Selective Oxidation of Glucose to Gluconic Acid in Aqueous Media Using Dye-Sensitized Photoelectrochemical Cells

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1. Experimental section

1.1. Materials

(E)-3-(5-(4-(bis(2',4'-dibutoxy-[1,1'-biphenyl]-4-yl) amino) phenyl) thiophen-2-yl)-2-cyanoacrylic acid (D35) was purchased from Dyenamo AB, Sweden. Fluorine-doped tin oxide (FTO) (F-SnO_2, 7 Ω/sq) glass was purchased from Hartford Glass Co. Inc. Boric acid, Potassium hydroxide, Gluconic acid, and D-(+)-glucose were purchased from Sigma-Aldrich. The (4-Acetamido-2,2,6,6-tetramethylpiperidine 1-oxyl) ACT, (2,2,6,6-tetramethylpiperidine 1-oxyl) TEMPO, and (9-Azabicyclo (3,3,1) nonan-3-one-9-oxyl) Keto-ABNO were purchased from AK scientific Inn.

1.2. Fabrication of photoanode (FTO/TiO_2/D35)

The photoanodes were fabricated and modified according to previous studies.[1,2] Briefly, FTO substrates were cleaned by sonicating with detergent followed by a mixture of acetone, isopropyl alcohol, and ethanol (1:1:1 ratio), separately, in an ultrasonic bath for 30 min and UV-ozone cleaned also for 30 min. Next, a TiO_2 blocking layer was deposited by screen printing onto FTO and annealed at 500 °C for 30 min. After that, the mesoporous structured TiO_2 (approximately 20 nm size) layer was coated by the screen-printing method with a thickness of 4 μm (measured by Alpha step D300). Then, the electrodes were annealed by multiple ramping methods at 100 °C for 15 min, 200 °C for 15 min, 300 °C for 15 min, 400 °C for 15 min, and 500 °C for 30 min to remove the organic binders from the TiO_2 paste and to achieve good electrical and interfacial contact between the FTO substrate and TiO_2.[3,4] Upon cooling down to 80 °C, the annealed TiO_2 films (FTO/TiO_2) were immersed in a 0.3 mM D35 solution in anhydrous ethanol for 5 h with continuous shaking at 40 °C. The FTO/TiO_2/D35 films were rinsed with anhydrous ethanol, then dried and used for the experiment.

1.3. Photoanode characterization

UV-visible absorption spectra of FTO/TiO_2/D35 films were collected using a Thermo Scientific Evolution 220 UV-vis spectrometer. Emission spectra measurement was performed using a Varian Cary Eclipse fluorescence spectrophotometer.

1.4. Product analysis

The glucose products were analysed by a Shimadzu LC-20AT high-performance liquid chromatography (HPLC) equipped with a UV detector (λ= 210 nm).[5] 5 mM H_2SO_4 at a flow rate of 0.6 mL/min was used as the mobile phase. The injection volume was 10 µL. In each analysis, five times diluted electrolyte withdrawn from the DSPEC cell was injected directly into a BioRad Aminex® HPX-87H column (300 x 7.8 mm) with a column temperature of 50 ºC. The glucose products were identified by comparing their retention times in the chromatograms with those of the standard solution. The given formulae were used to calculate the selectivity and Faradaic efficiency of gluconic acid conversion by using the calibration curves as given in supporting information.

$$Selectivity(\%) = \frac{mol\ of\ specific\ product}{mol\ of\ consumed\ reactant} \times 100\% \qquad (1)$$

$$\text{Faradaic efficiency} = \frac{N_{products}}{Q/_{ZF}} \times 100\% \qquad (2)$$

where $N_{products}$ is the gluconic acid concentration (calculated from calibration curve), Q is the charge passed (Q=I×t), Z is the number of electrons for glucose to gluconic acid conversion and F is Faraday constant (F=96485 C/mol).

1.5. Electrochemical measurements

All electrochemical measurements (VersaSTAT 4; Princeton Applied Research, USA) were performed in an aqueous solution with 0.1 M potassium borate buffer using a single-compartment three-electrode cell including a Pt wire counter electrode, Ag/AgCl as a reference electrode, and glassy carbon (GCE) as the working electrode. Voltammograms were recorded at a scan rate of 50 mV s^{-1}. Photocurrent-time trace measurements were performed in an aqueous solution with 0.1 M potassium borate buffer using a single-compartment three-electrode cell including a Pt disc counter electrode, Ag/AgCl as a reference electrode, and FTO/TiO_2/D35 as the working electrode, at light intervals of 60 s on/off and at 0 V *vs.* NHE under 1 sun illumination (100 mW/cm^2). Light irradiation was provided by an AM 1.5G solar simulator (Abet Technologies). The temperature in the photoanode was maintained at ambient conditions by cooling with forced air using an electric fan.

1.6. Photo-electrocatalytic oxidation of glucose

Glucose oxidation studies were performed using a solar simulator with 1 sun AM 1.5G (100 mW/cm^2) light intensity for 24 hours at 0 V *vs.* NHE. The light intensity was measured using a THORLABS PM400 optical power meter with a S415C thermal power sensor head. The electrolyte solution contained 10 mM ACT and 40 mM Glucose in 20 mL of 0.1 M Potassium borate buffer. A specifically designed Teflon cell suitable for back-illumination was used to assemble all the DSPECs.

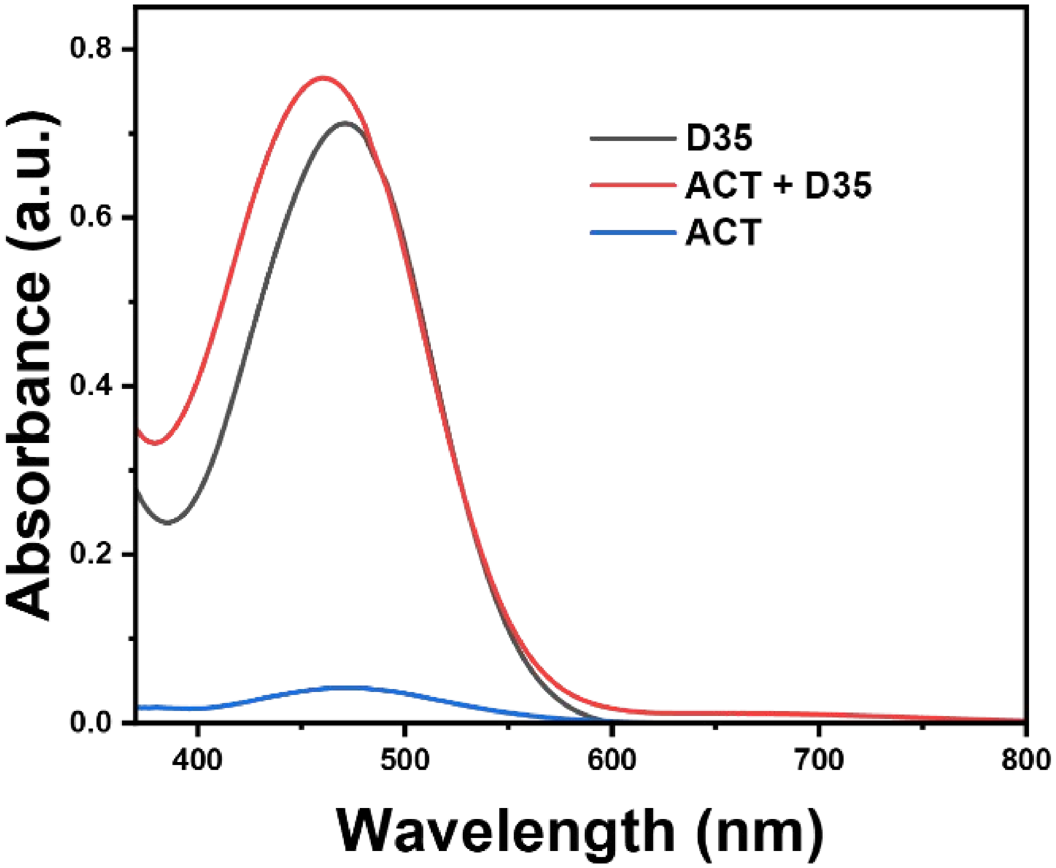

Figure S1. UV-visible absorption spectra of D35, ACT and ACT+D35 in acetonitrile.

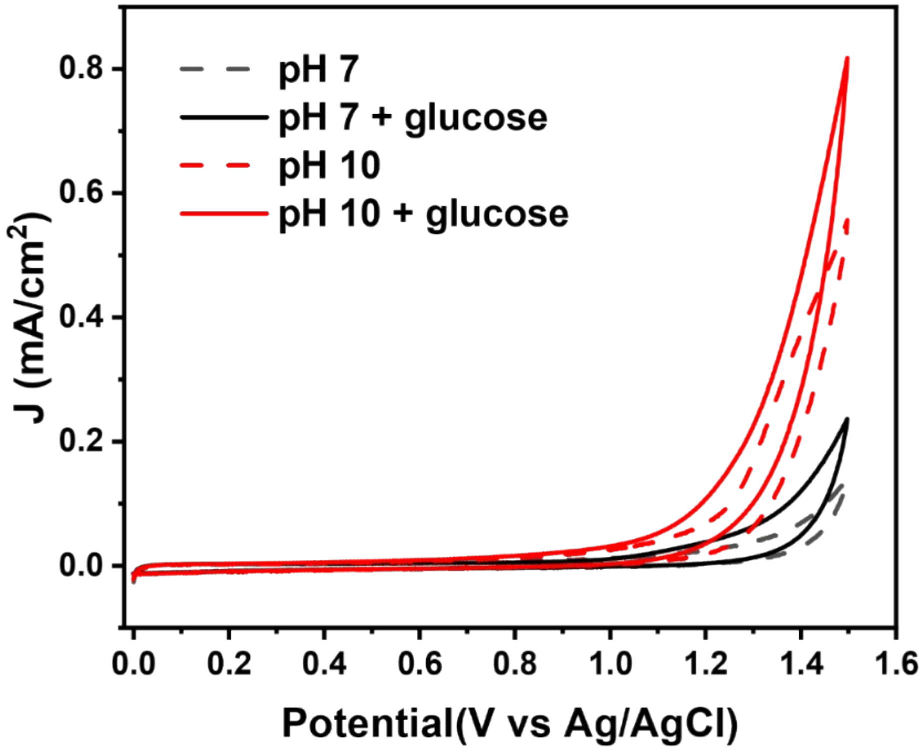

Figure S2. CV response with GCE measured in 0.1 M buffer solution for the effect of pH 7 (black curve) and pH 10 (red) in the absence (dotted line) and presence of 10 mM of glucose (solid line) at a scan rate of 50 mV/s.

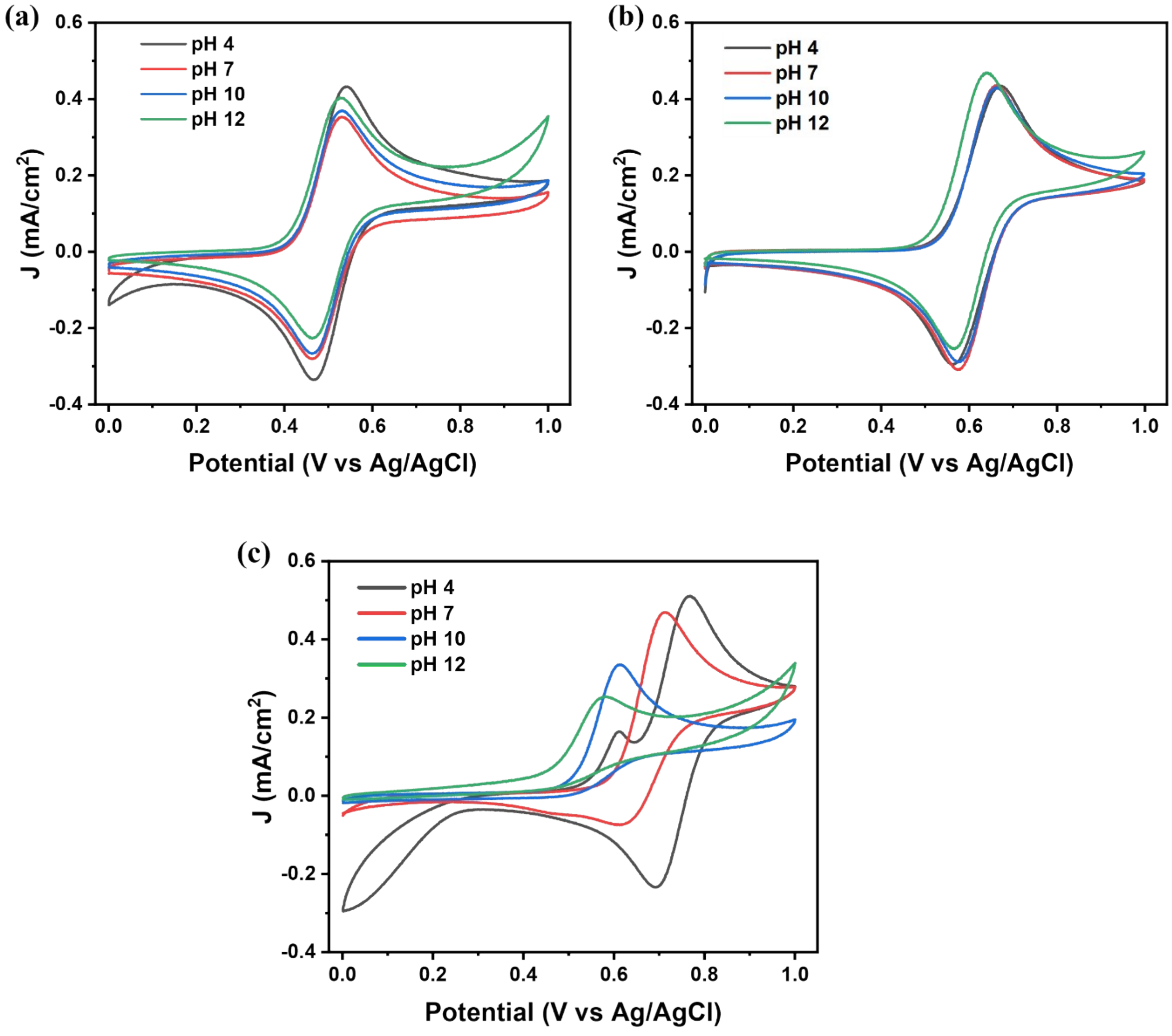

Figure S3. Cyclic Voltammograms of 3 mM of (a) TEMPO, (b) ACT and (c) Keto-ABNO in 0.1 M buffer solution at pH 4, 7,10 and 12 respectively, at a scan rate of 50 mV/s.

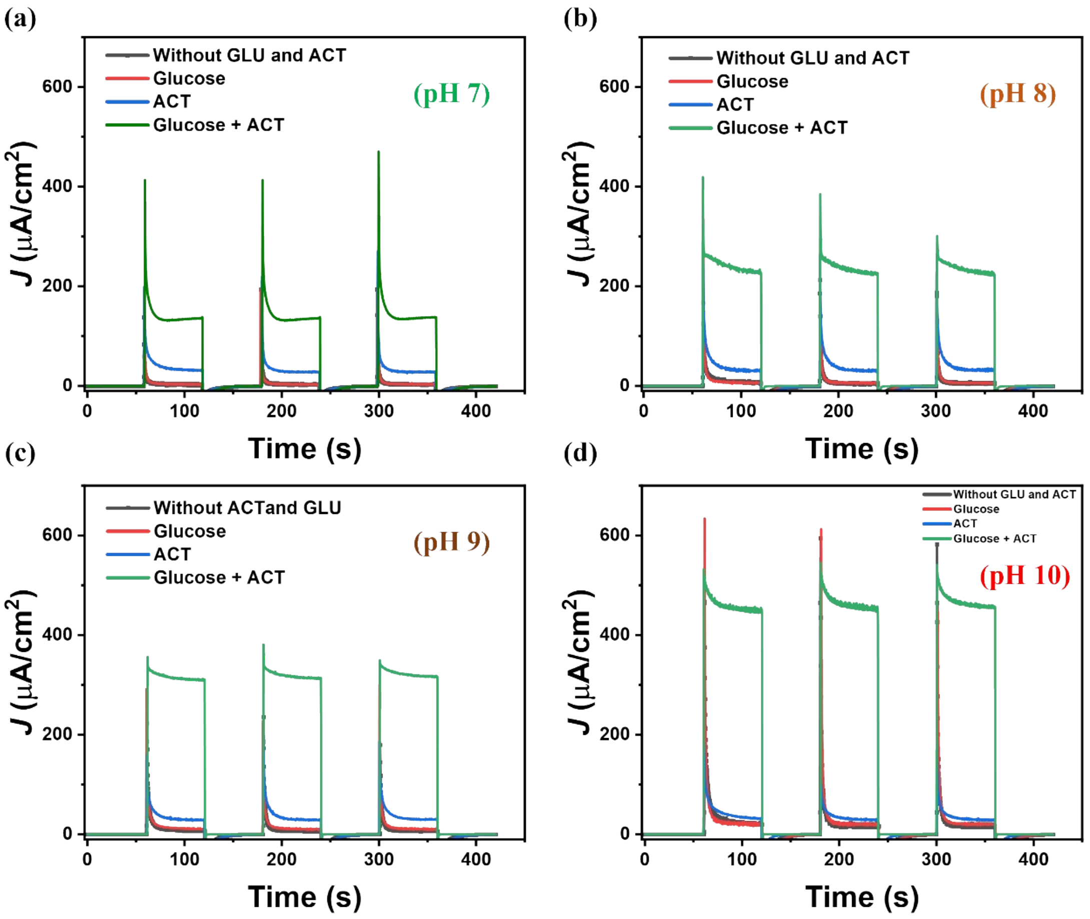

Figure S4. Photocurrent measurement with FTO/TiO_2/D35 electrode, with 10 mM of ACT and 40 mM of glucose, in 0.1 M buffer solution under 60 s on/off cycles at (a) pH 7 (b) pH 8 (c) pH 9 and (d) pH 10. The applied bias was 0 V vs NHE for all experiments and with illumination of 100 mW/cm^2, while a high energy cut-off at λ> 420 was applied.

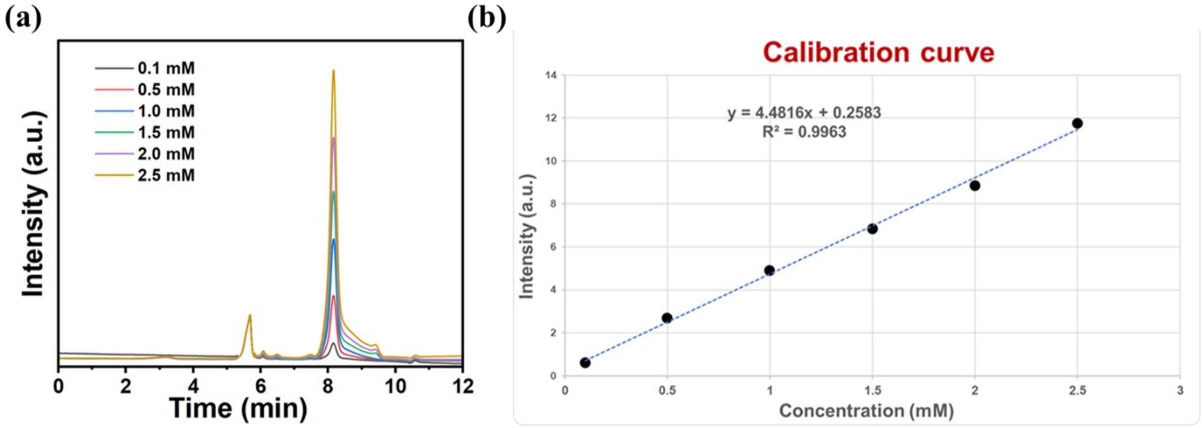

Figure S5. (a) HPLC chromatograms for the various concentrations (0.1 mM to 2.5 mM) of gluconic acid.[5,6] (b) Calibration curve used to estimate the concentration of gluconic acid.

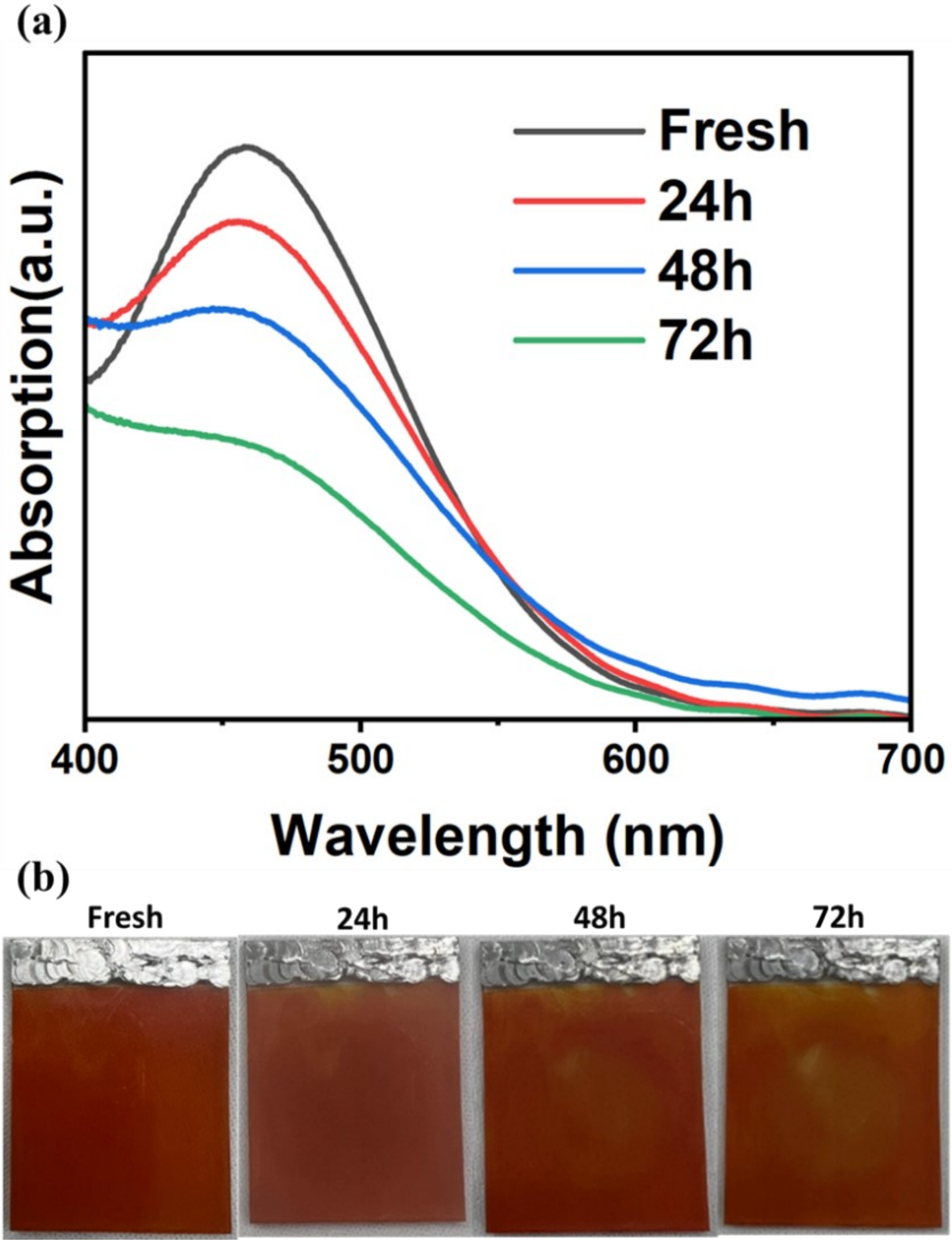
(a)
Absorption(a.u.)
Fresh
24h
48h
72h
400
500
600
700
Wavelength (nm)
(b)
Fresh
24h
48h
72h

Figure S6. (a) UV/Visible absorption spectrum of photoanode, FTO/TiO_2/D35, fresh and after using for every 24 h cycle. (b) Images of the electrode, FTO/TiO_2/D35, before and after using in 0.1 M buffer solution (pH = 7) at applied bias 0 V vs NHE, under 100 mW/cm^2 illumination with λ> 420 for 72 h.

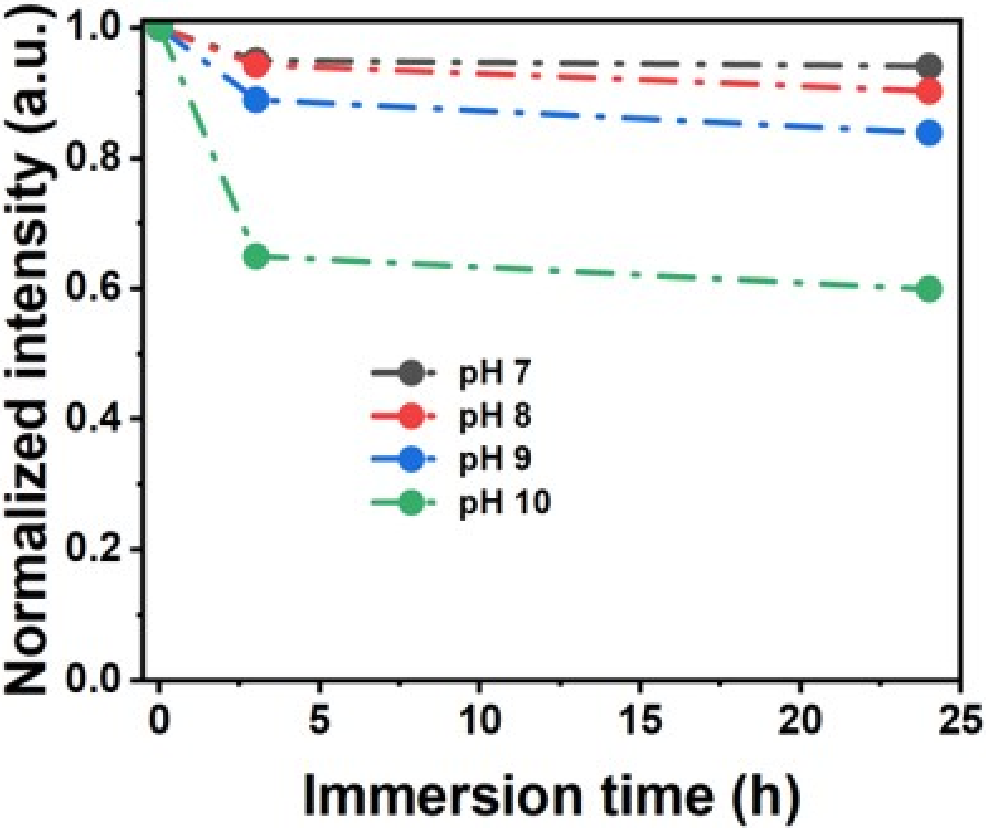

Figure S7. The decreasing absorption intensity of the FTO/TiO_2/D35 electrodes plotted after immersion tests in solutions of various pH (7, 8, 9, and 10) for 24 hours.

References

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