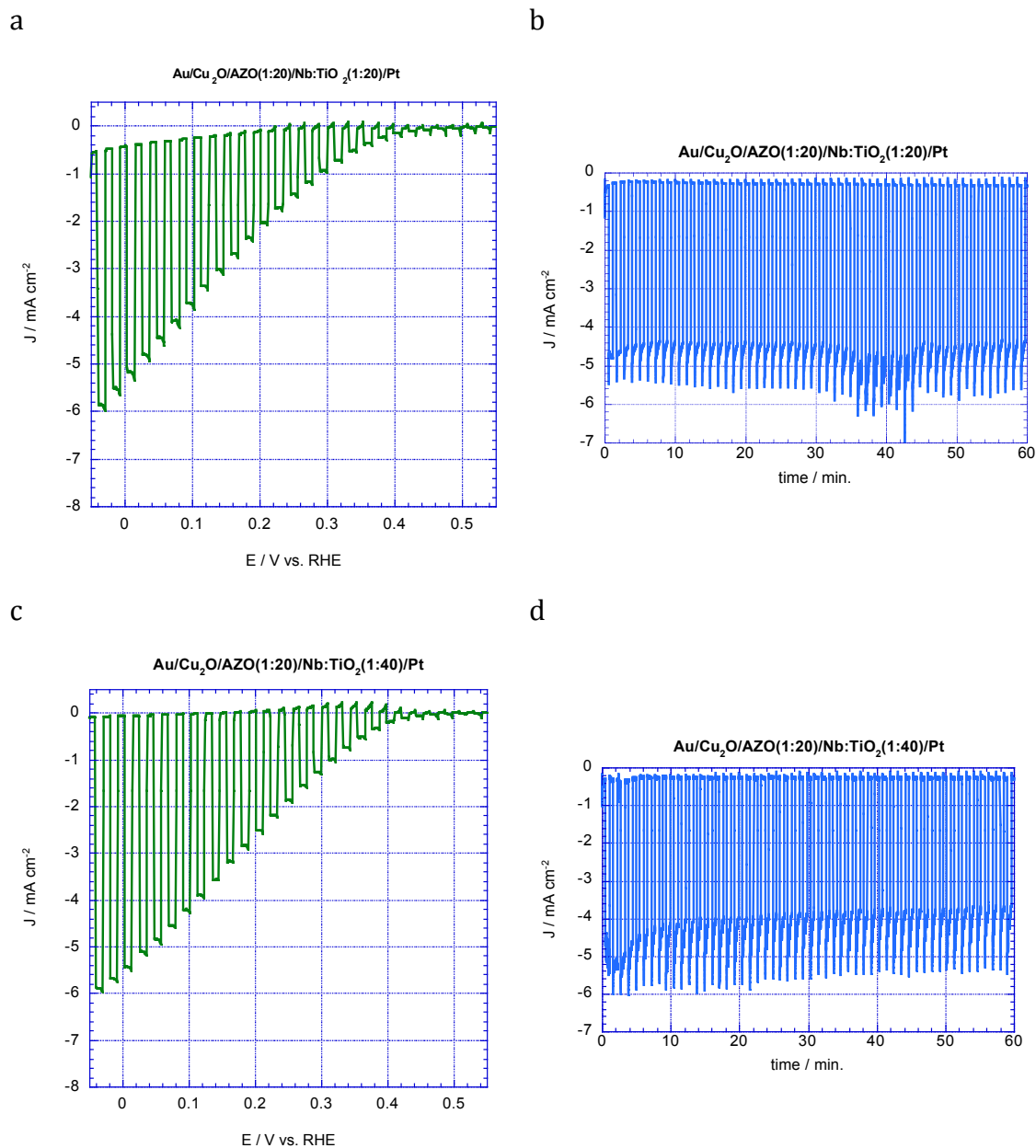
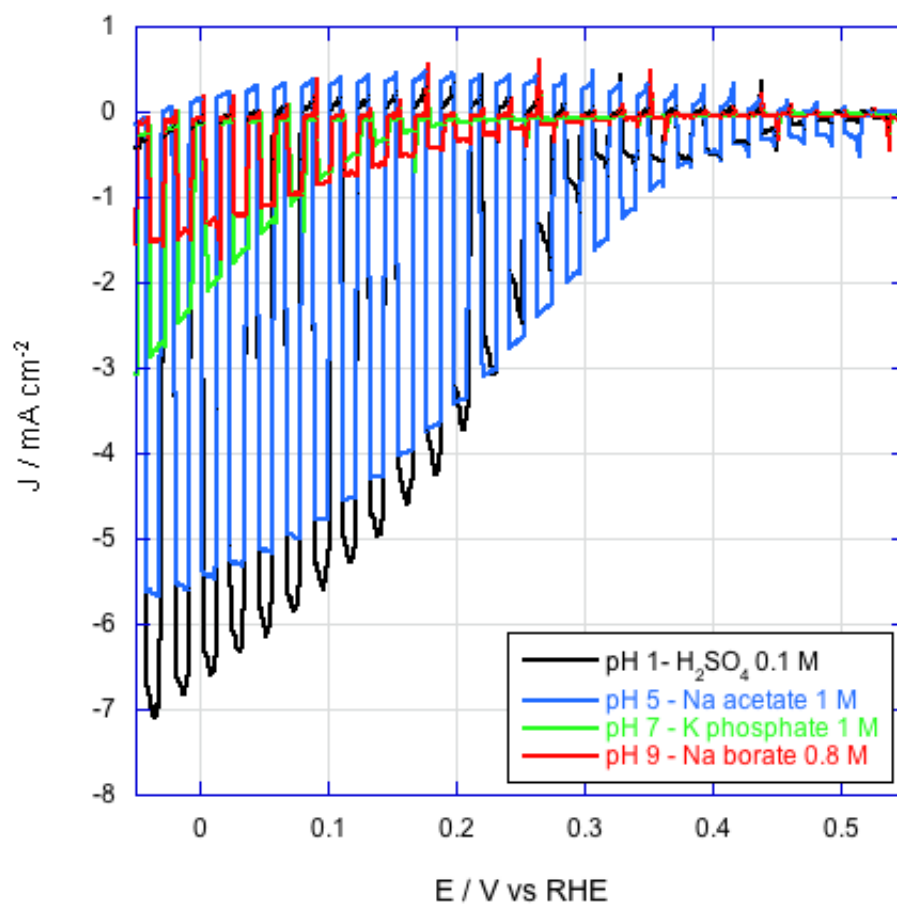


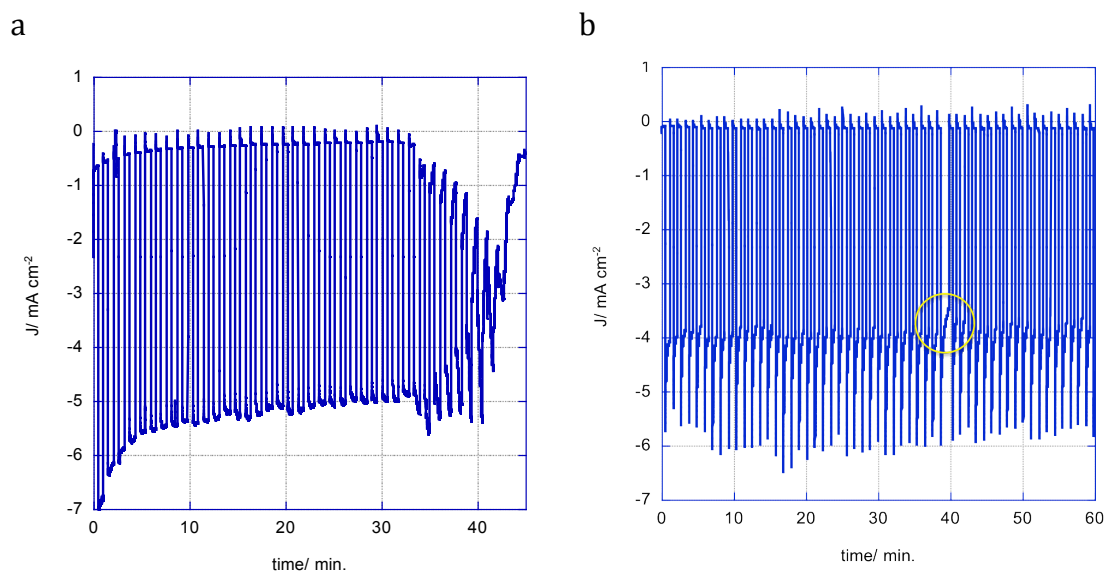
## Supporting information



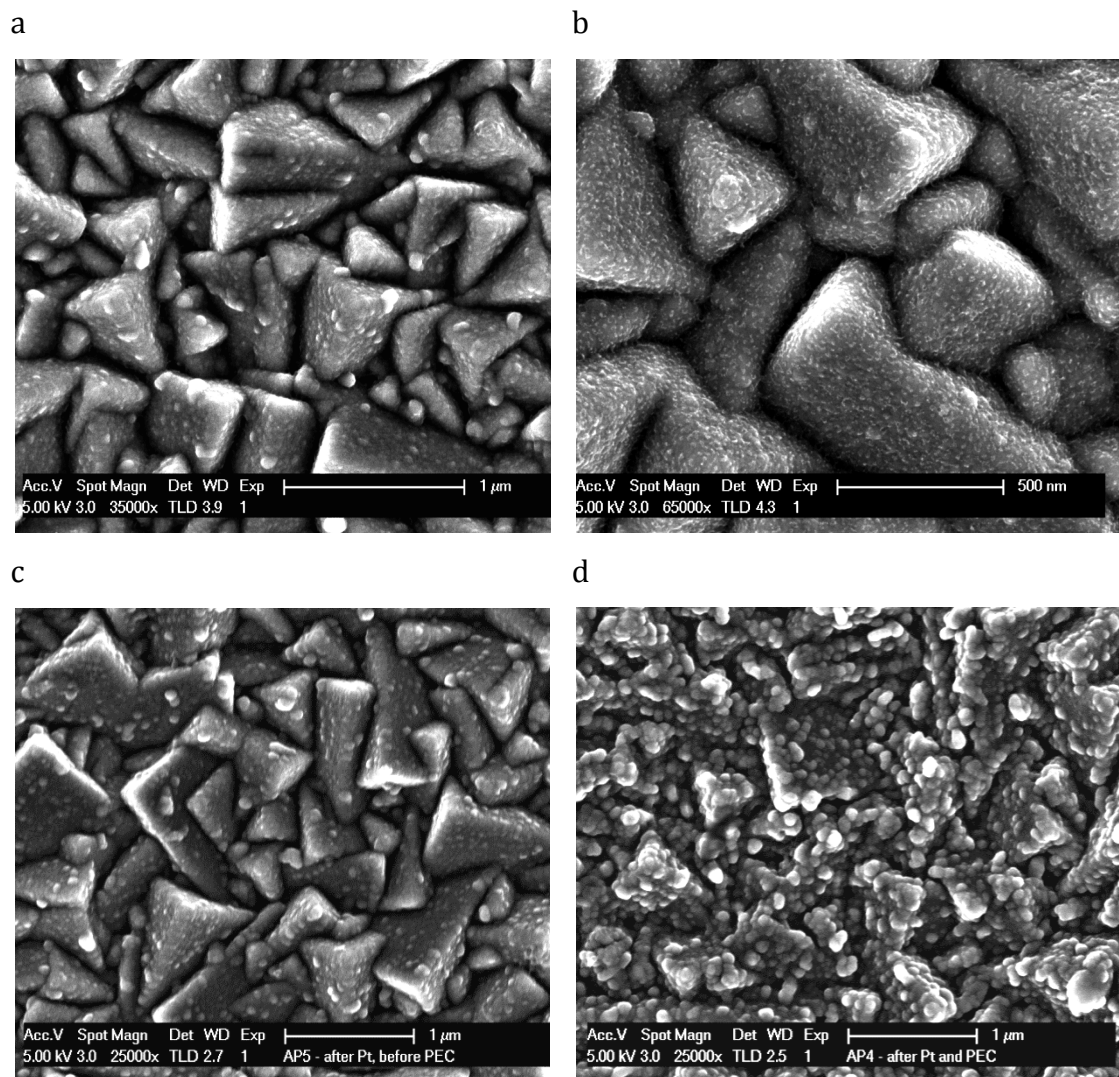
**Figure S1.** Cathodic potential sweep under chopped AM1.5 illumination in Na<sub>2</sub>SO<sub>4</sub> 0.5 M buffered at pH 5 for (a) a Cu<sub>2</sub>O/AZO(20 nm)/Nb:TiO<sub>2</sub> (1:20)(10 nm)/Pt photocathode (c) and a Cu<sub>2</sub>O/AZO(20 nm)/Nb:TiO<sub>2</sub> (1:40)(10 nm)/Pt photocathode. The respective stability test at 0 V/RHE in the same electrolyte are shown in (b) and (d).

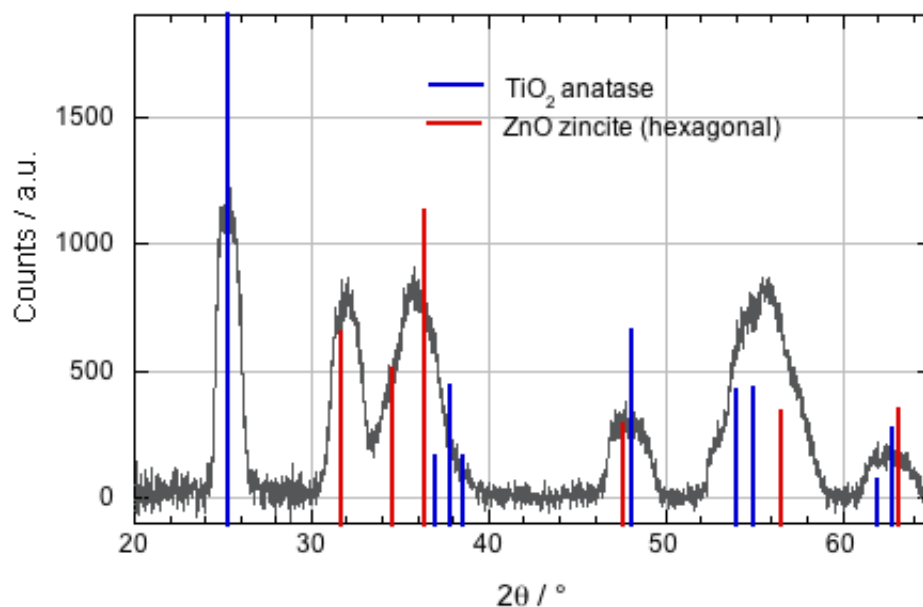


**Figure S2.** Cathodic potential sweep under chopped AM1.5 illumination for  $\text{Cu}_2\text{O}/\text{AZO}$  (20 nm)/ $\text{TiO}_2$  (10 nm)/Pt photocathodes in different electrolytes.

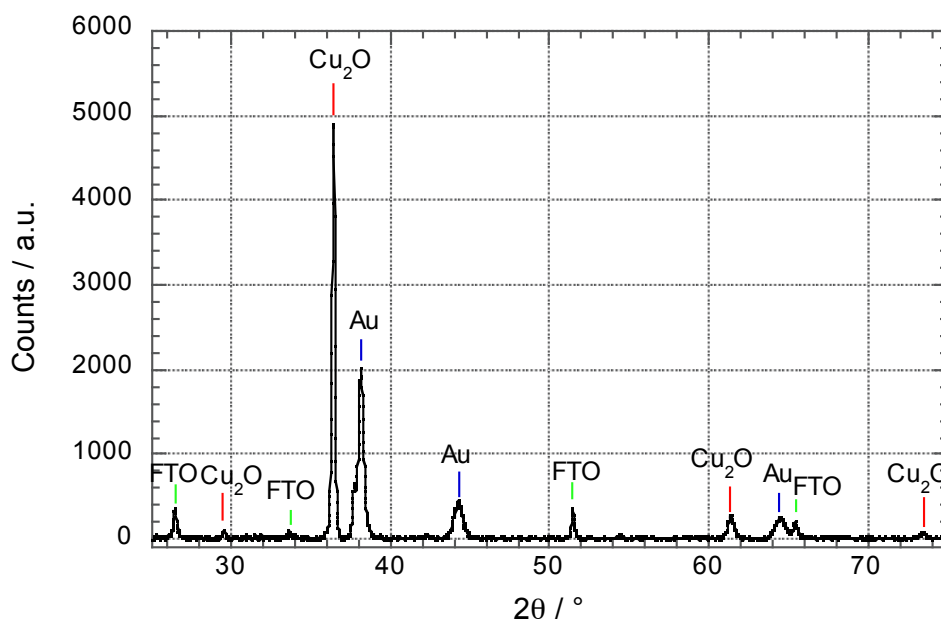


**Figure S3.** Stability tests for  $\text{Cu}_2\text{O}/\text{AZO}$  (20 nm)/ $\text{Nb}:\text{TiO}_2$  (10 nm)/Pt photocathodes in  $\text{H}_2\text{SO}_4$  0.1 M (pH 1) (a) and  $\text{Na}_2\text{SO}_4$  0.5 M (pH 5) (b). The large transients in (b) are due to proton depletion close to the photocathode surface, a phenomenon not occurring in the case of the highly acidic solution (a). The circle in panel (b) indicates the photocurrent decay observed when the chopping frequency is decreased in order to emphasize the proton-depletion phenomenon occurring in weakly acidic solutions.

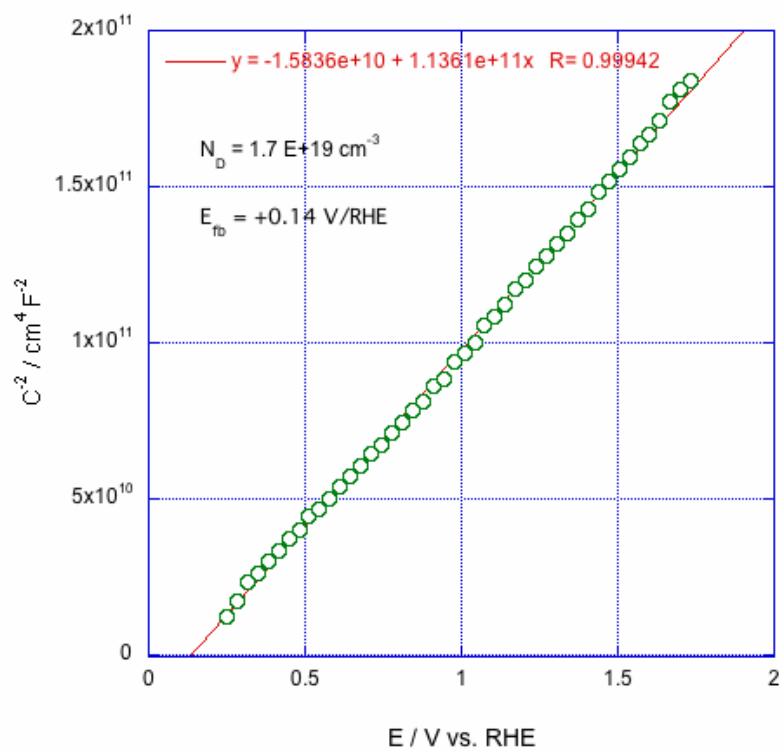




**Figure S5.** Grazing angle XRD for 20 nm of ALD TiO<sub>2</sub> grown at 200°C atop of 20 nm of AZO grown at 120°C on optically polished silicon. The as-deposited AZO was found to be substantially amorphous in another experiment. Here small crystalline domains start to appear due to the heating at 200°C. Also anatase domains are present. The large peak broadening for both phases indicates less than 5 nm-large crystallites dispersed in an amorphous mixture, as obtained from the calculation using the Scherrer equation.



**Figure S6.** XRD for a Cu<sub>2</sub>O/AZO/TiO<sub>2</sub>/Pt sample (with 20 nm ALD TiO<sub>2</sub> grown at 200°C) after a 10 hours stability measurement at 0 V/RHE.



**Figure S7.** Mott-Schottky plot in 1 M NaOH for ALD TiO<sub>2</sub> (50 nm) deposited at 200°C and annealed in oxygen for 2 hours.