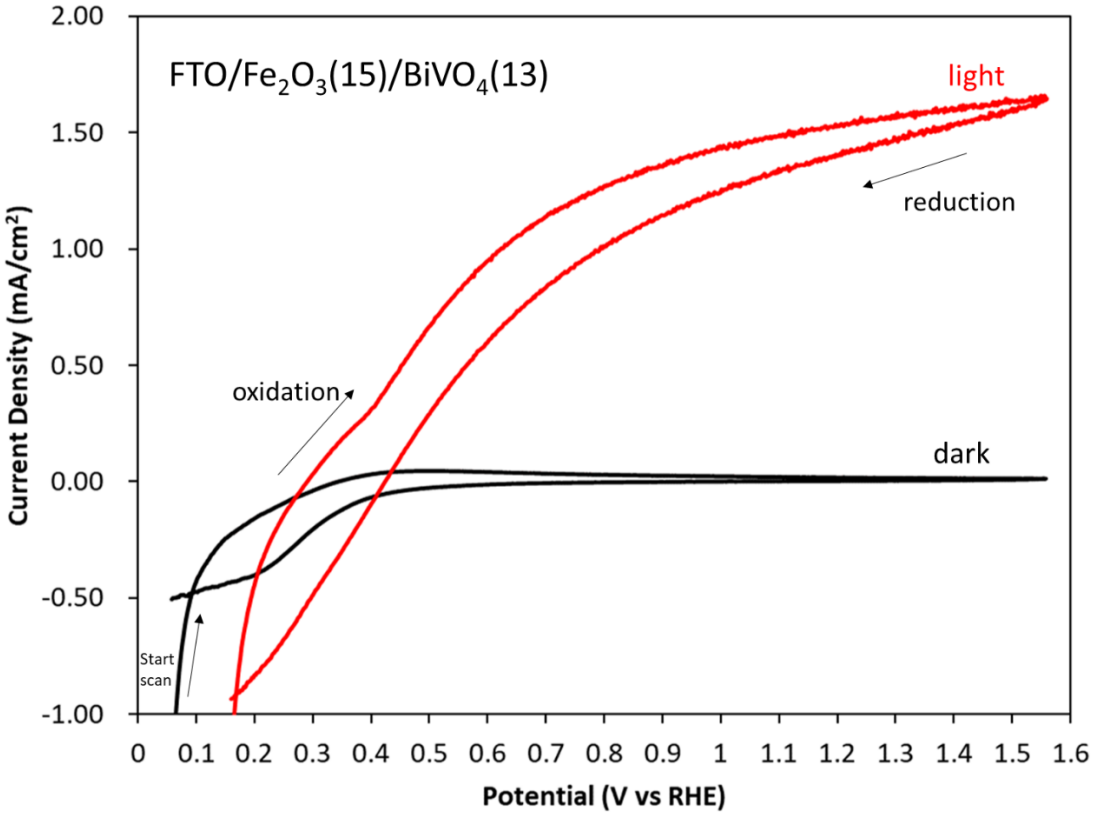


Fig. S8. CV curves of the FTO/Fe_2O_3(15)/$BiVO_4$(13) anode. The light CV curve is collected in 0.5 M H_3BO_3 adjusted to pH 9.5 with KOH under AM1.5G with 1 sun of front illumination. The scan rate was 20 mV/s.

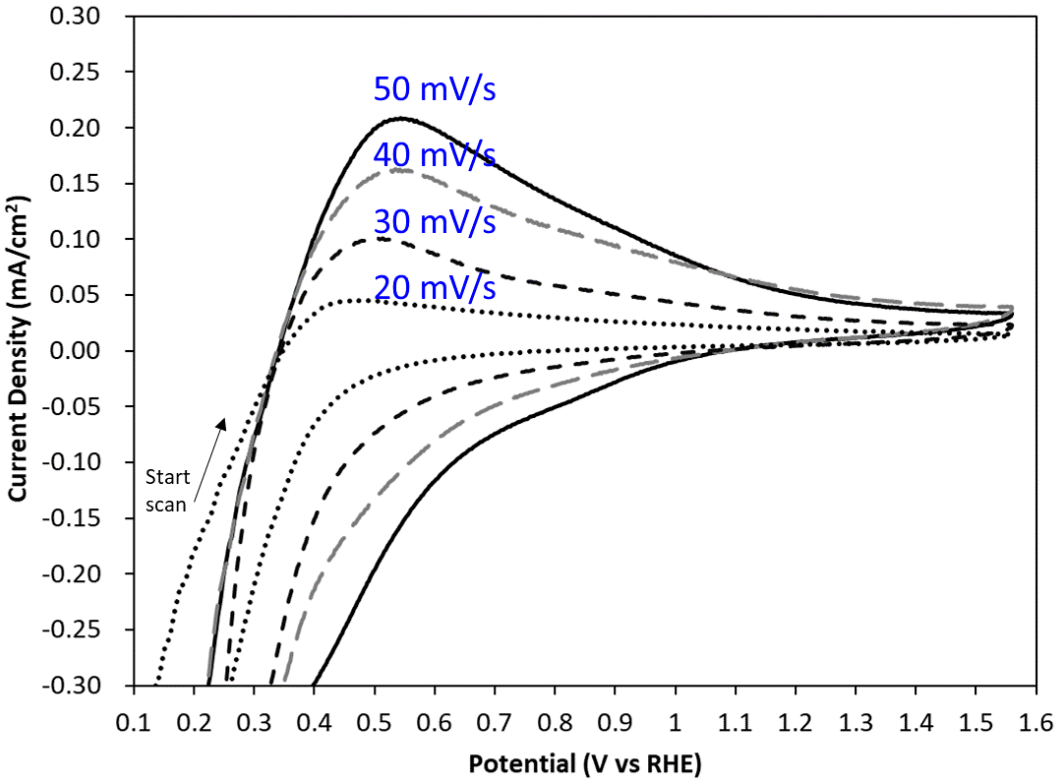


Fig. S9. Dark CV curves of the FTO/Fe_2O_3/$BiVO_4$ anode at different scan rates.

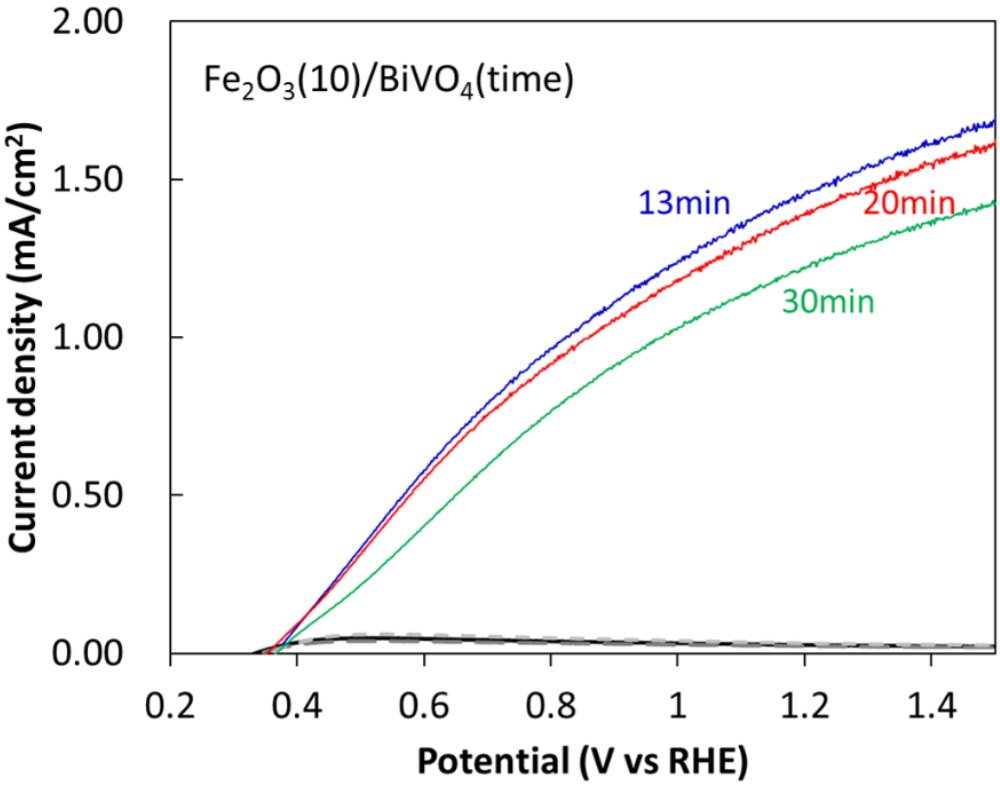


Fig. S10. PEC properties. J-V curves of the FTO/Fe_2O_3(**10**)/$BiVO_4$(time) anode with deposition duration of the upper layer $BiVO_4$ for 13, 20 and 30 min. The deposit duration of the Fe_2O_3 underlayer was **10 min**. Measurements were recorded under AM1.5G 1 sun light of front irradiation in a 0.5 M potassium borate (pH 9.5) solution.

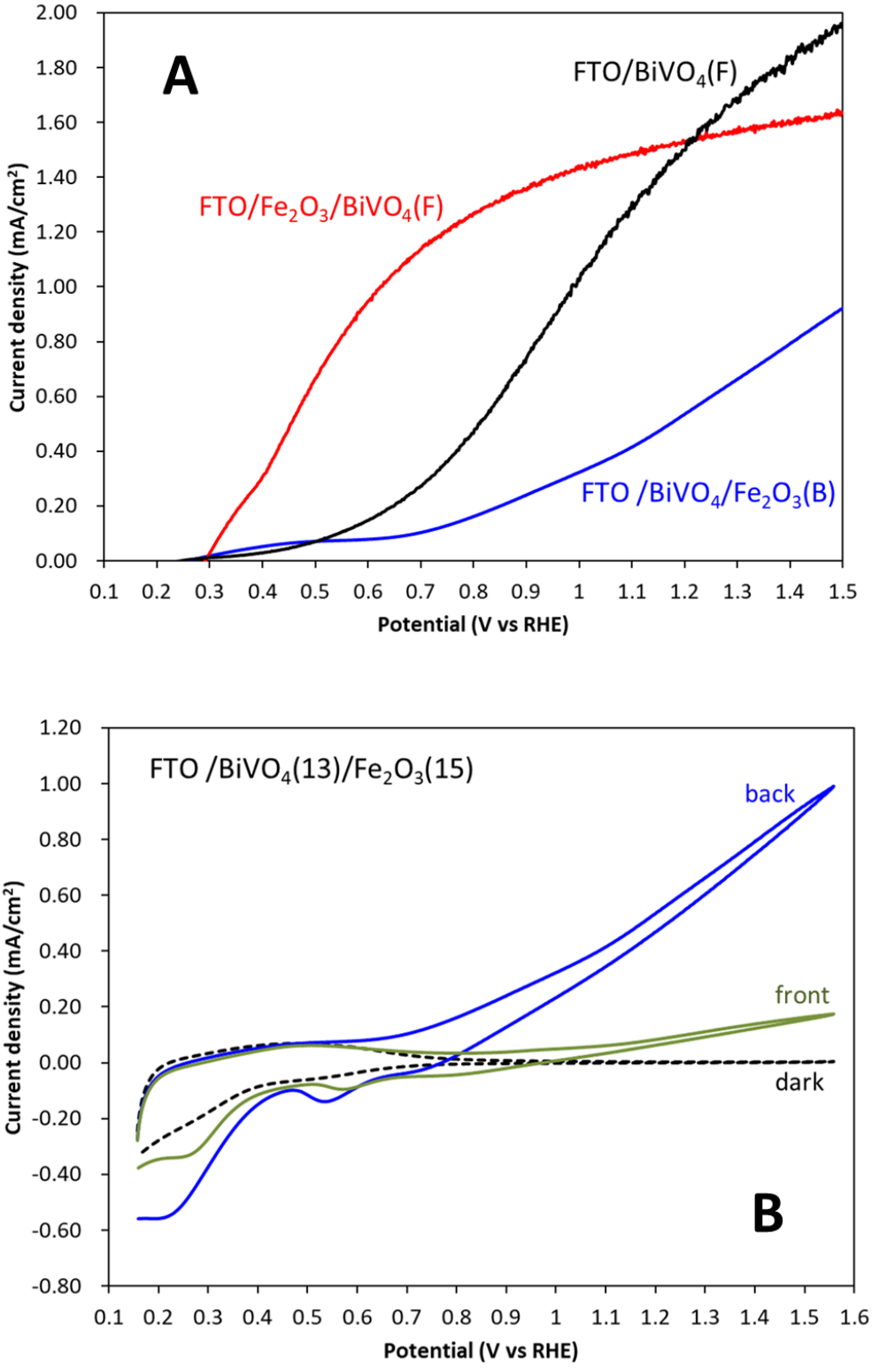
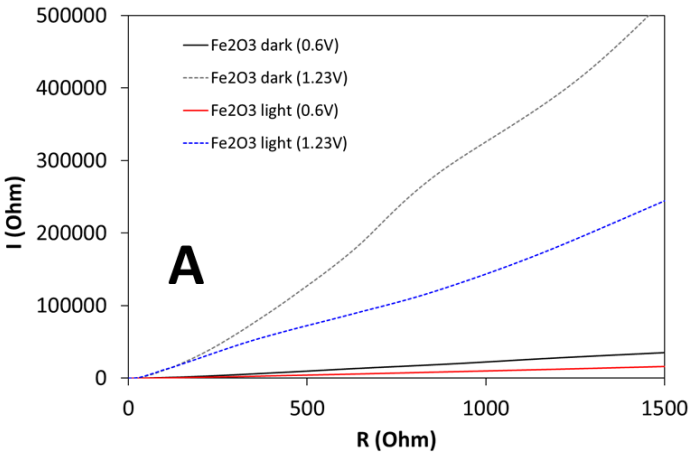
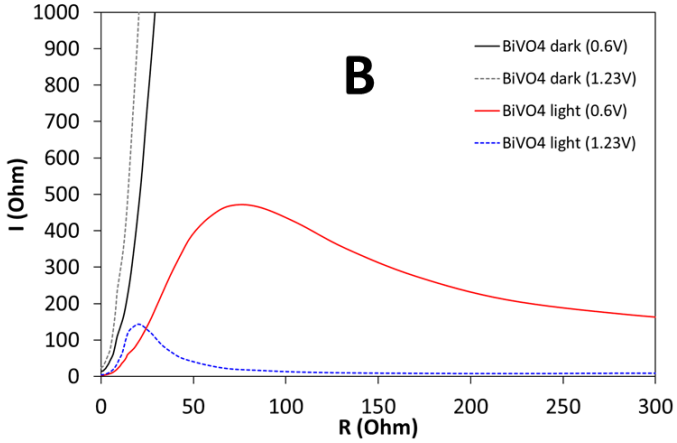


Fig. S11. (A) J-V curves of the FTO/$BiVO_4$(13)/Fe_2O_3(15), FTO/$BiVO_4$ and FTO/Fe_2O_3(15)/$BiVO_4$(13) anodes. (B) CV curves of the FTO/$BiVO_4$(13)/Fe_2O_3(15) anode.





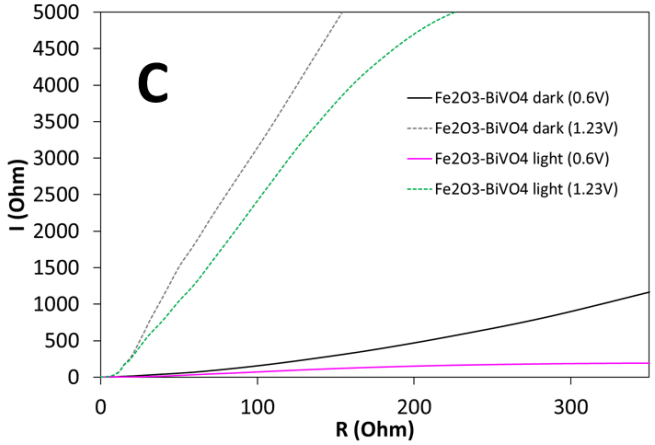


Fig. S12. Nyquist plots of (A) FTO/Fe_2O_3, (B) FTO/$BiVO_4$ and (C) FTO/Fe_2O_3/$BiVO_4$ anodes. Data were collected in the dark and under one sun light illumination at 0.6 V and 1.23 V *vs*. RHE from 10 kHz to 10 mHz.

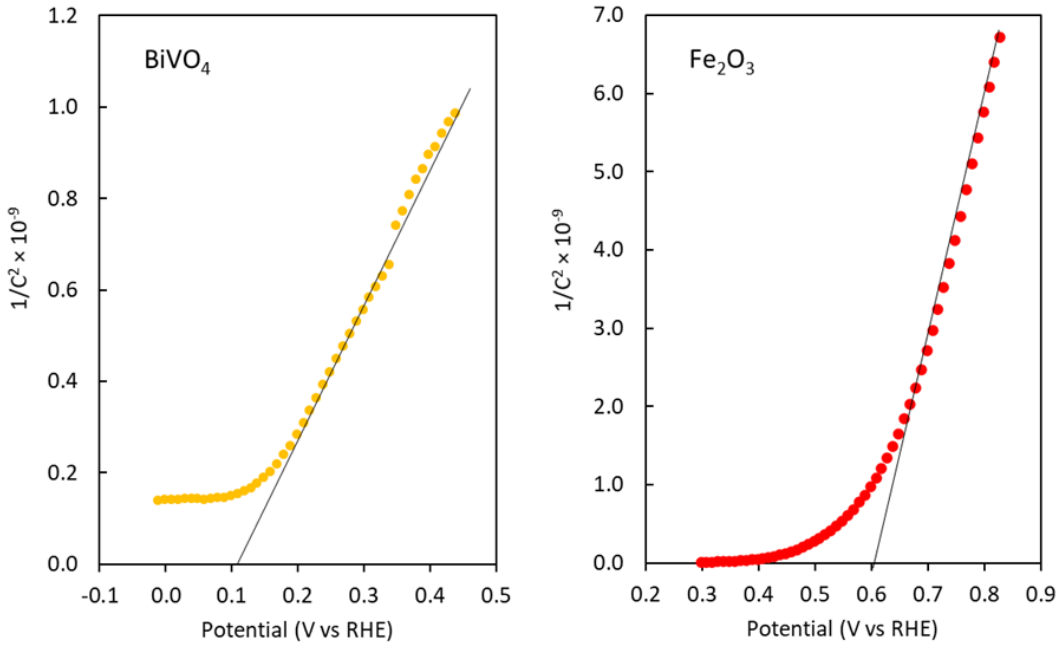


Fig. S13. Mott–Schottky plots for the FTO/$BiVO_4$ and FTO/Fe_2O_3 anodes measured in 0.5 M potassium borate (pH 9.5) solution at 1 kHz in the dark.