

## Supporting Information

# Boosting Water Oxidation Layer-by-Layer

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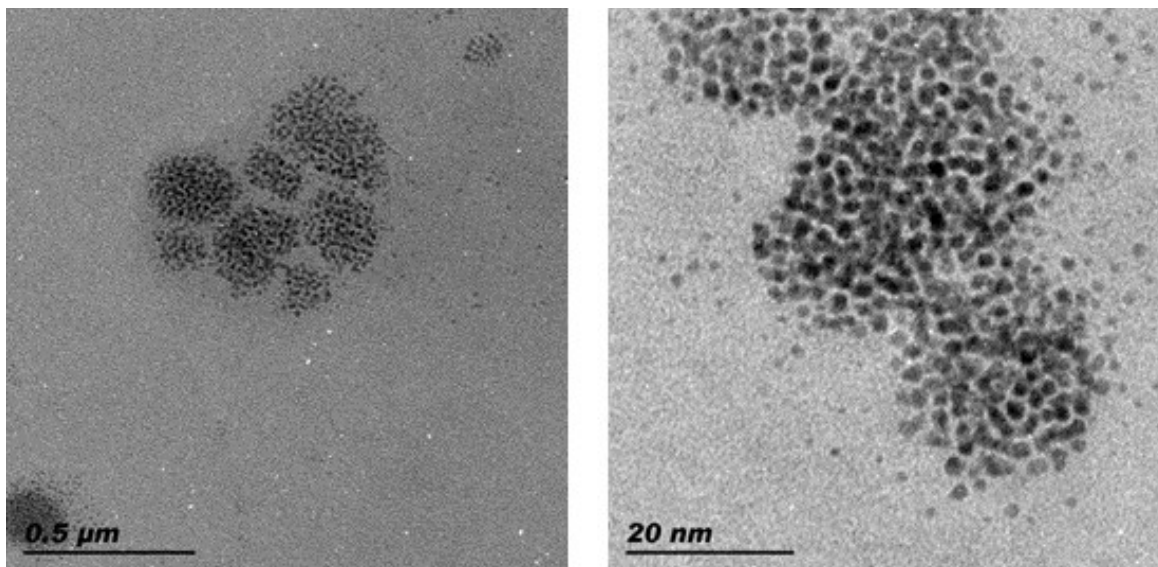
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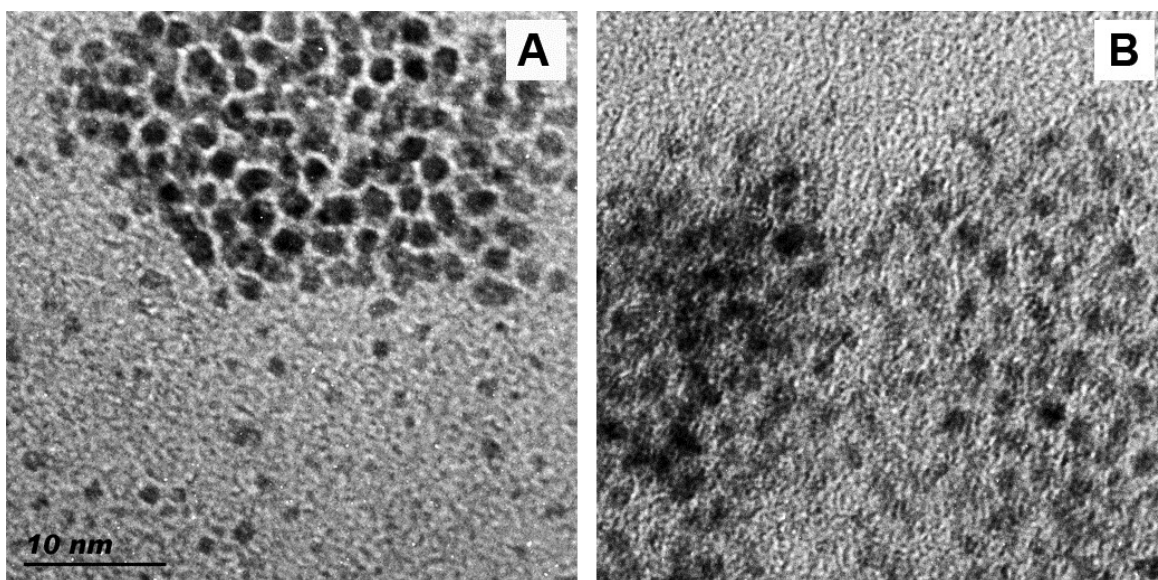
## Table of Contents

Section	Page
• Transmission electron microscopy (TEM) of colloidal IrO <sub>2</sub> nanoparticles	3
• UV/vis spectroscopy of colloidal IrO <sub>2</sub> nanoparticles	4
• “Aging” of the Layer-by-Layer (LbL) deposited IrO <sub>2</sub> /PDDA bilayer on FTO electrodes under ambient conditions with time	5
• Disappearance of the Ir(IV)-Ir(IV)/Ir(IV)-Ir(V) redox transition after <i>i</i> R compensation	6
• Bulk electrolysis cell: experimental setup	7
• Experimental determination of amounts of molecular oxygen (O <sub>2</sub> ) evolved during bulk electrolysis experiments at IrO <sub>2</sub> /PDDA-modified FTO electrodes	8
• Long term electrolysis experiments	10

## Transmission electron microscopy (TEM) of colloidal IrO<sub>2</sub> nanoparticles

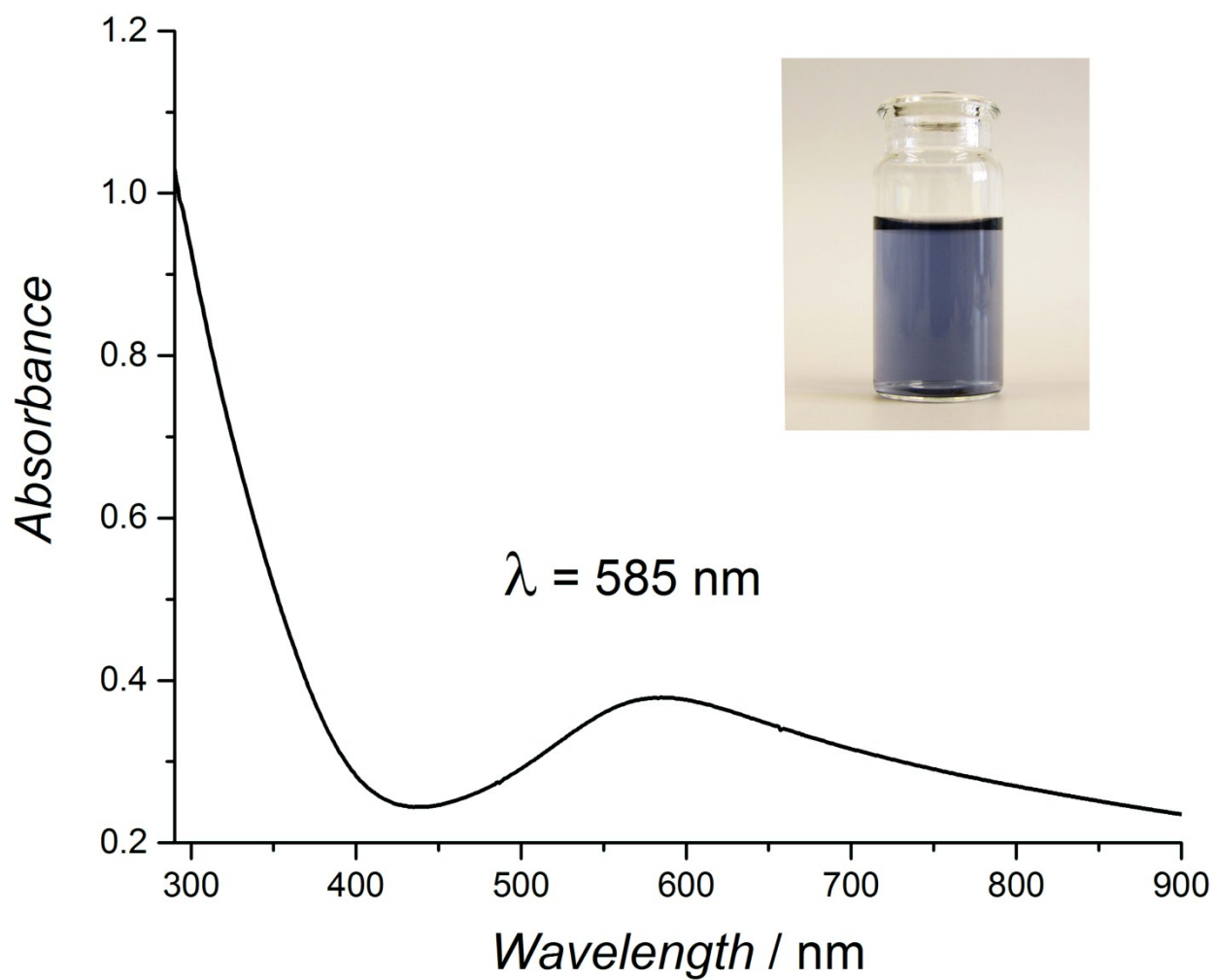


**Figure S1.** TEM images of the as-synthesized citrate stabilized IrO<sub>2</sub> NPs at two different magnifications.



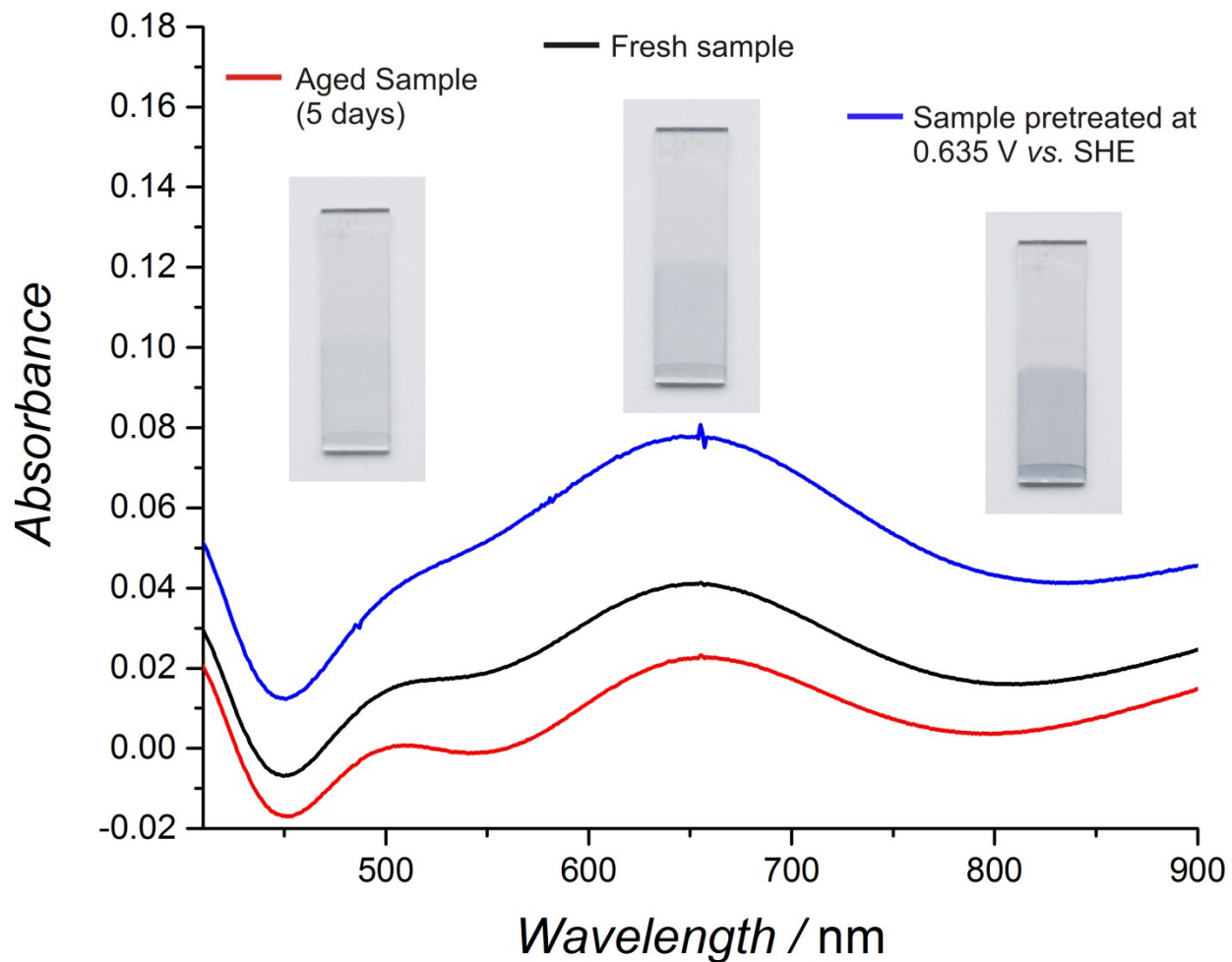
**Figure S2.** TEM images of (A) as-synthesized citrate stabilized IrO<sub>2</sub> NPs and (B) residue obtained after sonicating an FTO electrode modified with 14 IrO<sub>2</sub>/PDDA bilayers for 4 hours in ethanol.

## UV/vis spectroscopy of colloidal IrO<sub>2</sub> nanoparticles



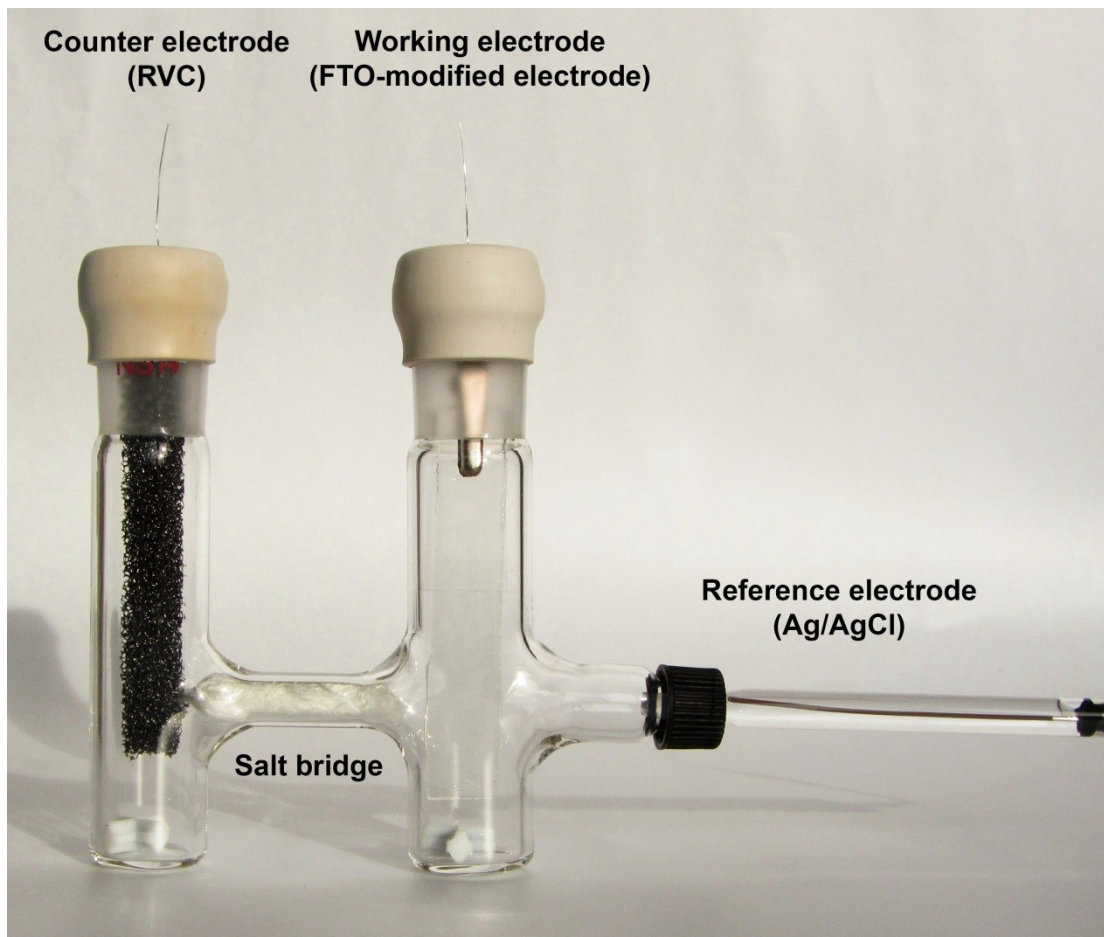
**Figure S3.** UV/vis absorbance spectra of the as-synthesized citrate stabilized IrO<sub>2</sub> nanoparticles (NPs). A cell containing the blue colloid is shown in the inset.

**“Aging” of the Layer-by-Layer (LbL) deposited IrO<sub>2</sub>/PDDA bilayer on FTO electrodes under ambient conditions with time**



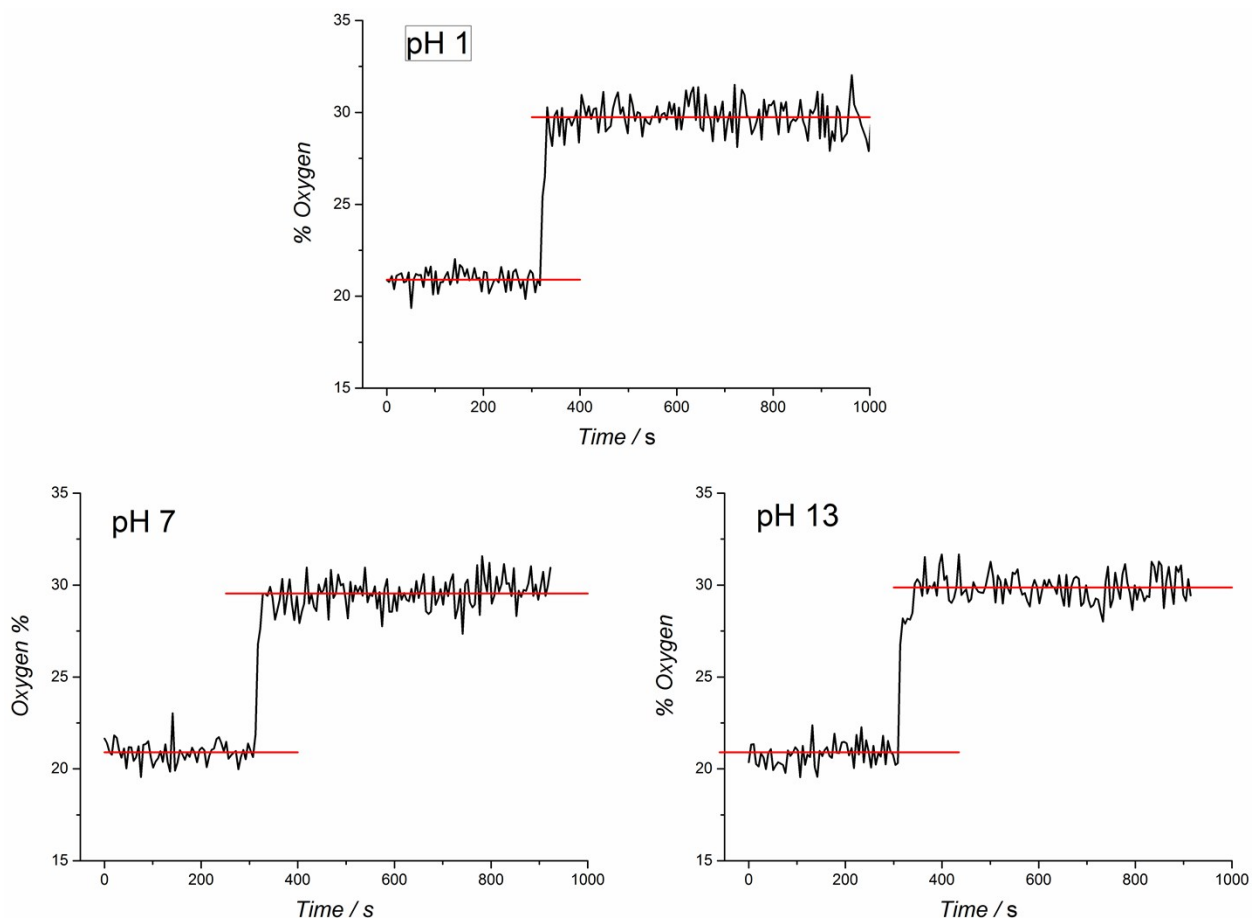
**Figure S4.** UV/vis spectra obtained from an FTO electrode modified with 14 IrO<sub>2</sub>/PDDA bilayers immediately after the synthesis (black line), after 5 days of “aging” (blue line), and after pretreatment by application of a potential of 0.635 V vs. SHE for 90 s *via* chronoamperometry in 0.5 M phosphate buffer solution (pH 7).

## Bulk electrolysis cell: experimental setup



**Figure S5.** Gas-tight bulk electrolysis cell used for electrocatalytic O<sub>2</sub> generation and quantification during IrO<sub>2</sub>/PDDA bilayer stability and OER Faradaic efficiency experiments.

## Experimental determination of the amounts of molecular oxygen (O<sub>2</sub>) evolved during bulk electrolysis experiments at IrO<sub>2</sub>/PDDA-modified FTO electrodes



**Figure S6.** O<sub>2</sub> determination was achieved using a FOXY fluorescent O<sub>2</sub> sensor after bulk electrolysis at each pH investigated.

Quantitative determination of the amounts of O<sub>2</sub> evolved from each FTO electrode modified with 14 IrO<sub>2</sub>/PDDA bilayers as a function of pH was achieved using a FOXY fluorescent O<sub>2</sub> sensor from Ocean Optics. The probe was inserted through a septum into the headspace of the working electrode compartment of the electrolysis cell at the end of each bulk electrolysis

experiment. In each case the amounts of O<sub>2</sub> dissolved in solution were considered negligible and not considered in the following calculations.

For practical reasons bulk electrolysis experiments were performed under aerobic conditions. Thus, in order to determine the amounts of O<sub>2</sub> evolved in moles during bulk electrolysis ( $\eta_{O_2(\text{evolved})}$ ), it was necessary to calculate the total number of moles of O<sub>2</sub> present at the beginning ( $\eta_{O_2(\text{initial})}$ ) and at the end ( $\eta_{O_2(\text{final})}$ ) of each experiment.  $\eta_{O_2(\text{initial})}$  was calculated from the ideal gas equation, taking into account that the initial gas in the head space contains 20.9 % O<sub>2</sub>:

$$\eta_{O_2(\text{initial})} = \left( \frac{P_{\text{atm}} \times V_{\text{HS}}}{R \times T} \right) \times 0.209 \quad (\text{S1})$$

where  $P_{\text{atm}}$  is the atmospheric pressure,  $V_{\text{HS}}$  is the volume of the head space,  $T$  is the room temperature and  $R$  the gas constant.  $\eta_{O_2(\text{final})}$  was calculated as follows:

$$\eta_{O_2(\text{final})} = \left( \frac{\%O_2}{100 - \%O_2} \right) \left( \frac{P_{\text{atm}} \times V_{\text{HS}}}{R \times T} \right) (1 - 0.209) \quad (\text{S2})$$

Therefore,

$$\eta_{O_2(\text{evolved})} = \eta_{O_2(\text{final})} - \eta_{O_2(\text{initial})} \quad (\text{S3})$$

Finally, the Faradaic efficiency was calculated as the ratio between the experimentally determined value of  $\eta_{O_2(\text{evolved})}$  and the theoretical value of  $\eta_{O_2(\text{evolved})}$  determined from Faraday's law based on the quantities of charge ( $Q / C$ ) passed during bulk electrolysis ( $\eta_{O_2(\text{evolved})} = Q / nF$  where  $z$ , the number of electrons transferred per water molecule oxidized, is equal to 4), see Table S2.



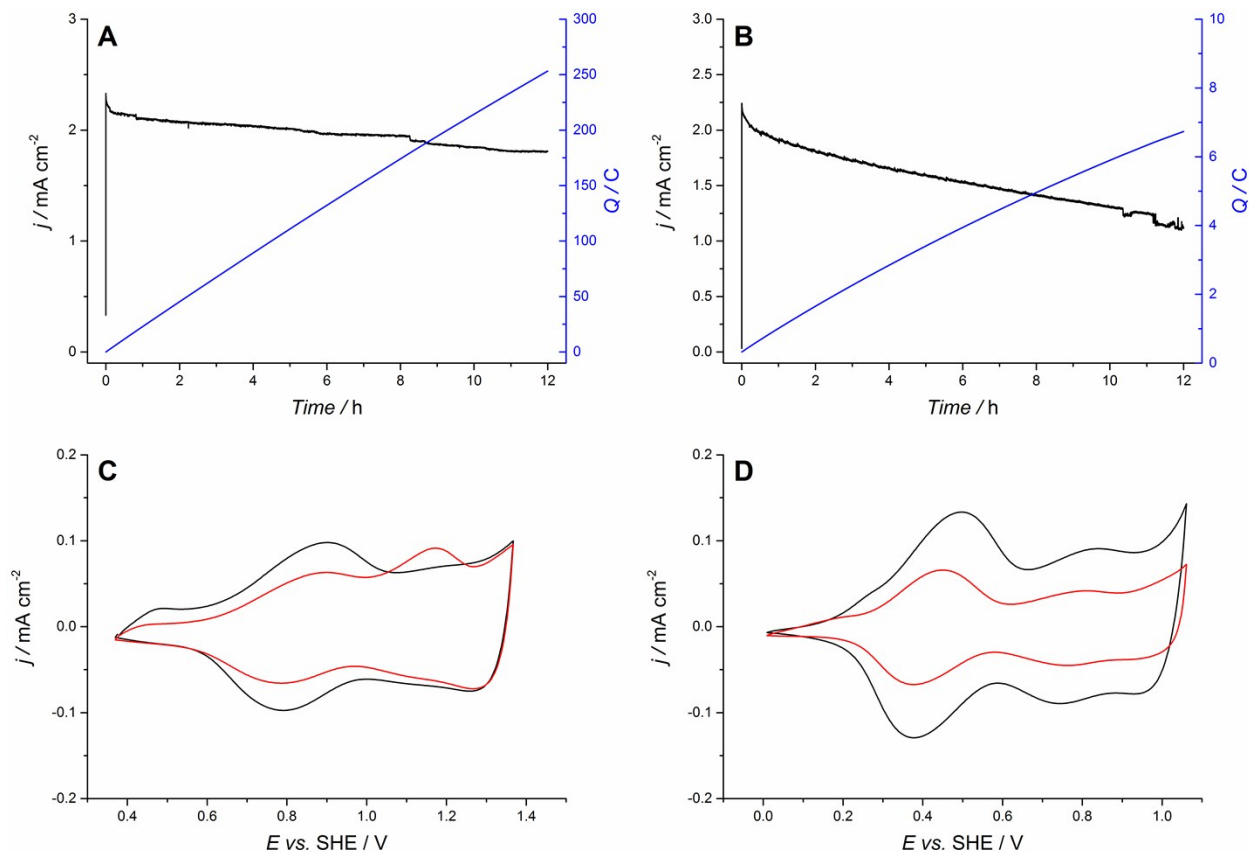
**Table S1.** Summary of the experimentally observed amounts of O<sub>2</sub> evolved ( $\eta_{\text{O}_2(\text{evolved})}$  /  $\mu\text{mol}$ ) using a FOXY fluorescent O<sub>2</sub> sensor from an FTO electrode modified with 14 IrO<sub>2</sub>/PDDA bilayers after bulk electrolysis experiments carried out in 0.1 M HClO<sub>4</sub> (pH = 1), 0.5 M phosphate buffer solution (pH = 7) and 0.1 M NaOH (pH = 13) with applied potentials of 1.57, 1.22 and 0.80 V vs. SHE, respectively.

<b>Experimental Conditions</b>	<b>%O<sub>2</sub>(measured)</b>	<b>Experimentally determined <math>\eta_{\text{O}_2(\text{evolved})}</math> / <math>\mu\text{mol}</math></b>
<b>pH 1</b>	8.98	16.6
<b>pH 7</b>	8.85	17.4
<b>pH 13</b>	9.18	15.6

**Table S2.** Summary of the theoretical amounts of O<sub>2</sub> evolved ( $\eta_{\text{O}_2(\text{evolved})}$  /  $\mu\text{mol}$ ) determined from Faraday's Law at pH 1, 7, and 13, and determination of the Faradaic efficiency as the ratio of the experimentally measured and theoretically predicted values of  $\eta_{\text{O}_2(\text{evolved})}$ .

<b>Experimental Conditions</b>	<b>Charge (Q) / C</b>	<b>Theoretically predicted <math>\eta_{\text{O}_2(\text{evolved})}</math> / <math>\mu\text{mol}</math></b>	<b>Faradaic efficiency / %</b>
<b>pH 1</b>	6.85	17.7	94
<b>pH 7</b>	6.85	17.7	98
<b>pH 13</b>	6.85	17.7	88

## Long term bulk electrolysis experiments at IrO<sub>2</sub>/PDDA-modified FTO electrodes



**Figure S7: Long-term bulk electrolysis experiments.** (A, B) Chronoamperometric plots of the current (black line) and charge (blue line) during water electrolysis using an FTO electrode modified with 14 IrO<sub>2</sub>/PDDA bilayers in a classic bulk electrolysis cell. In each case an overpotential ( $\eta$ ) of +600 mV *versus* the thermodynamic potential for the OER was applied to the working electrode. The experiments were carried out in (A) 0.1 M HClO<sub>4</sub> and (B) 0.5 M phosphate buffer solution (pH = 7). The figures (C, D) depict the CVs recorded before (black line) and after (red line) electrolysis for the systems described in (A, B). The scan rate used was 10 mV·s<sup>-1</sup>.