Supporting Information for Selective Water Oxidation to H₂O₂ on TiO₂ Surfaces

with Redox-Active Allosteric Sites

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Section S1. Surface Model Structures

To identify the most stable configurations of the introduced metal and hydrogen atom in TiO₂, we calculated the relative energies of the models with the proton at different adjacent O around the introduced metal atoms by setting the lowest energy as zero. Due to the symmetry of the slab models, the O at the short axes are equivalent along the [001] direction. Therefore, we only considered four situations here as shown in Figure S1 and S2. The results indicate that the proton would be more favorable to appear at the O in the long axis of the introduced metals in most cases. Specially, for the models with Co alloyed at B site, the proton at the short axis O is slightly more stable than at the long axis. However, since their energies are very close, we still use the models with proton at the long axis O for all calculations. Furthermore, we have also proved that the catalytic properties of these Co alloyed models with the proton at different positions are quite similar as shown in Figure S10.



Cr, Mn, Fe, and Co at A site in TiO₂

Figure S1. The relative energies of the A site alloyed models with H at different positions. Color scheme for atoms: light blue for Ti, red for O, white for H, green for Cr, purple for Mn, yellow for Fe, and dark blue for Co.



Cr, Mn, Fe, and Co at B site in TiO₂

Figure S2. The relative energies of the B site alloyed models with H at different positions. The color scheme is the same as Figure S1.

Section S2. Density of States

Figure S3 displays the element-projected density of states (DOS) of all surface models relative to the potential of standard hydrogen electrode (SHE). For the B site alloyed models (i.e. Cr_B, Mn_B, Fe_B, and Co_B), the proton and the reduced metal ion would induce a dipole along the normal direction of the surface. This dipole could affect the electrostatic potential distribution in the surface models and lead to a shift of the DOS curves toward the negative potential direction.



Figure S3. Element-projected DOS of all surface models. The grey lines represent the total DOS of the systems and the filled regions indicate these states are occupied. Color scheme of lines: light blue for Ti, red for O, green for Cr, purple for Mn, yellow for Fe, and dark blue for Co.

Section S3. Spin Density Distributions

Figure S4-S8 display the structures and spin density distributions of the water oxidation intermediates on clean and alloyed TiO_2 surface models, and their relationship in the reactions are also drawn. The atomic magnetic moments are given to illustrate the oxidation states of the relevant species, which are equivalent to their spin populations. The results indicate that the introduced redox-active metals would be oxidized from +3 to +4 valence state in the first reaction step of HO* formation. While in the next reaction step from HO* to O*, the intermediate itself would be oxidized on all surface models. Moreover, we found that the antiferromagnetic coupling between the intermediates and substrates is more stable than ferromagnetic coupling.



Figure S4. Structures and spin density distributions of the water oxidation intermediates on clean TiO₂ surface models. The yellow region is the spin density distribution with the iso-surface level of 0.03 e/bohr⁻³ and the magnetic moments of the relevant atoms are shown in $\mu_{\rm B}$.



Figure S5. Structures and spin density distributions (with the iso-surface level of 0.03 e/bohr⁻³) of the water oxidation intermediates on Cr(III) alloyed TiO₂ surface models. Yellow and blue regions represent the spin up and spin down electrons, respectively. The magnetic moments of the relevant atoms are shown in $\mu_{\rm B}$.



Figure S6. Structures and spin density distributions (with the iso-surface level of 0.03 e/bohr⁻³) of the water oxidation intermediates on Mn(III) alloyed TiO₂ surface models. Yellow and blue regions represent the spin up and spin down electrons, respectively. The magnetic moments of the relevant atoms are shown in $\mu_{\rm B}$.



Figure S7. Structures and spin density distributions (with the iso-surface level of 0.04 e/bohr⁻³) of the water oxidation intermediates on Fe(III) alloyed TiO₂ surface models. Yellow and blue regions represent the spin up and spin down electrons, respectively. The magnetic moments of the relevant atoms are shown in $\mu_{\rm B}$.



Figure S8. Structures and spin density distributions (with the iso-surface level of 0.03 e/bohr⁻³) of the water oxidation intermediates on Co(III) alloyed TiO₂ surface models. Yellow and blue regions represent the spin up and spin down electrons, respectively. The magnetic moments of the relevant atoms are shown in $\mu_{\rm B}$.

Section S4. Reaction Energy Diagrams

Figure S9 displays the reaction free energy diagrams of water oxidation on alloyed TiO₂ surface models accompanied with the results on clean TiO₂ for comparison. It reveals that the introduced redox-active metals could simultaneously reduce the ΔG_{HO*} and ΔG_{O*} while maintain the rest variables. Figure S10 shows that the catalytic properties of the models with Co at B site are barely affected by the position of the proton.



Figure S9. Reaction free energy diagrams of water oxidation on alloyed TiO_2 surface models. The results on clean TiO_2 are drawn for comparison.



Figure S10. Reaction free energy diagrams of water oxidation on Co_B alloyed TiO₂ surface models with the proton at different positions. The names of the models are consistent with Figure S2.

Section S5. H₂O₂ Product Quantification

Figure S11 shows the UV-visible (UV-Vis) spectroscopy data of different amounts of KMnO4 in the operating electrolyte. The intensity at 500nm was plotted against the volume of KMnO4 solution added to enable the precise calculation of the titration endpoint through quantification of the quantification of over titration.



Figure S11. UV-vis over titration data of 20, 40, 60, 80, 100 μ L of a known concentration of KMnO₄ in 0.5M PBS.



Figure S12. Regression of background corrected intensity at 500 nm vs quantity of titrant added

from Figure S11.

Equation	$y = a + b^*x$
Plot	Absorption at 500
Weight	No Weighting
Intercept	0 ±
Slope	$0.00366 \pm 2.46703E-5$
Residual Sum of	6.69E-05
Squares	
Pearson's r	0.99989
R-Square (COD)	0.99977
Adj. R-Square	0.99973

 Table S1: Statistical results from Figure S12.

The generated H_2O_2 molar quantity was quantified by using KMnO₄ titration. The linear relationship between the UV-vis adsorption intensity and Mn⁷⁺ concentration was determined (**Figure S11**). During KMnO₄ titration, dark purple MnO₄⁻ will be reduced to a clear solution by H_2O_2 . The reaction is presented as **Equation S1**:

$$2MnO_4^- + 5H_2O_2 + 6H^+ \to 2Mn^{2+} + 5O_2 + 8H_2$$
(S1)

Therefore, the total molar quantity (n) of H_2O_2 generated can be calculated by,

$$n(H_2O_2) = \frac{5}{2}n(MnO_4^-)$$
 (S2)

A 1mL aliquot of the sample was taken from a blank reactor solution and mixed with 2 mL of $1M H_2SO_4$ in order to lower the pH to prevent Mn(VII) disproportionation. That solution was then added with 20, 40, 60, 80, and 100 uL of KMnO4 titrant solution so that the quantity of excess KMnO4 remaining after titration could be quantified.

Faraday efficiency (FE) for H_2O_2 production, measured in percentage, can be calculated by Equation S3:

$$FE = \frac{Amount \text{ of experimentally generated } H_2O_2(mol)}{Amount \text{ of theoretically generated } H_2O_2(mol)} \times 100\%$$
(S3)

where the amount of experimentally generated H_2O_2 can be calculated by titration (Equation S3), and the amount of theoretically generated H_2O_2 can be calculated based on the measured total charge passed at the electrode, assuming a FE=100% for 2e⁻ water oxidation (Equation S4).

Amount of *theoretically* generated
$$H_2O_2(mol) = \frac{Q(C)}{F(C/mol) \times 2}$$
 (S4)

where Q is the charge (C) passed during electrolysis, F is the Faraday constant (96485.3 C·mol⁻¹), 2 is for the 2e⁻ transfer process.

Section S6. Electrocatalytic Stability Test

The electrocatalytic stability, shown in Figure S11, of the TiMnOx catalyst was measured by fixing the current at 1.0 mA/cm² and allowing the cell voltage to vary to maintain that current density. The increase in cell voltage is related to the amount of overpotential needed to drive the reaction, increasing as the catalyst deactivates. This increase in cell voltage is relatively small, only 50 mV between the time points of 5 and 50 hours, suggesting minimal deactivation in that time window. Figure S12 shows that the surface morphology and the relative atomic percentages of O, Ti, and Mn of the catalyst remains constant before and after the 50 hours. EDS mapping, Figure S13, shows that the relative distribution of the elements on the surface also remains constant.



Figure S11 Chronoamperometry of TiMnOx/FTO at 1 mA/cm² in 0.5M Phosphate Buffer Solution, pH 7.4 with stirring at 500 RPM. Conducted in a one compartment cell, with a SCE reference electrode, and carbon rod counter electrode. $V_{RHE} = V_{SCE} + 0.242 + .059*7.4$,



Figure S12 Plan view SEM and overall EDS spectra of the TiMnOx/FTO electrode used in Figure S11, before (a, c) and after, (b, d). The morphology and elemental composition of the TiMnOx structure is predominately unchanged after 50 hours.

Element	Peak Position	TiMnOx Before	TiMnOx After
	(keV)	(Normalized Intensity)	(Normalized Intensity)
Oxygen	0.4-0.6	0.00187 +/001	0.00192 +/001
Manganese	4.5-4.7	0.02487 +/001	0.02497 +/001
Titanium	5.8-6.0	0.01077 +/001	0.01067 +/001

Table S2 Total spectra normalized peak intensities of O, Mn, and Ti before and after 50 hours of electrolysis.



Figure S13 Plan-view EDS of the TiMnOx/FTO electrode used in Figure S11. The Mn and Ti elemental distribution within the amorphous TiMnO_x structure is predominately unchanged after 50 hours.

Section S7. Linear Sweep Voltammetry

Linear Sweep Voltammetry conducted in 0.5M pH 7.4 Phosphate Buffer Solution, with TiMnOx working electrode, carbon rod counter electrode, and SCE reference electrode show the onset potential near the thermodynamic potential for H_2O_2 production, 1.77 V_{RHE} .



Figure S14 LSV of TiMnOx with and without post-reaction iR correction

Section S8. X-Ray Diffraction

X-Ray Diffraction, Figure S15, of TiMnOx show the absence of any peaks associated with crystallinity, verifying that the TiMnOx is amorphous, consistent with the low temperature ALD growth process.



Figure S15 X-ray Diffraction of TiMnOx