Supporting Information

Highly-Crystallized α-FeOOH for Stable and Efficient Oxygen Evolution Reaction

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Simulation method

The U value of 5.0 eV was used as it is, similar to other values used in the literature for goethite.[1-3]The experimental and lowest energy antiferromagnetic ordering was used for the magnetic structure. Van der Waals interactions were included by using the DFT-D3 method of Grimme*et al.*.[4] Reaction energies are extremely similar using DFT-D2 and DFT-D3 treatments, we therefore report details using only the latter treatment. All atoms were fully relaxed until the change in force upon ionic displacement was less than 0.01 eV/Å, with the change in energies no greater than 10^{-5} eV. The lattice parameters of goethite, which we model using the *Pnma*spacegroup (this is equivalent to *Pbnm*), were obtained by generating energy-volume data from a series of constant volume cell shape optimisation calculations, and fitting this data to the Murnaghan equation of state. This was performed using a (3×5×5) Monkhorst-Pack net. We found a = 10.061 Å, b = 4.645 Å, and c = 3.059 Å, overestimates of 1.5% (a), 1.5% (b) and 1.4% (c) with respect to experiment.[5] The (021) surface was modelled using (1×1) surface supercells, with the surface composed of four Fe layers, with the surface Brillouin zone sampled using a (4×4×1) k-point mesh. The system contains 64 atoms. A vacuum spacing of 10 Å was used in all

calculations. Water adsorption on both surfaces of the slab was modelled, with dipole correction implemented. One molecule or functional group was added to each undercoordinated Fe atom.

The reaction free energy per water molecule G_R for first hydroxylation is calculated using:

$$G_R = G_{FeOOH+H_2O} - G_{FeOOH} - G_{H_2O}$$

where G_{F+H_2O} is the free energy of the (021) surface binding H_2O/OH+H, G_{FeOOH} is the free energy of the bare slab, and G_{H_2O} is the free energy of the water molecule. Successive hydroxylation reaction energies are calculated in a similar fashion. In practice, we approximate $G_{FeOOH+H_2O}$ and G_{FeOOH} to the electronic energies obtained from DFT, as the vibrational contributions to the free energy from both slabs are assumed to be the same, i.e. the phonon density of states is unaltered and vibrational contributions cancel out. Pressure terms are also assumed to be negligible. The free energy of water, G_{H_2O}, in the liquid state is taken to be

$$G_{H_2O} = E_{H_2O}^{el} + \Delta g_{H_2O}^{solv}$$

where $E_{H_2O}^{el}$ is a well converged electronic energy and $\Delta g_{H_2O}^{solv}$ is the experimental Gibbs free energy of solvation, taken to be –0.274 eV/molecule at standard conditions.[6]

In our calculations, if the free energy of reaction is negative then it is exothermic. We find that the first hydroxylation is quite strong at –1.038 eV/H_2O. This is reflective of the chemical bond formed between the OH and Fe. In contrast, there is a significant reduction in the reaction energy for the second hydroxylation, at –0.620 eV/H_2O. From inspection, we note that the Fe–O distance is significantly longer than bulk, at 2.415 Å compared to the bulk value of 2.057 Å, suggesting that no chemical bond has formed. Rather, we note the presence of significant hydrogen bonding, as indicated by a short O…H bond length of 1.643 Å, and charge density difference analysis.
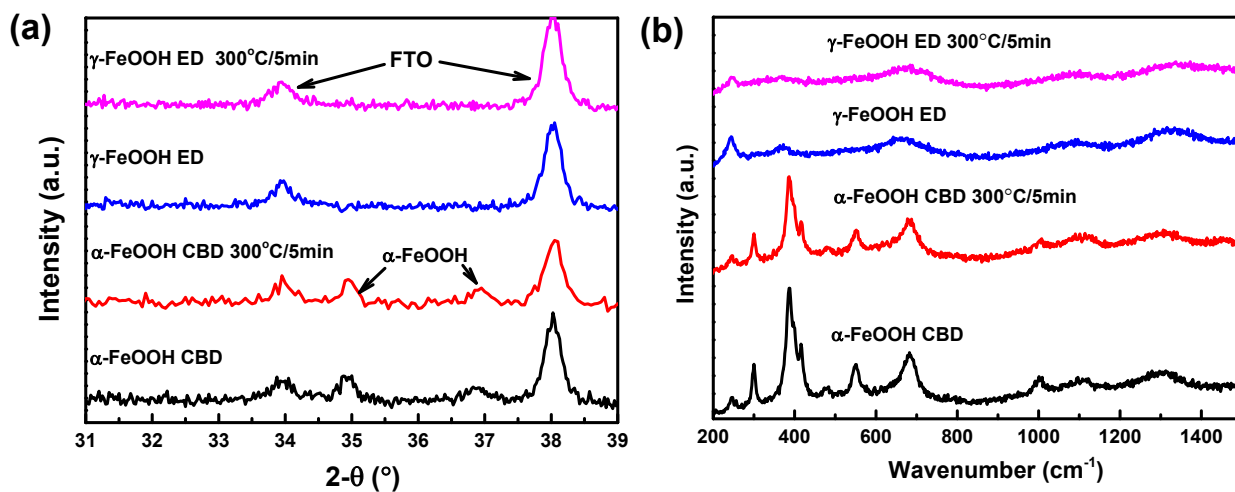
Figure S1 XRD (a) and Raman (b) of α-FeOOH by CBD method and γ-FeOOH by ED method before and after calcination at 300°C for 5 min

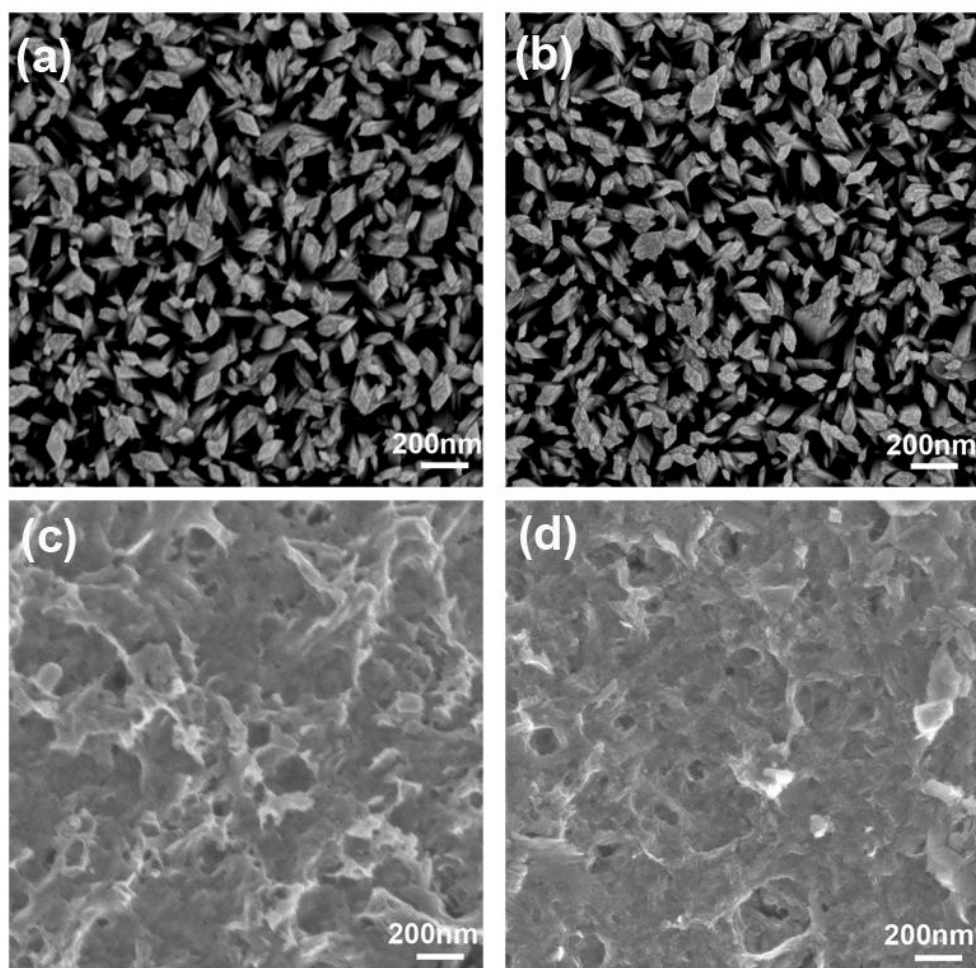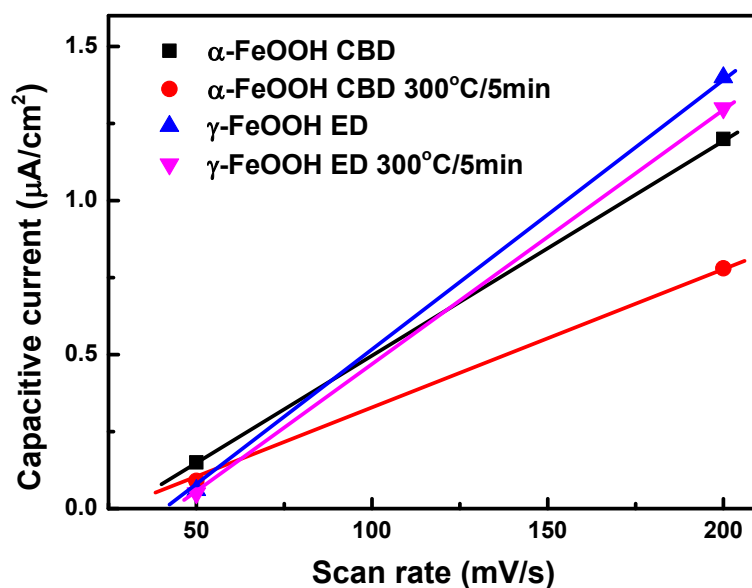Figure S2 SEM images of α-FeOOHbefore (a) and after (b),γ-FeOOH before (c) and (d) after calcinationat 300°C for 5min.

Figure S3 Electrochemical surface area of α-FeOOH and γ-FeOOH before and after calcination at 300°C for 5min. The relative electrochemical surface area was obtained from capacitance measurements by cyclic voltammetry between 0.8 V_{RHE} and 1.2 V_{RHE} in 1M KOH aqueous solution. The scan rateswere 50 and 200 mV s^{-1}.
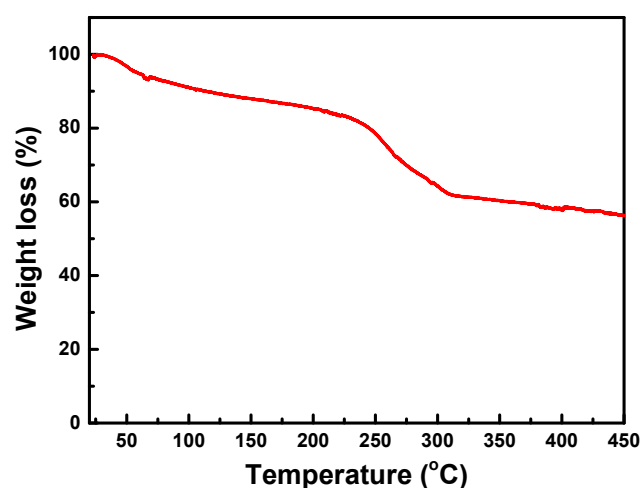
Figure S4 A TG curve of powders collected from deposition vessels. 0.02M FeSO$_4$ solution, 70°C for 72h
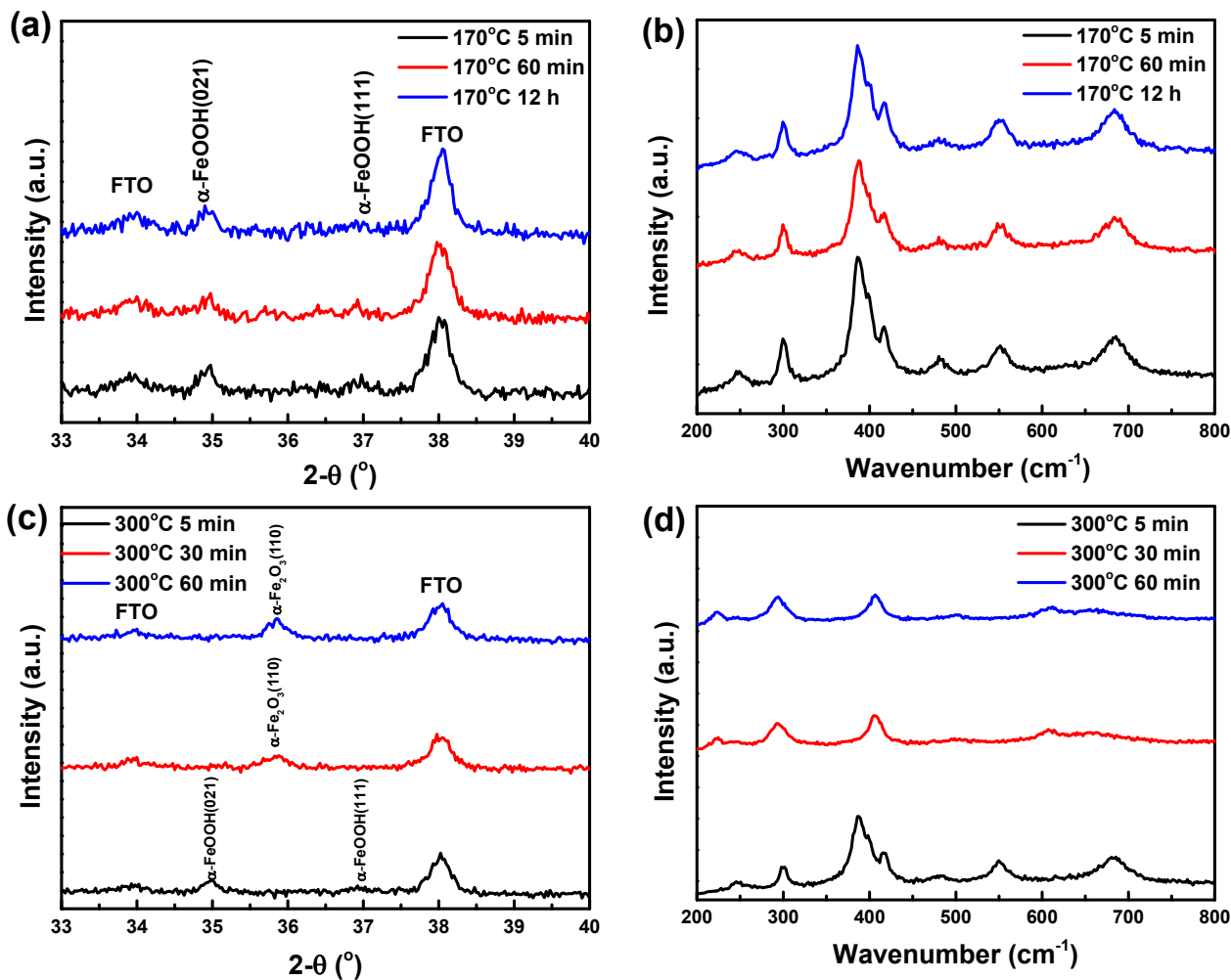
Figure S5 XRD patterns (a) and Raman spectra (b) of the α-FeOOH calcined at 170°C for different times ; XRD patterns (c) and Raman spectra (d) of the α-FeOOH calcined at 300°C for different times
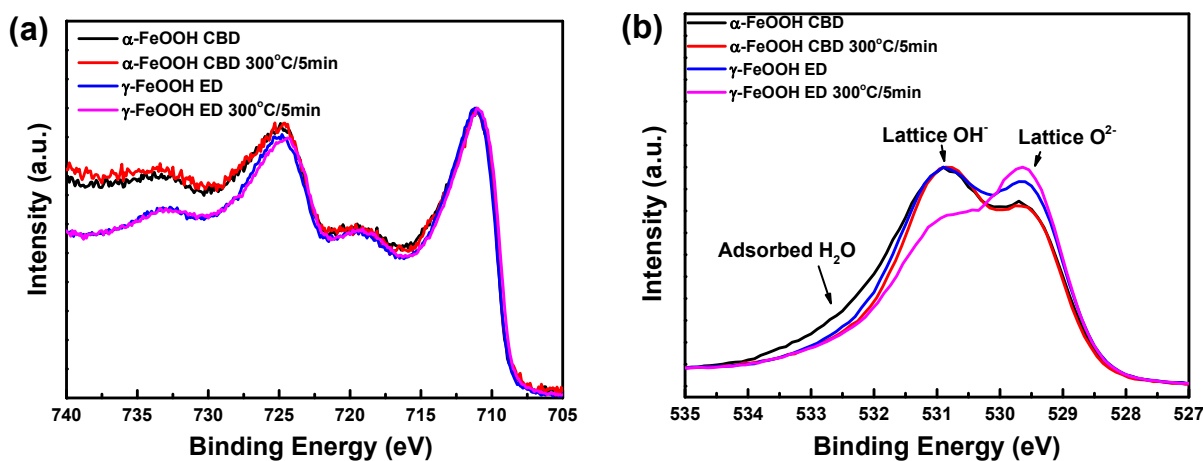

Figure S6 Normalized XPS spectra of Fe2p (a), O1s (b) on the surfaces of α-FeOOHand γ-FeOOH samples before and after calcination at 300°C for 5 min.
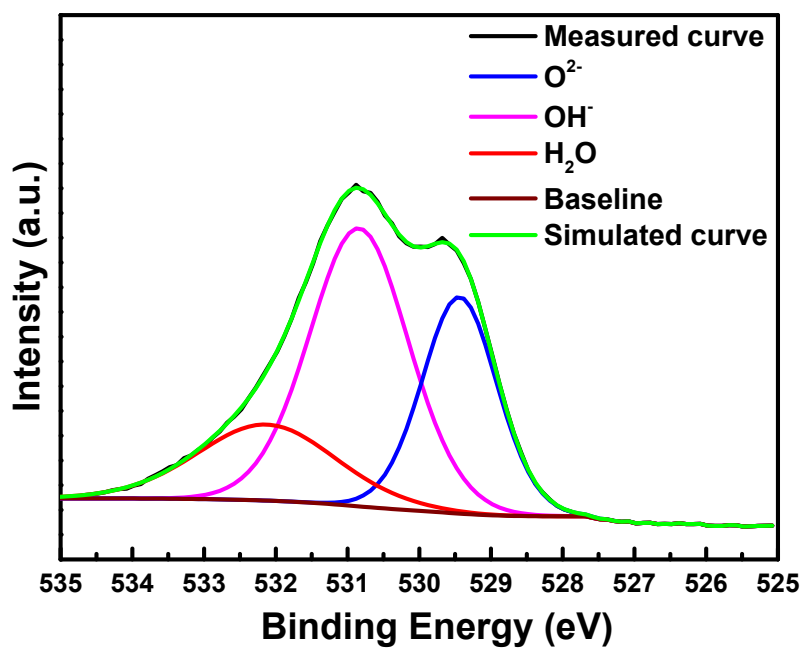
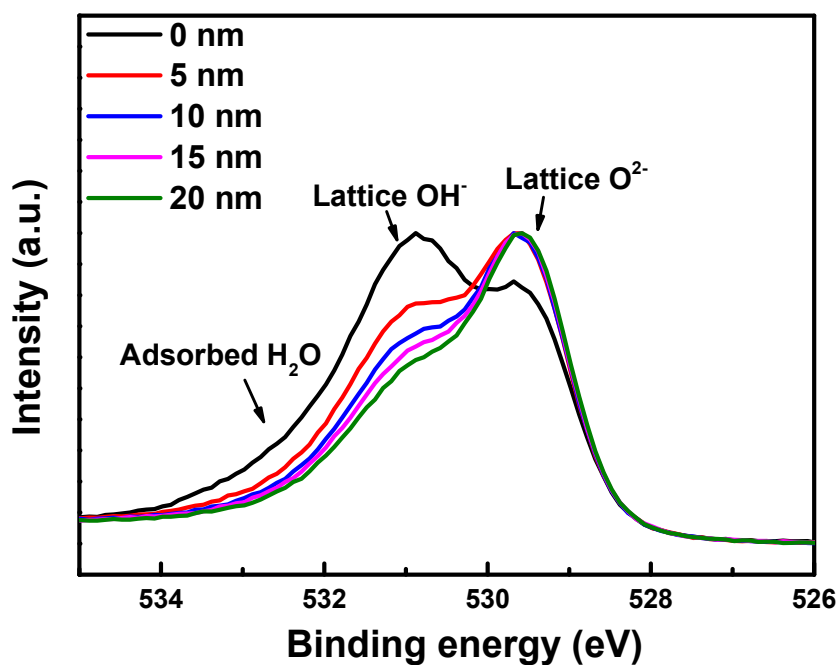Figure S7 Measured and simulated XPS spectra of O1s on the surface of as-deposited α-FeOOH.

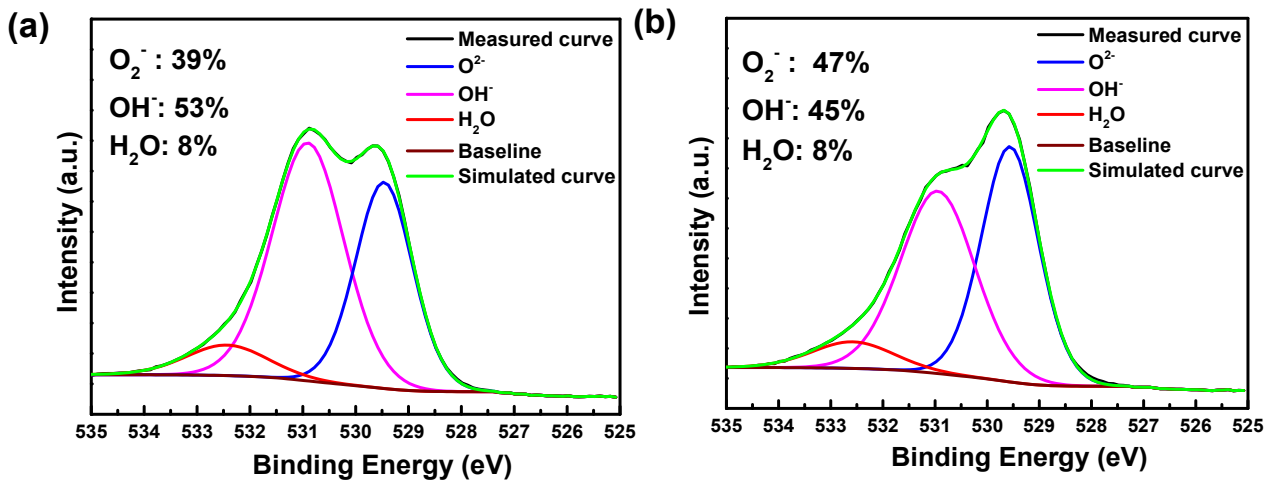Figure S8 XPS of O1s in the different depths of as-deposited α-FeOOH.

Figure S9 Measured and simulated XPS spectra of O1s on the surface of γ-FeOOH before (a) and after (b) calcined at 300°C for 5 min.
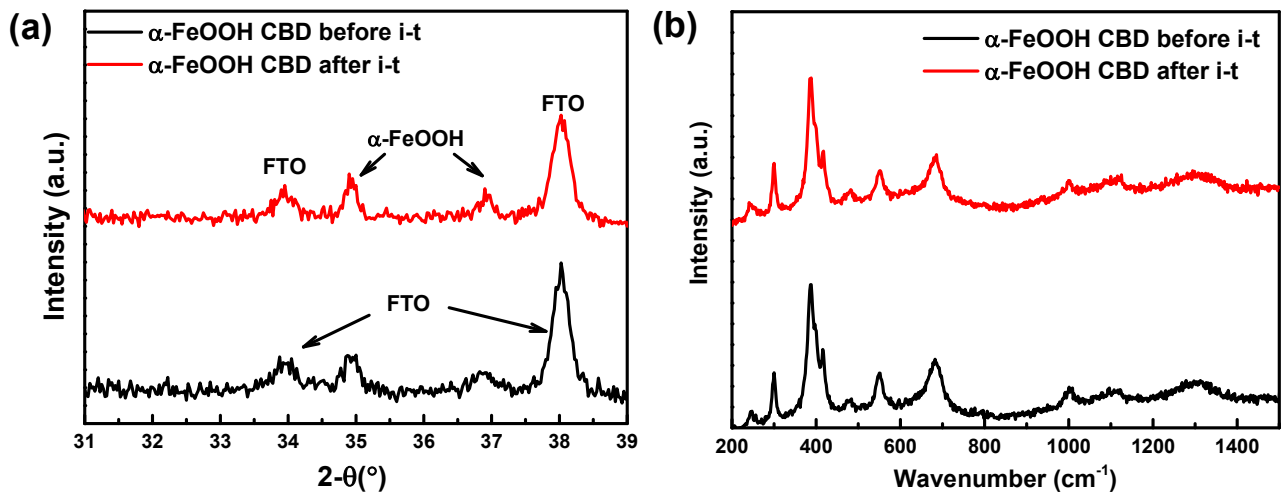

Figure S10 XRD (a) and Raman (b) of as-deposited α-FeOOH before and after i-t measurement. Electrolyte: 1M KOH aqueous solution, potential: 2.1 V_{RHE}.

References

[1] Russell, B., Payne, M. &Ciacchi, L. C. Phys. Rev. B 79, 14 (2009).

[2] Guo, H. B. & Barnard, A. S. Phys. Rev. B 83, 18 (2011).

[3]Otte, K., Schmahl, W. W. &Pentcheva, R. Surf. Sci. 606, 1623-1632 (2012).

[4] Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. J. Chem. Phys. 132, 19 (2010).

[5]Gualtieri, A. F. &Venturelli, P. Am. Miner.84, 895-904 (1999).

[6] Bennaim, A. & Marcus, Y. J. Chem. Phys. 81, 2016-2027 (1984).