

Catalytic Water Oxidation on Derivatized *nanoITO*

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Supporting Information

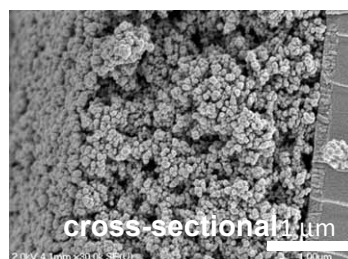
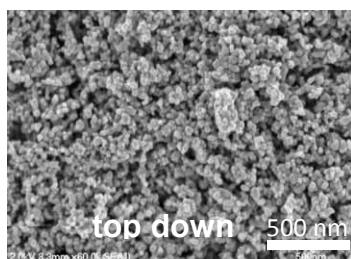
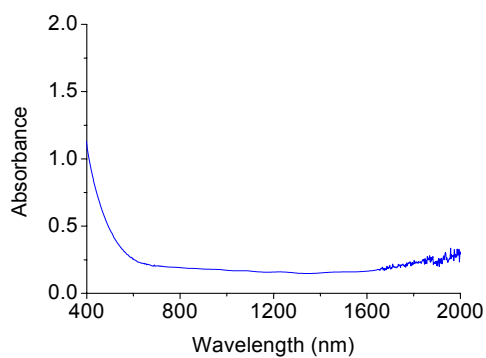


Figure S1. UV-vis-near IR spectrum and SEM images of *oxidized ITO|nanoITO*.

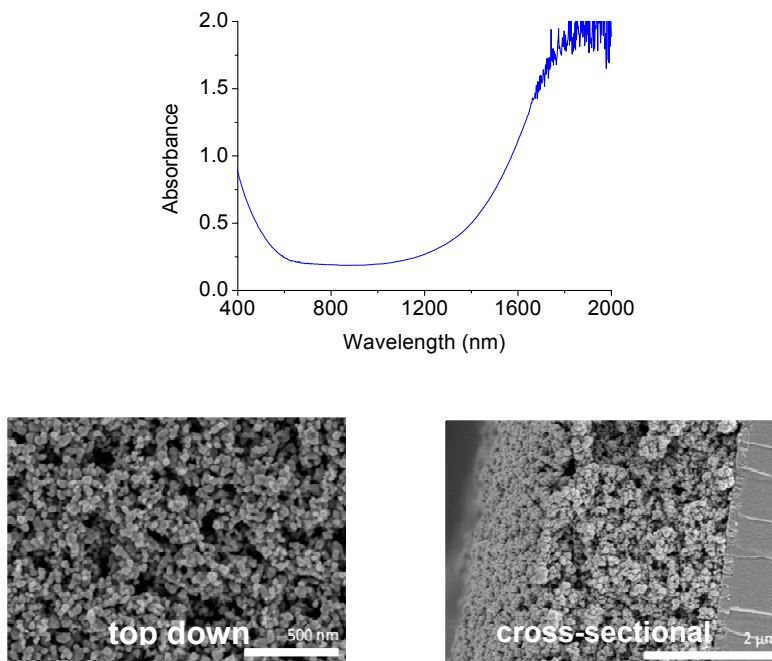


Figure S2. UV-vis-near IR spectrum and SEM images of *reduced ITO|nanoITO*.

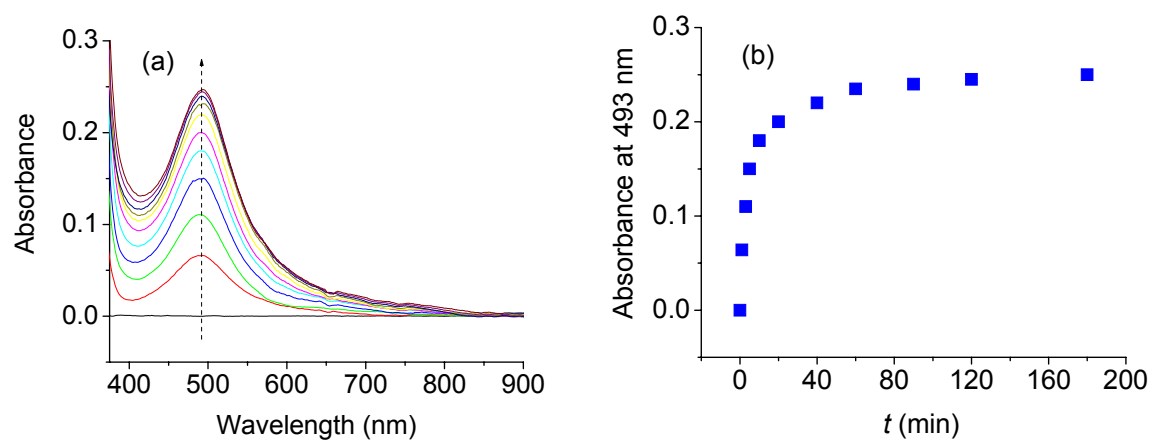


Figure S3. (a) UV-vis spectra of ITO|nanoITO|1-PO₃H₂ after various soaking times in 0.1 mM solution in methanol. (b) Dependence of the absorbance at 493 nm on the soaking time. $\Gamma_0 = 1.7 \times 10^{-8} \text{ mol/cm}^2$ (2.5 \square m, $6.8 \times 10^{-9} \text{ mol/cm}^2 \cdot \square$ m).

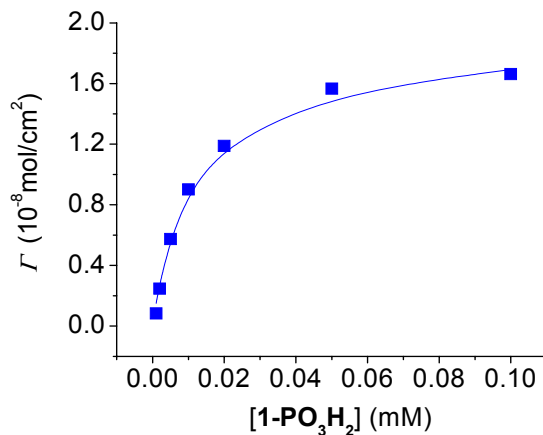


Figure S4. Adsorption isotherm for **1-PO₃H₂** on ITO|*nano*ITO after soaking in methanol stock solution of different concentration for 72 h at 25 °C.

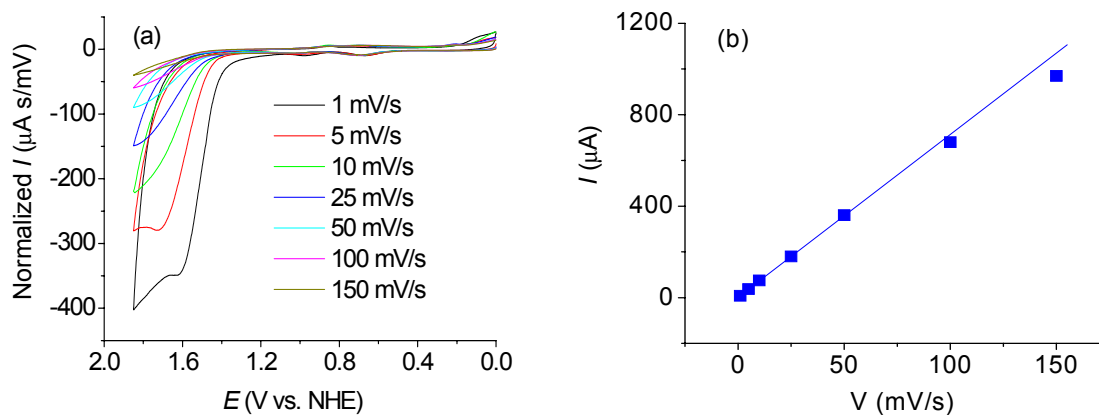


Figure S5. (a) Normalized cyclic voltammograms of ITO|*nano*ITO|**1-PO₃H₂** at pH 5 (0.036 M CH₃CO₂H-0.064 M CH₃CO₂Na) at different scan rates. The currents are normalized for scan rate, i/v . (b) Dependence of the current of the Ru(III/II) redox couple at ITO|*nano*ITO|**1-PO₃H₂** on the scan rate.

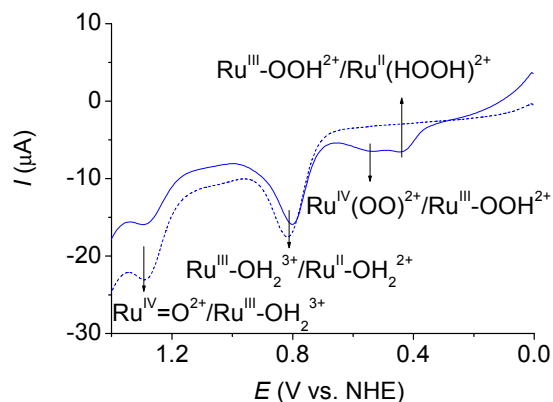


Figure S6. Square wave voltammogram of $\text{Ru}^{\text{IV}}(\text{OO})^{2+}$ (generated by adding $\times 3$ $\text{Ce}(\text{IV})$ to 0.5 mM $\text{Ru}^{\text{II}}\text{-OH}_2^{2+}$) in 0.1 M HNO_3 at a glassy carbon electrode. Incremental potential at each point, 0.004 V; square wave amplitude, 0.025 V; square wave frequency, 15 Hz. The dotted line represents the square wave voltammogram before $\text{Ce}(\text{IV})$ oxidation.

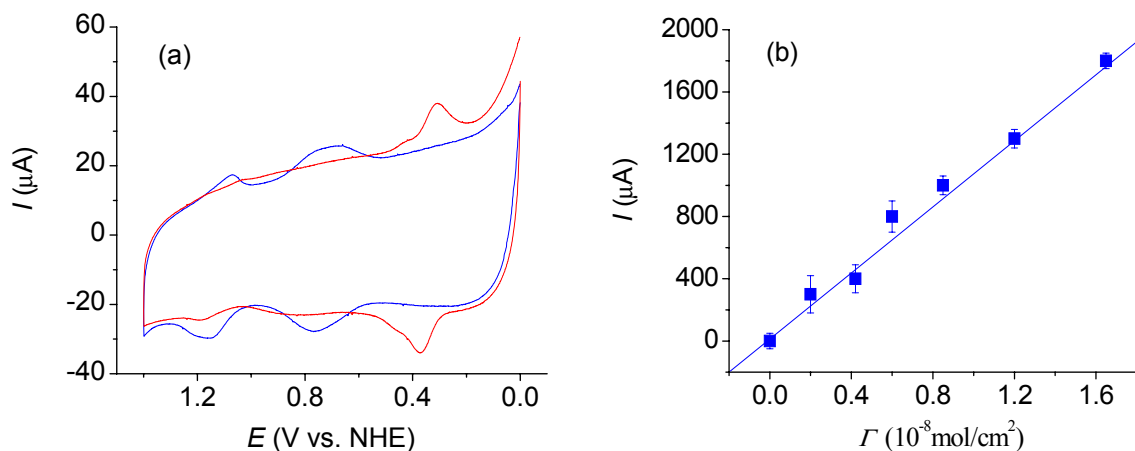


Figure S7. (a) Cyclic voltammograms of $\text{ITO}|\text{nanoITO}|1\text{-PO}_3\text{H}_2$ at pH 3 (0.1 M phosphate buffer) before (blue line) and after (red line) scanning to 1.85 V. Scan rate, 10 mV/s; $\Gamma = 1.8 \times 10^{-9}$ mol/cm² ($2.5 \square$ m, 7.2×10^{-10} mol/cm²· \square m). (b) Dependence of the electrocatalytic

current (*nano*ITO background subtracted) at 1.85 V vs NHE at pH 5 (0.036 M CH₃CO₂H-0.064 M CH₃CO₂Na) on surface complex loading. Scan rate, 10 mV/s.

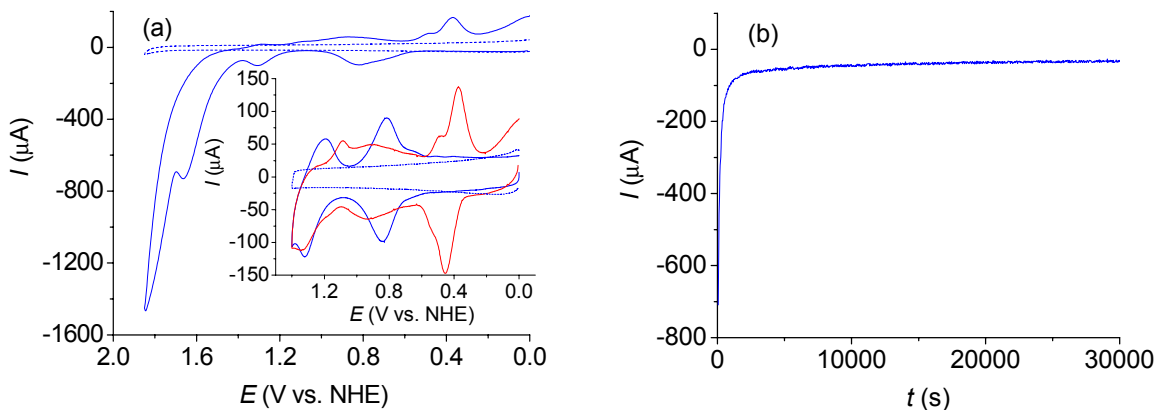


Figure S8. (a) Cyclic voltammogram of ITO|*nano*ITO|1-PO₃H₂ at pH 1 (0.1 M HNO₃) at a scan rate of 10 mV/s. The dotted line is the ITO|*nano*ITO background under the same experimental conditions. The inset shows cyclic voltammograms of ITO|*nano*ITO|1-PO₃H₂ at pH 1 before (blue line) and after (red line) scanning to 1.85 V. (b) Electrolysis of ITO|*nano*ITO|1-PO₃H₂ at 1.85 V vs NHE at pH 1. Number of turnovers ≈ 180 , turnover frequency $\approx 0.006 \text{ s}^{-1}$ (background subtracted). $\Gamma = 1.7 \times 10^{-8} \text{ mol/cm}^2$, area = 1.25 cm², current density $\approx 40 \text{ } \square \text{ A/cm}^2$ (16 $\square \text{ A/cm}^2 \cdot \square \text{ m}$).

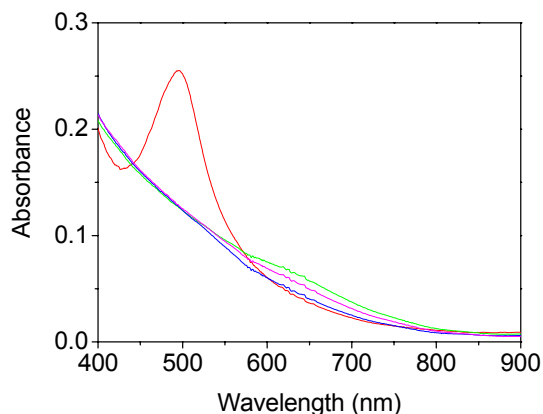


Figure S9. UV-vis spectra of ITO|*nano*ITO|1-PO₃H₂ (red line), and following potential scans to 1.1 V (green line), 1.40 V (blue line) and 1.85 V (magenta line) vs NHE. Solution, pH 1 (0.1 M HNO₃); scan rate, 10 mV/s.

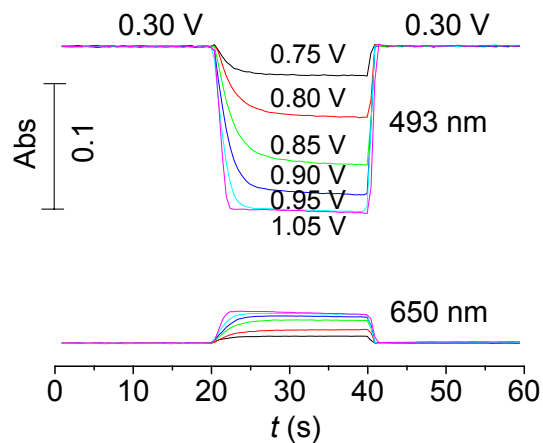


Figure S10. Changes in absorbance of ITO|*nano*ITO|1-PO₃H₂ at 493 nm and 650 nm with time during a potential step from 0.30 V vs NHE to the potentials indicated in the figure, followed by step backward to 0.30 V. Solution, pH 1 (0.1 M HNO₃).

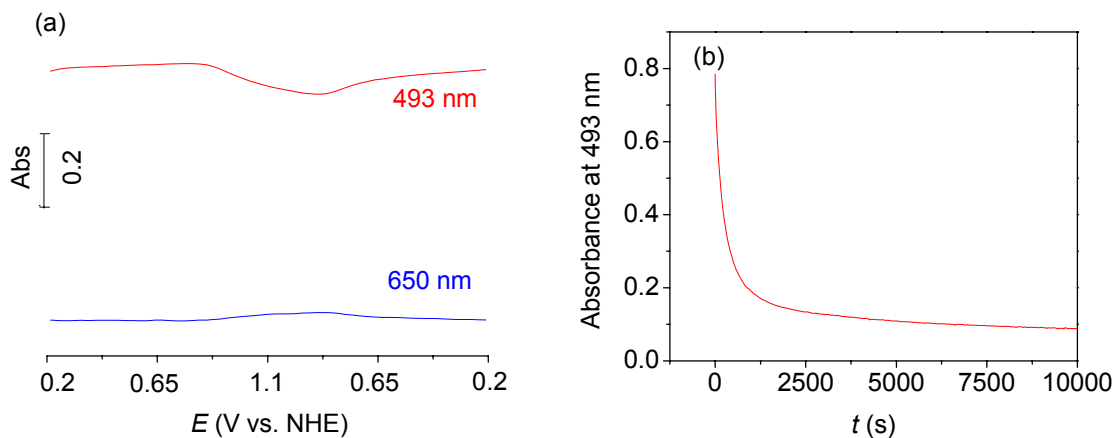


Figure S11. (a) Spectra evolution of FTO|*nano*TiO₂|1-PO₃H₂ at pH 1 (0.1 M HNO₃) during CV scan between 0.2 - 1.1 V. The monitoring wave lengths are $\lambda_{\text{max}} = 493$ nm for Ru^{II}-OH₂²⁺ (red line), and $\lambda_{\text{max}} = 650$ nm for Ru^{III}-OH₂³⁺ (blue line). Scan rate, 10 mV/s. *nano*TiO₂ $\Gamma = 5.3 \times 10^{-8}$ mol/cm² (10 \square m, 5.3×10^{-9} mol/cm²· \square m). Only ~8% of the available sites were electroactive as calculated from the absorption decrease at $\lambda_{\text{max}} = 493$ nm during 10 mV/s cyclic scan. (b) Absorbance change (493 nm) of FTO|TiO₂|1-PO₃H₂ at pH 1 (0.1 M HNO₃) with potential hold at 0.95 V vs NHE past $E_{1/2}$ for Ru^{III}-OH₂³⁺/Ru^{II}-OH₂²⁺ couple.