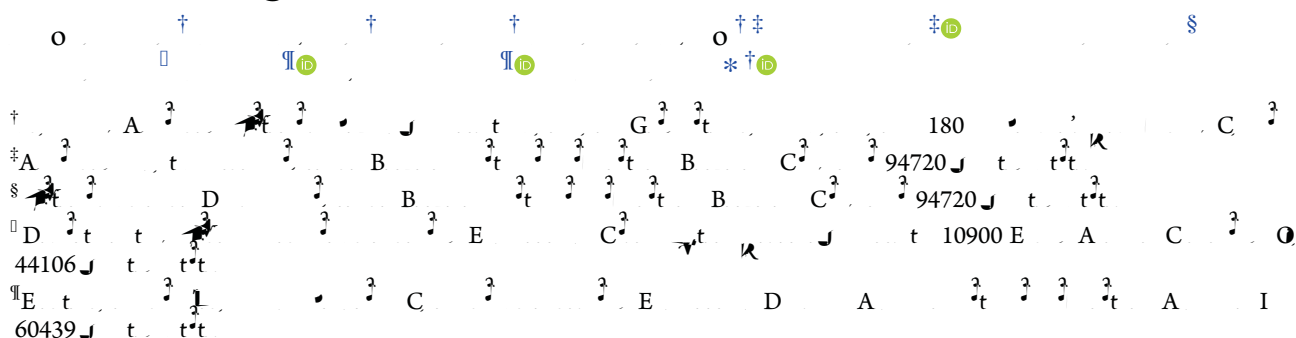


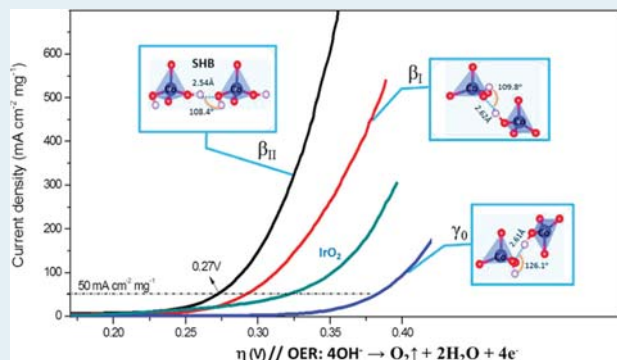
Short Hydrogen Bond on Reconstructed Nanocrystal Surface Enhance Oxygen Evolution Activity



Supporting Information

ABSTRACT:

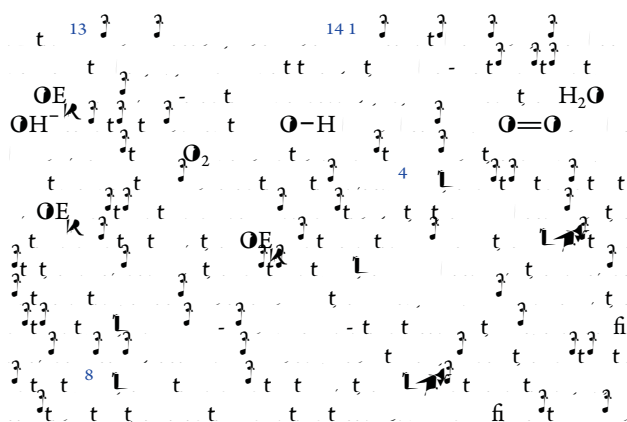
The oxygen evolution reaction (OER) is a key process in renewable energy conversion. In this work, we report a reconstructed nanocrystal surface of $\beta_{II'}\text{-Li}_2\text{CoSiO}_4$ that exhibits enhanced OER activity. The surface is characterized by short hydrogen bonds (SHB) and proton transfer and dissociation, which significantly improve the OER activity. The OER activity is evaluated by the current density (mA cm⁻² mg⁻¹) as a function of the potential (V) for the OER: $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$. The OER activity is significantly enhanced on the reconstructed surface compared to the bulk material. The OER activity is also evaluated by the Tafel slope (mV dec⁻¹ log j) as a function of the potential (V) for the OER: $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$. The Tafel slope is significantly reduced on the reconstructed surface compared to the bulk material. The OER activity is also evaluated by the overpotential (mV) as a function of the current density (mA cm⁻² mg⁻¹) for the OER: $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$. The overpotential is significantly reduced on the reconstructed surface compared to the bulk material.



KEYWORDS: $\beta_{II'}\text{-Li}_2\text{CoSiO}_4$, nanocrystal surface, short hydrogen bond, proton transfer and dissociation, oxygen evolution activity

INTRODUCTION

The oxygen evolution reaction (OER) is a key process in renewable energy conversion. In this work, we report a reconstructed nanocrystal surface of $\beta_{II'}\text{-Li}_2\text{CoSiO}_4$ that exhibits enhanced OER activity. The surface is characterized by short hydrogen bonds (SHB) and proton transfer and dissociation, which significantly improve the OER activity. The OER activity is evaluated by the current density (mA cm⁻² mg⁻¹) as a function of the potential (V) for the OER: $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$. The OER activity is significantly enhanced on the reconstructed surface compared to the bulk material. The OER activity is also evaluated by the Tafel slope (mV dec⁻¹ log j) as a function of the potential (V) for the OER: $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$. The Tafel slope is significantly reduced on the reconstructed surface compared to the bulk material. The OER activity is also evaluated by the overpotential (mV) as a function of the current density (mA cm⁻² mg⁻¹) for the OER: $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$. The overpotential is significantly reduced on the reconstructed surface compared to the bulk material.



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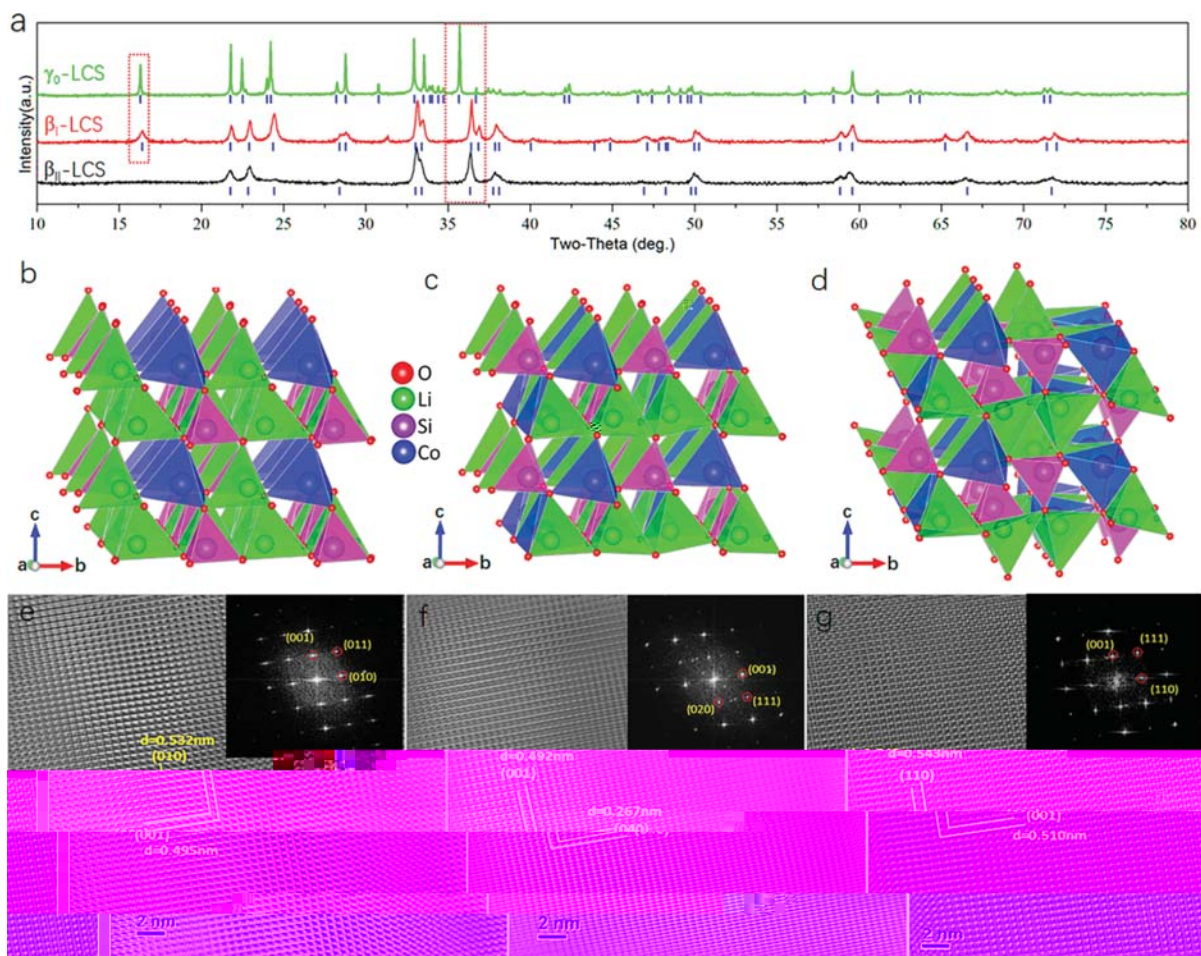
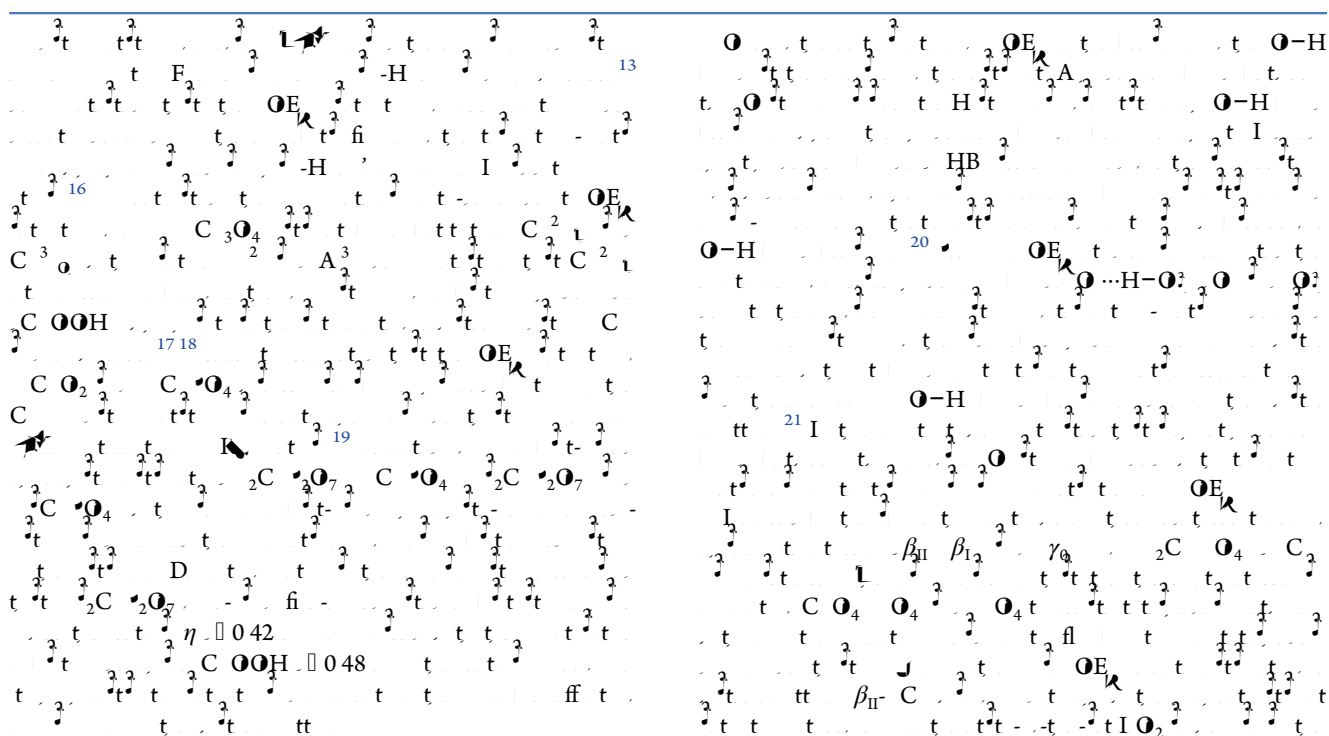


Figure 1. (a) XRD patterns of β_{II} -LCS, β_I -LCS, and γ_0 -LCS phases. (b) Crystal structure of β_{II} -LCS. (c) Crystal structure of β_I -LCS. (d) Crystal structure of γ_0 -LCS. (e) HRTEM image and SAED pattern of β_{II} -LCS. (f) HRTEM image and SAED pattern of β_I -LCS. (g) HRTEM image and SAED pattern of γ_0 -LCS.



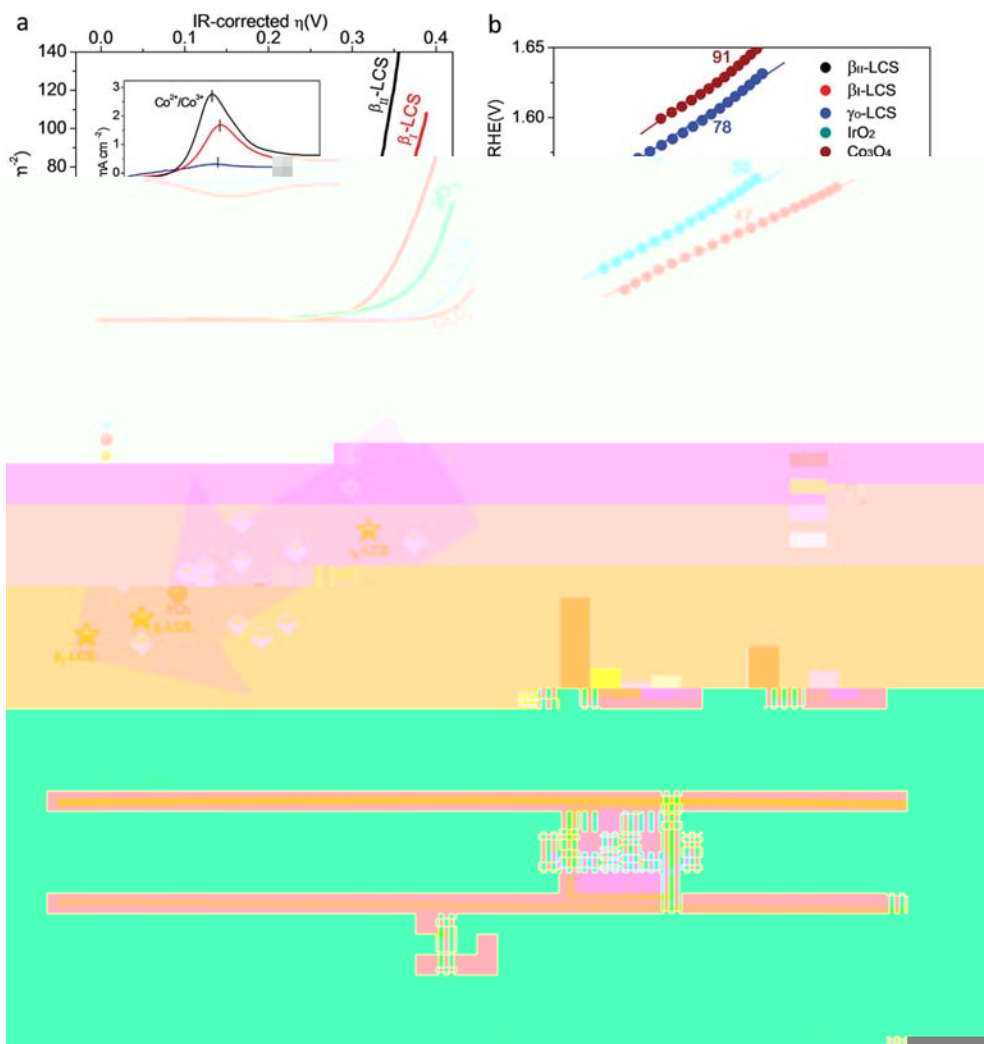


Figure 2. (a) IR-corrected η (V) vs. potential for β_{II} -LCS and β_I -LCS. (b) RHE(V) vs. potential for β_{II} -LCS, β_I -LCS, γ_0 -LCS, IrO_2 , and Co_3O_4 . The schematic shows the electrocatalytic system.

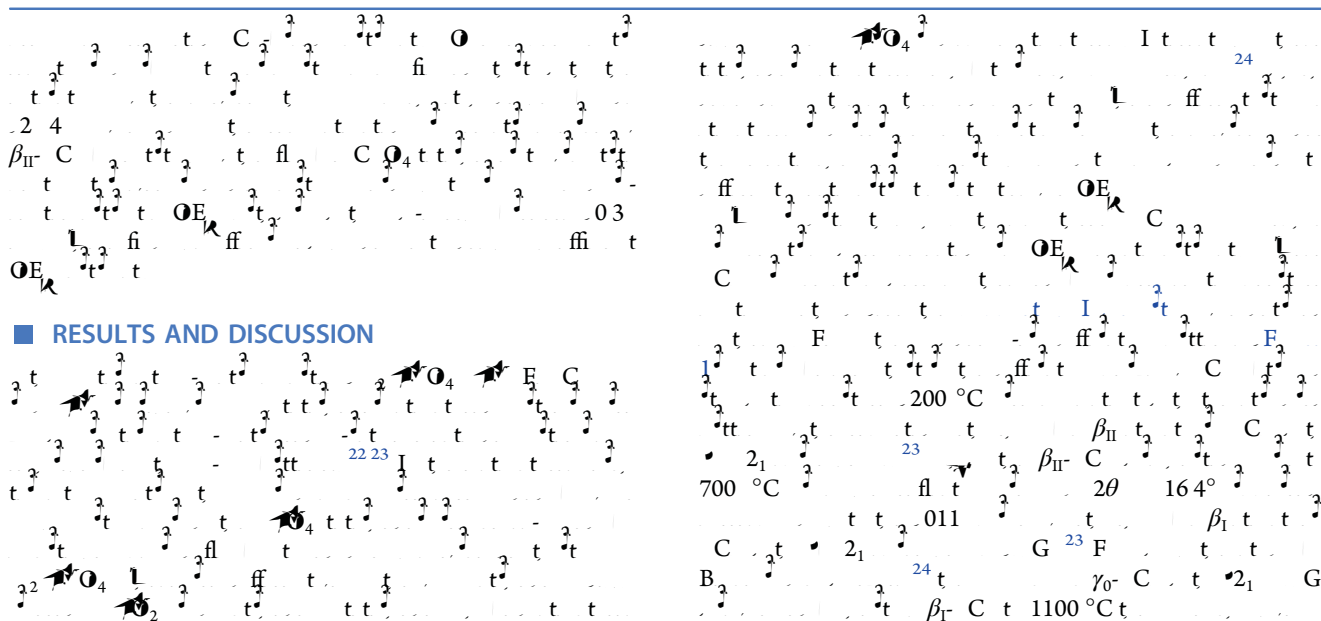


Figure 3. (a) XRD patterns of β_{II} -LCS, β_I -LCS, γ_0 -LCS, IrO_2 , and Co_3O_4 . (b) XRD patterns of β_{II} -LCS, β_I -LCS, γ_0 -LCS, IrO_2 , and Co_3O_4 . The schematic shows the electrocatalytic system.

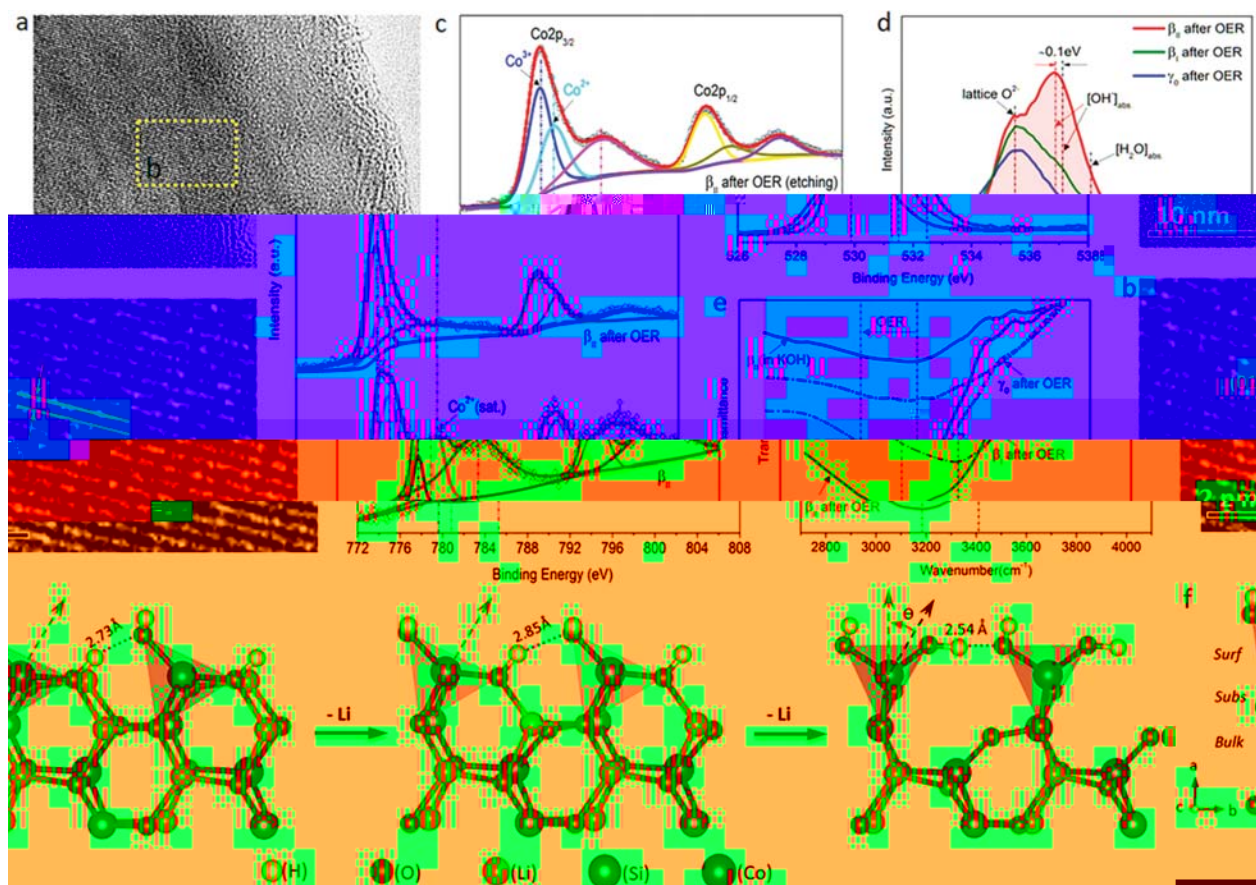
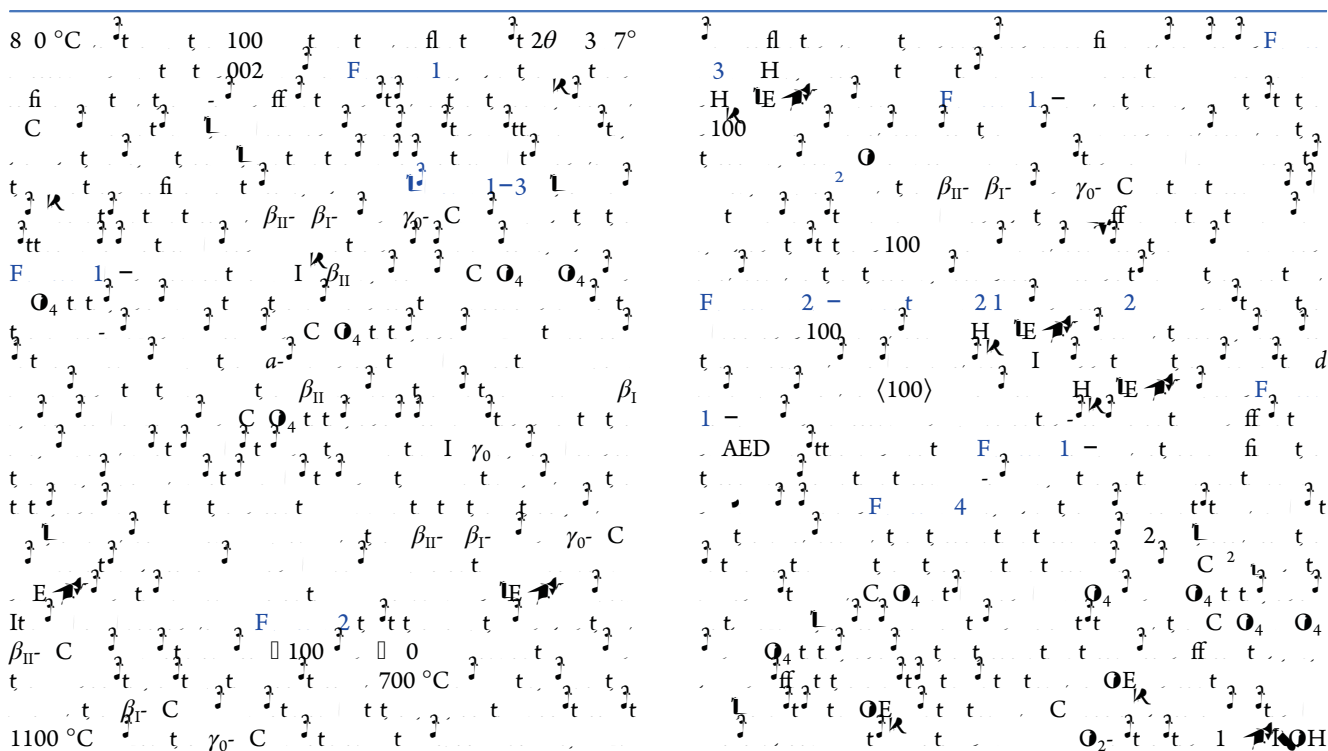


Figure 3. (a) TEM image of Co₂p₃₂ after OER. (b) HRTEM image of a single crystal. (c) Co₂p₃₂ XPS spectra showing peaks for Co₂p₃₂, Co₂p_{3/2}, and Co₂p_{3/2} after OER (etching). (d) O₂ 1s XPS spectra showing peaks for lattice O₂, [OH]_{ads}, and [H₂O]_{ads}. (e) O₂ 1s XPS spectra showing peaks for [OH]_{ads}, [H₂O]_{ads}, and [H₂O]_{ads} after OER. (f) IR spectra showing peaks for [OH]_{ads}, [H₂O]_{ads}, and [H₂O]_{ads} after OER. (g) Schematic diagram of the crystal structure showing the removal of Li ions from the layers.



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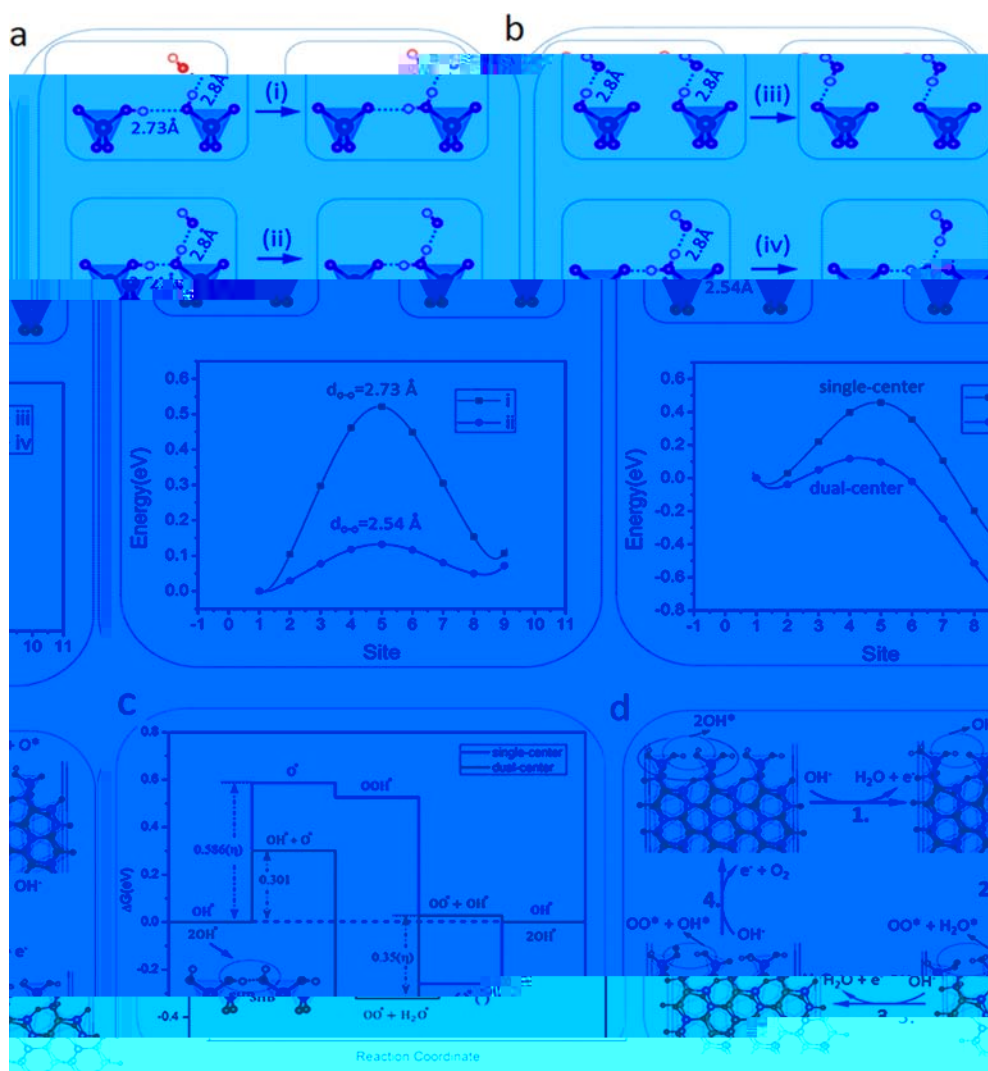
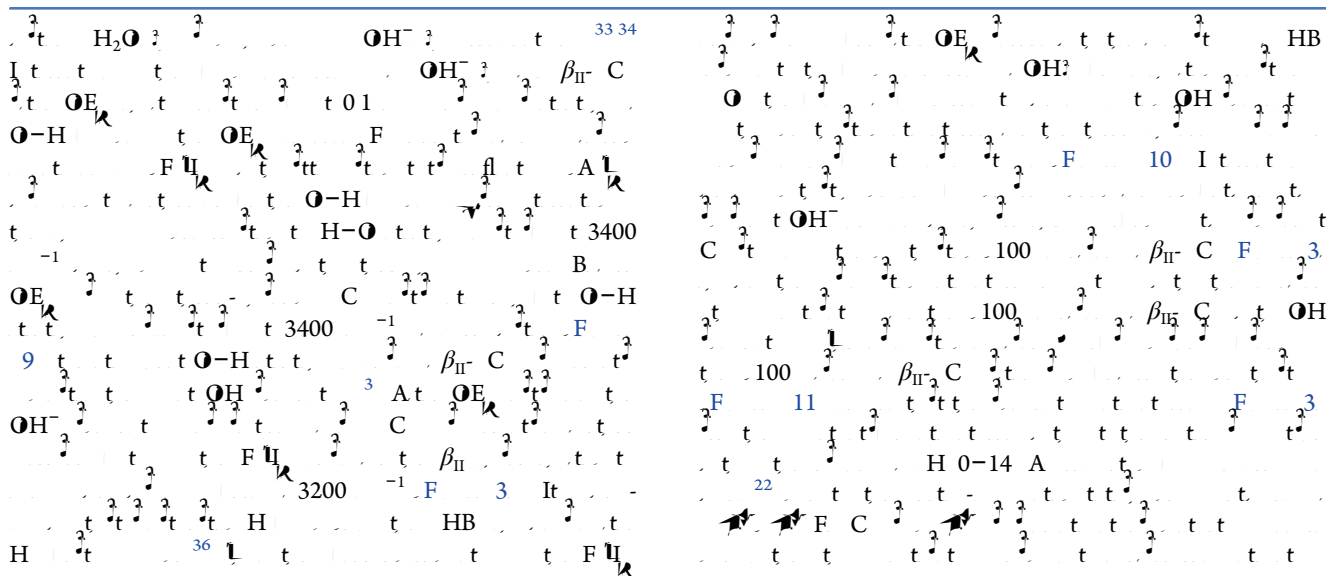
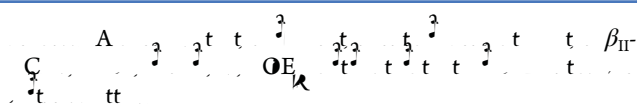
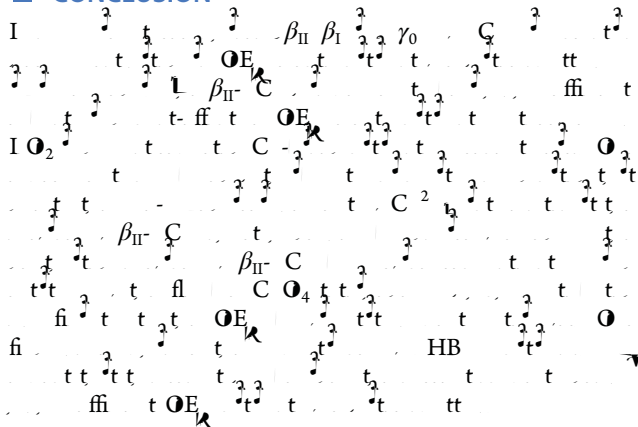


Figure 4. (a) Initial state of O_2 adsorption on two adjacent sites (2.73 Å). (b) Transition state (iii) and final state (iv) of O_2 reduction to two hydroxyl groups (2.54 Å). (c) Free energy diagram (ΔG in eV) versus reaction coordinate for the reduction of O_2 on a catalyst surface. (d) Catalytic cycle for the reduction of O_2 on a catalyst surface.





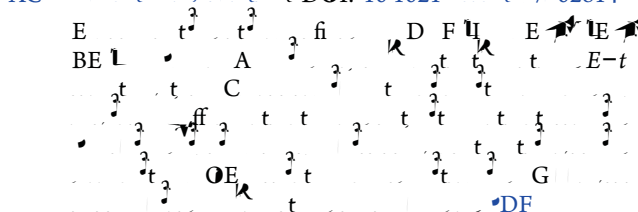
CONCLUSION



ASSOCIATED CONTENT

S. Supporting Information

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AUTHOR INFORMATION

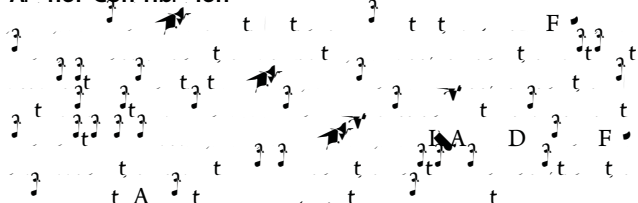
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