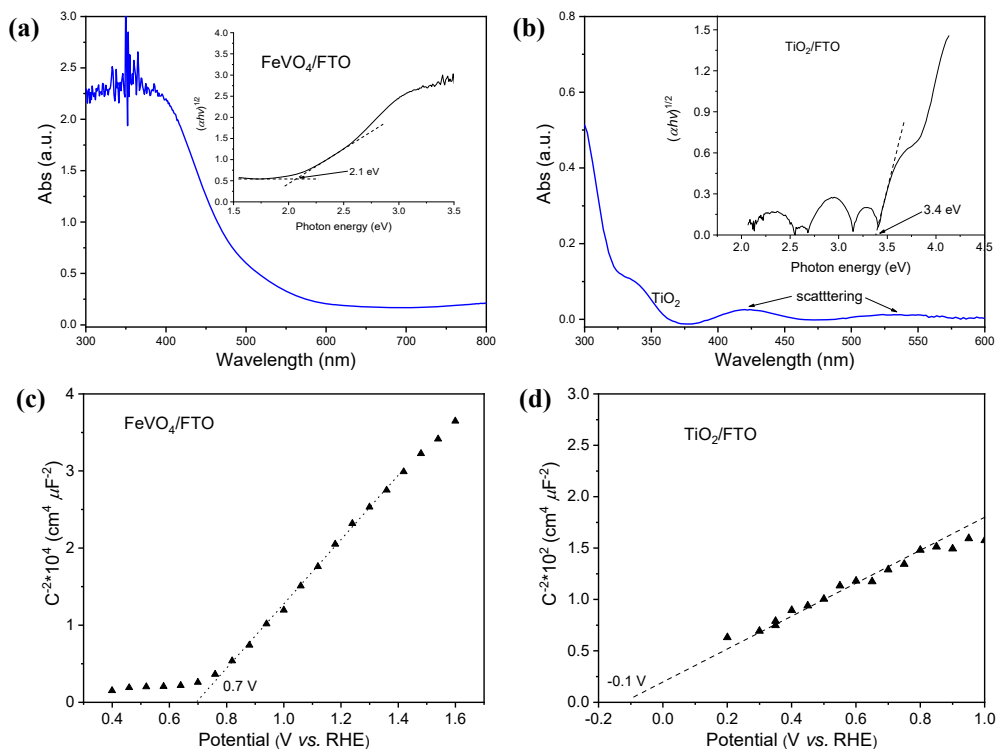
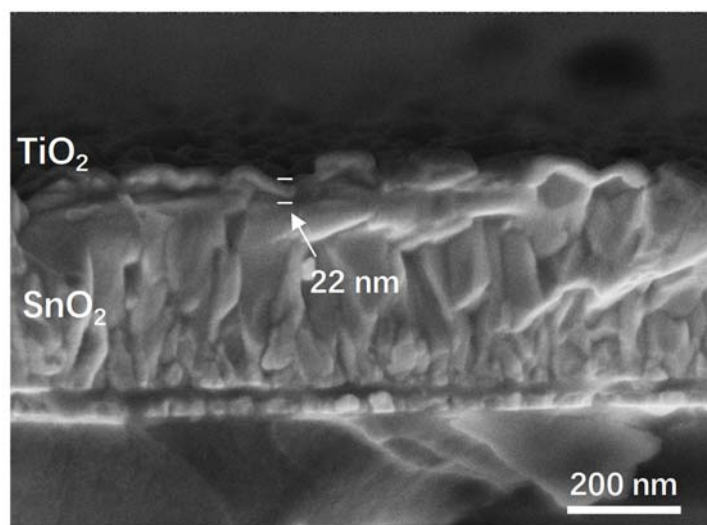


## Electronic Supplementary Information

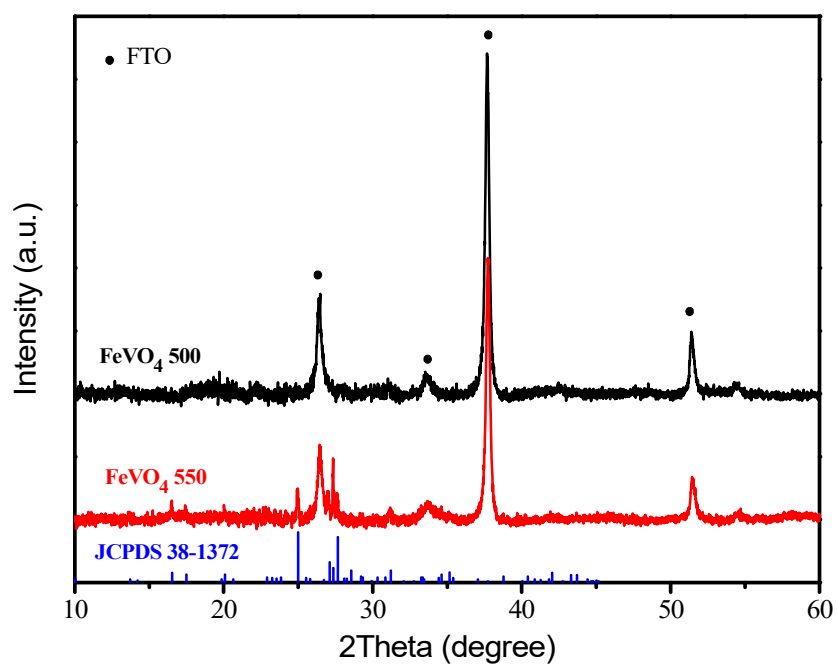
### Ultrathin TiO<sub>2</sub> Interfacial Layer Enhancing the Performance of FeVO<sub>4</sub> Photoanode for Water Splitting



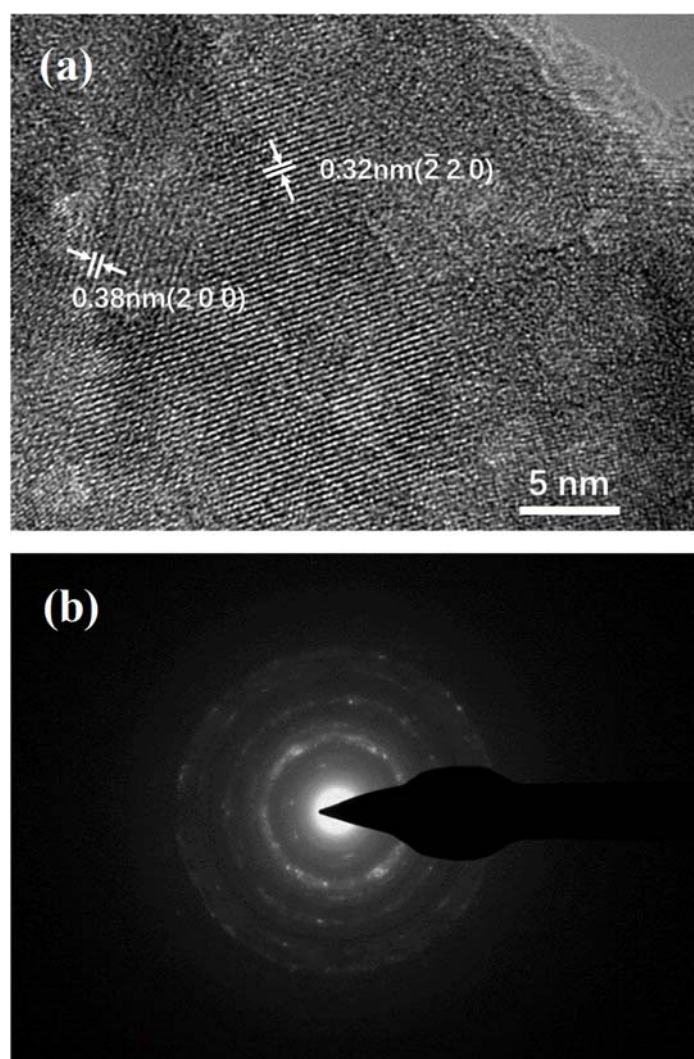
**Fig. S1** (a-b) UV-Vis absorption spectra for the samples, the insets showed the plots of  $(\alpha h\nu)^{1/2}$  versus the photon energy, and the bandgap energies of FeVO<sub>4</sub> and TiO<sub>2</sub> were estimated to be 2.1 and 3.4 eV, respectively. (c-d) Mott-Schottky plots for the samples, the flat-band potentials of FeVO<sub>4</sub> and TiO<sub>2</sub> were determined to be 0.7 and -0.1 VRHE, respectively.



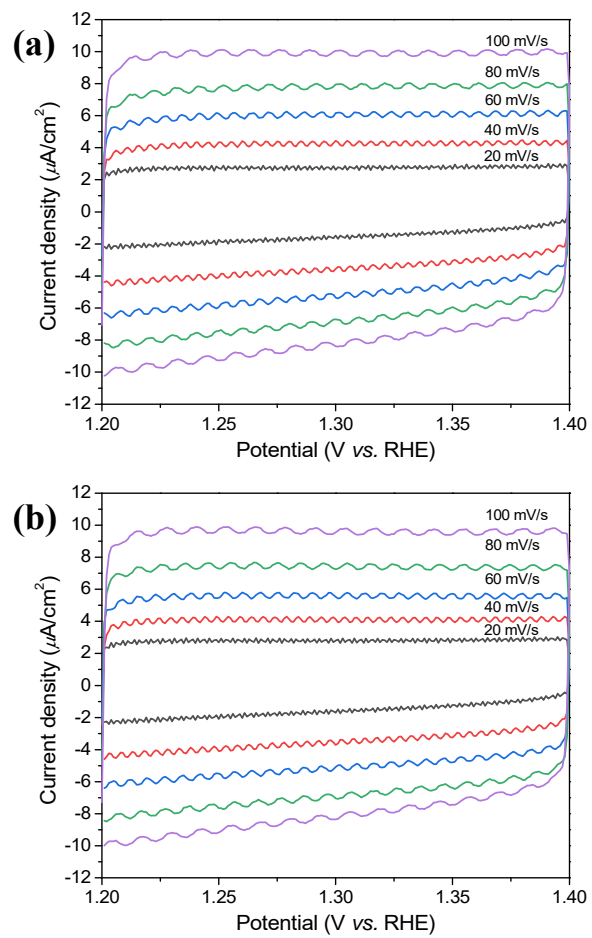
**Fig. S2** Cross-sectional SEM image of FTO with a 300-cycle  $\text{TiO}_2$  deposition layer



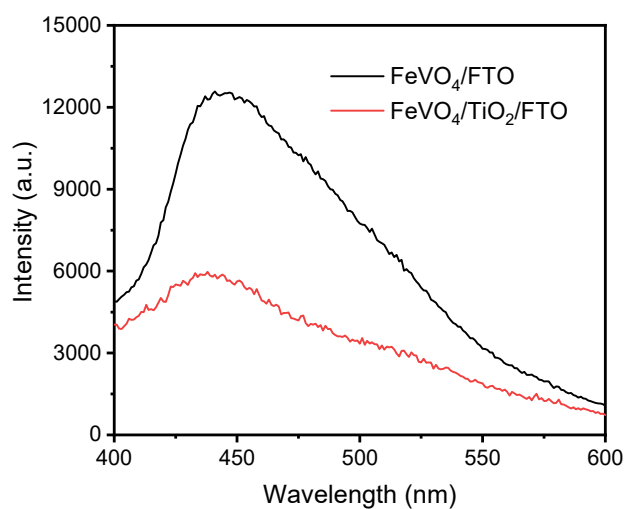
**Fig. S3** XRD patterns of  $\text{FeVO}_4$  photoanodes annealed at 500 °C and 550 °C



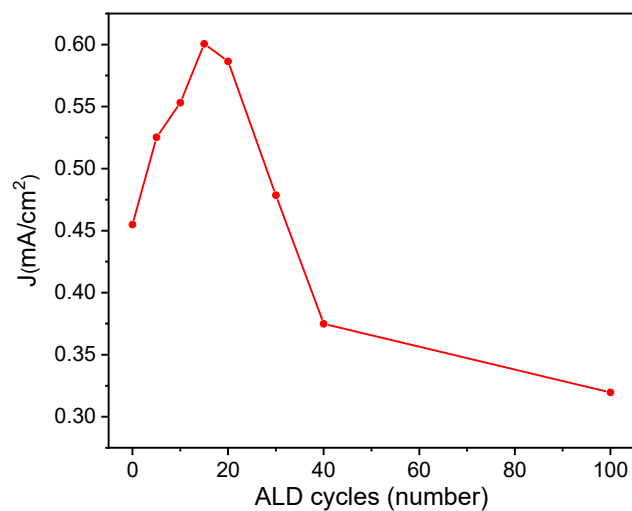
**Fig. S4** (a) HRTEM and (b) Electron diffraction patterns of FeVO<sub>4</sub> scratched from FeVO<sub>4</sub>/TiO<sub>2</sub>/FTO



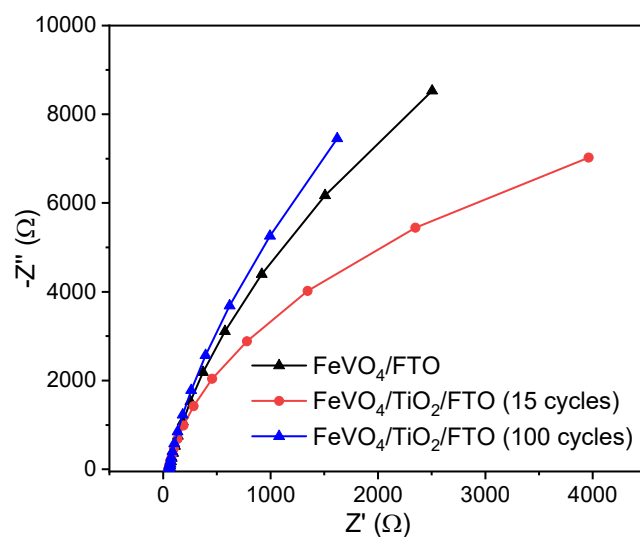
**Fig. S5** Cyclic voltammetry curves of (a) FeVO<sub>4</sub> and (b) FeVO<sub>4</sub>/TiO<sub>2</sub>/FTO electrodes under dark.



**Fig. S6** The photocurrent density at 1.6 V<sub>RHE</sub> for FeVO<sub>4</sub>/TiO<sub>2</sub>/FTO electrode with different thickness of TiO<sub>2</sub> underlayers



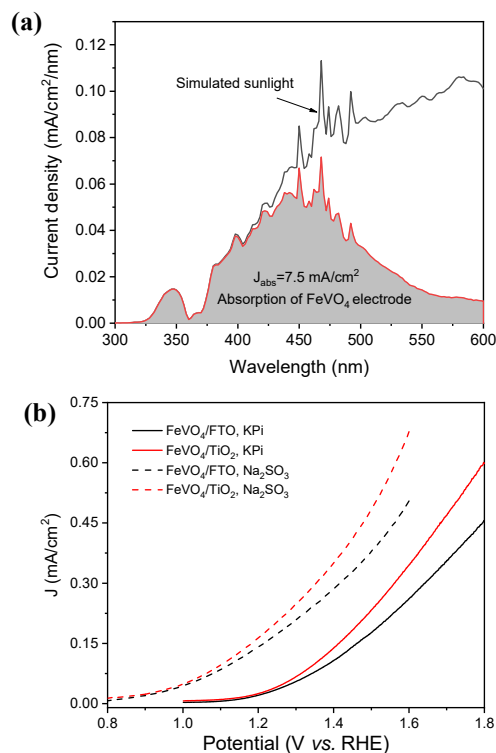
**Fig. S7** The photoluminescence spectra for the electrodes, with the excitation wavelength at 350 nm.



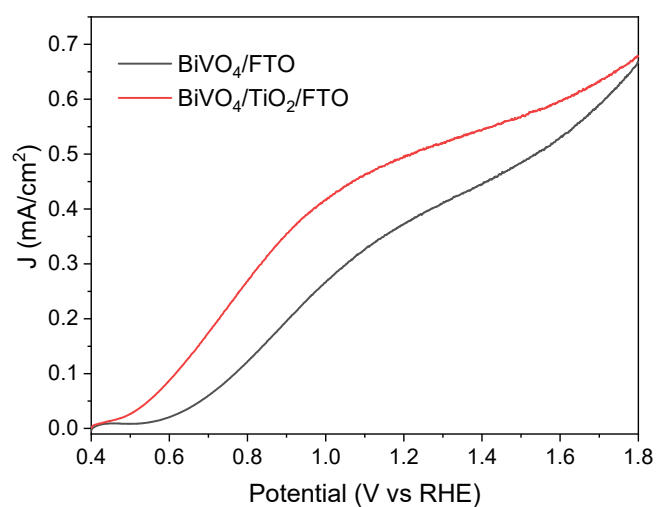
**Fig. S8** Nyquist plots of the electrodes.

**Table S1** The resistance values estimated by fitting the EIS data for the electrodes

Sample	$R_s(\Omega)$	$R_B(k\Omega)$	$R_I(k\Omega)$
FeVO <sub>4</sub> /FTO	$54.3 \pm 0.2$	$3.23 \pm 0.04$	$60.9 \pm 0.1$
FeVO <sub>4</sub> /TiO <sub>2</sub> /FTO (15 cycles)	$54.0 \pm 0.2$	$2.27 \pm 0.05$	$21.4 \pm 0.1$
FeVO <sub>4</sub> /TiO <sub>2</sub> /FTO (100 cycles)	$54.6 \pm 0.2$	$8.26 \pm 0.09$	$80.3 \pm 0.4$



**Fig. S9** The theoretical photocurrent spectrum for  $\text{FeVO}_4$  electrode obtained by multiplication of its light absorbance spectrum with photoflux spectrum of the simulated sunlight, with the theoretical photocurrent density of  $7.5 \text{ mA/cm}^2$ , (b) the photocurrent density-applied potential curves of the photoelectrodes in potassium phosphate (KPi) buffer solution or  $\text{Na}_2\text{SO}_3$  solution.



**Fig. S10** The photocurrent density-applied potential curves over the photoelectrodes for PEC water oxidation reaction