Electronic Supplementary Information

Comparison of Heterogenized Molecular and Heterogeneous Oxide Catalysts for Photoelectrochemical Water Oxidation

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Figure S1. Normalized IMPS response of (a) bare hematite (b) hematite with het-WOC (c) hematite with IrOx. Low frequency intercept was determined by extrapolating the semicircle.
Figure S2. TEM images of hematite with IrO$_x$ surface (with 5 s, 25 s and 90 s deposition time respectively). All transmission electron micrographs were taken on a JEOL 2010F microscope operating at an acceleration voltage of 200 kV.

A layer of amorphous IrO$_x$ can be observed in the TEM images, which is not the case for the het-WOC. A thicker film is observed from left to right, as expected with gradually higher deposition times, indicating the increasing loading of IrO$_x$.

Figure S3. Steady-state current-voltage curves of bare hematite, hematite with het-WOC (overnight) and hematite with IrO$_x$ (90 s).
The loading amount of het-WOC was determined by ICP-OES (Agilent 5100 ICP-OES, Agilent Technologies). The catalyst was detached by soaking het-WOC-covered hematite in a 1 M NaOH solution for 24 h. Then, the solution was acidified with nitric acid for ICP-OES measurement. Since het-WOC adsorption is a self-limiting process, optimized surface-binding of the catalyst should be expected when soaking the hematite substrate for a sufficiently long time. The irregular trend at 5 h of het-WOC soaking time is an artifact from hematite etching, caused by the acidic catalyst precursor solutions.
Figure S5. (a) Charge transfer efficiency (TE) and (b) Steady-state current-voltage curves of hematite with het-WOC with different soaking time. (c) Charge transfer efficiency (TE) and (d) Steady-state current-voltage curves of hematite with IrOₓ with shorter deposition times (<90 s) and (e) longer deposition times (>90 s).
According to Hamann and Bisquert’s analysis, surface state capacitance can be expressed into the following equation:

\[ C_{\text{trap}} = A_s N_{\text{ss}} q \frac{\partial f_{\text{ss}}}{\partial E_{\text{Fn}}} = A_s N_{\text{ss}} q^2 \frac{k_B T}{f_{\text{ss}}^2} f_{\text{ss}}(1 - f_{\text{ss}}) \]

\( N_{\text{ss}} \) is density of the surface states, \( f_{\text{ss}} \) is the occupancy of the states, and \( E_{\text{Fn}} \) is the electron Fermi level of the state. The \( C_{\text{trap}} \) will trace a peak with respect to Fermi level variation at the point \( E_{\text{Fn}} = E_{\text{ss}}(f_{\text{ss}} = 0.50) \), where \( E_{\text{ss}} \) is the energy level of the surface state. Consequently, \( R_{\text{ct,trap}} \) can be defined as \( R_{\text{ct,trap}} = \frac{1}{k_{\text{ss}} C_{\text{trap}}} \) (\( k_{\text{ss}} \) is rate constant for charge transfer). From the plot, the increase of \( C_{\text{trap}} \) is correlated with the decrease of \( R_{\text{ct,trap}} \), and the photocurrent onset is also coincident with the charging of surface states and the decrease of \( R_{\text{ct,trap}} \). The results here imply that holes transfer for water oxidation takes place through surface states, which is consistent with Hamann and Bisquert’s previous work.
Figure S7. (a) Nyquist plot of hematite with IrO₅ (90 s). Three semicircles can be observed and can’t be unambiguously fit. Nyquist plots (squares) measured at an applied potential of 0.93 V vs RHE and fitting results (solid lines) of (b) bare hematite and hematite with het-WOC (overnight) (c) bare hematite and hematite with IrO₅ (10 s). Two semi-circles can be observed.
Figure S8. (a) $C_{\text{het-WOC}}$ of hematite with het-WOC (overnight) and $C_{\text{trap}}$ of bare hematite (b) $C_{\text{IrOx}}$ of hematite with IrO$_x$ (10 s) and $C_{\text{trap}}$ of bare hematite obtained from EIS. (c) $R_{\text{ct,het-WOC}}$ of hematite with het-WOC (overnight) and $R_{\text{ct,trap}}$ of bare hematite (d) $C_{\text{IrOx}}$ of hematite with IrO$_x$ (10 s) and $R_{\text{ct,trap}}$ of bare hematite obtained from EIS.
In the case of bare hematite, due to severe surface Fermi-level pinning, photovoltage gained under illumination is limited. Moreover, the charge transfer from surface states to water is slow and recombination at the surface states is fast. With het-WOC decoration, the nature of surface states inherent to bare hematite remains, so that the recombination still takes place at the surface states and remains the same as bare hematite. However, molecular het-WOC provides a new reaction route, speeding up charge transfer towards water oxidation due to its high turnover frequency and resulting in improved charge transfer efficiency and PEC performance. With the decoration of IrO$_x$, surface states are almost completely passivated, thus the photovoltage gained is much larger. What’s more, IrO$_x$ can serve as a hole storage layer to enhance the charge separation and suppress the charge recombination. Because of the high activity of the IrO$_x$ catalyst, charge transfer from IrO$_x$ layer to water is also increased. Combining these reasons together, IrO$_x$ decoration also gives a better performance than bare hematite.
Figure S10. (a) $C_{\text{bulk}}$ obtained from EIS performed in dark (b) Mott-Schottky plots obtained from Nyquist plots for bare hematite, hematite with IrO$_x$ and hematite with het-WOC.

From Mott-Schottky plots, a deviation at $1.0 \sim 1.2$ V vs. RHE for hematite with IrO$_x$ is observed that is not present for bare hematite and hematite with het-WOC. This deviation in capacitive measurements can be generally related to surface states, as noted by Sukigara *et al.*$^5$ based on calculated and experimental data. Although IrO$_x$ covers the hematite surface and passivates the original surface states of hematite, it forms a new IrO$_x$/electrolyte interface. The formation of this interface introduces new surface states that are distinct from those present at the hematite/electrolyte interface and possess different capacitive behavior in this voltage range.

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<th>Flat band potential</th>
<th>Donor Conc.</th>
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<tr>
<td>Bare hematite</td>
<td>0.50 $\text{V}_{\text{RHE}}$</td>
<td>$3.96 \times 10^{18}$ cm$^{-3}$</td>
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<tr>
<td>Hematite/het-WOC</td>
<td>0.48 $\text{V}_{\text{RHE}}$</td>
<td>$3.49 \times 10^{18}$ cm$^{-3}$</td>
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<tr>
<td>Hematite/IrO$_x$</td>
<td>0.35 $\text{V}_{\text{RHE}}$</td>
<td>$2.79 \times 10^{18}$ cm$^{-3}$</td>
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Table S1. Flat band potentials and donor concentration of bare hematite, hematite with IrO$_x$ and hematite with het-WOC derived from Mott-Schottky plots.

Supplementary References:


