Catalytic Water Oxidation on Derivatized \textit{nano}ITO

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Supporting Information

\textbf{Figure S1.} UV-vis-near IR spectrum and SEM images of oxidized ITO|\textit{nano}ITO.
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. $I_o = 1.7 \times 10^{-8}$ mol/cm² (2.5 μm, 6.8 × 10⁻⁹ mol/cm²·μm).
**Figure S4.** Adsorption isotherm for $1$-$PO_3H_2$ on ITO$|$nanoITO after soaking in methanol stock solution of different concentration for 72 h at 25 °C.

**Figure S5.** (a) Normalized cyclic voltammograms of ITO$|$nanoITO$|$1-$PO_3H_2$ at pH 5 (0.036 M CH$_3$CO$_2$H-0.064 M CH$_3$CO$_2$Na) 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$|$nanoITO$|$1-$PO_3H_2$ on the scan rate.
Figure S6. Square wave voltammogram of Ru$^{IV}$(OO)$^{2+}$ (generated by adding $\times$ 3 Ce(IV) to 0.5 mM Ru$^{II}$-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 Ce(IV) oxidation.

Figure S7. (a) Cyclic voltammograms of ITO|nanoITO|1-PO$_3$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/cm$^2$ (2.5 m, 7.2 $\times$ 10$^{-10}$ mol/cm$^2$). (b) Dependence of the electrocatalytic
current (nanoITO 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|nanoITO|1-PO₃H₂ at pH 1 (0.1 M HNO₃) at a scan rate of 10 mV/s. The dotted line is the ITO|nanoITO background under the same experimental conditions. The inset shows cyclic voltammograms of ITO|nanoITO|1-PO₃H₂ at pH 1 before (blue line) and after (red line) scanning to 1.85 V. (b) Electrolysis of ITO|nanoITO|1-PO₃H₂ at 1.85 V vs NHE at pH 1. Number of turnovers ≈ 180, turnover frequency ≈ 0.006 s⁻¹ (background subtracted). $I = 1.7 \times 10^{-8}$ mol/cm², area = 1.25 cm², current density ≈ 40 A/cm² (16 A/cm²·m).
Figure S9. UV-vis spectra of ITO|nanoITO|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|nanoITO|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|nanoTiO$_2$|1-PO$_3$H$_2$ at pH 1 (0.1 M HNO$_3$) during CV scan between 0.2 - 1.1 V. The monitoring wave lengths are $\lambda_{\text{max}} = 493$ nm for Ru$^{II}$-OH$_2^{2+}$ (red line), and $\lambda_{\text{max}} = 650$ nm for Ru$^{III}$-OH$_2^{3+}$ (blue line). Scan rate, 10 mV/s. nanoTiO$_2$ $\Gamma = 5.3 \times 10^{-8}$ mol/cm$^2$ (10 $\mu$m, $5.3 \times 10^{-9}$ mol/cm$^2$·$\mu$m). Only $\sim$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|TiO$_2$|1-PO$_3$H$_2$ at pH 1 (0.1 M HNO$_3$) with potential hold at 0.95 V vs NHE past $E_{1/2}$ for Ru$^{III}$-OH$_2^{3+}$/Ru$^{II}$-OH$_2^{2+}$ couple.