Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.


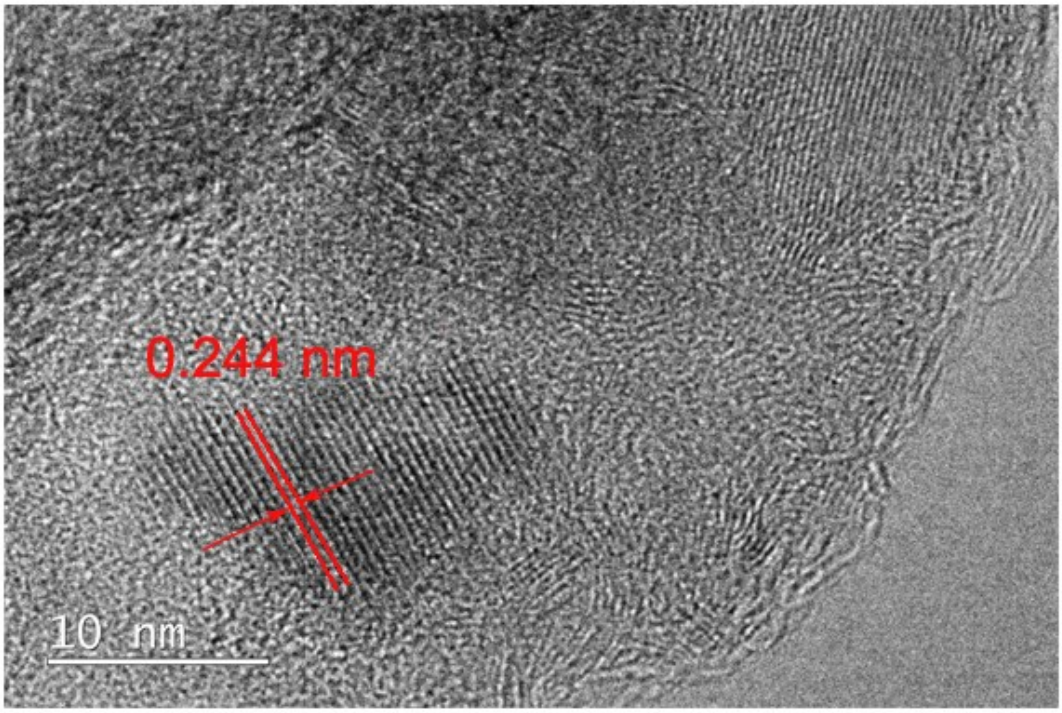


**Fig. S1.** HRTEM image of CoOx/CNTs electrocatalyst.

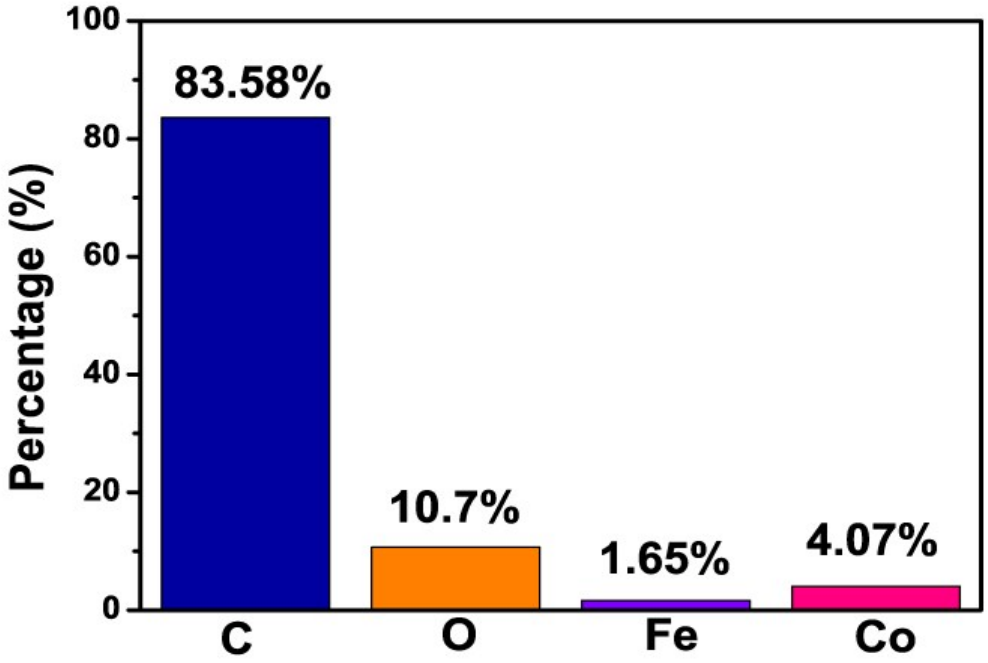


**Fig. S2.** XPS element contents of CoOx/FeOx/CNTs.

**Table S1.** Comparison of the electrocatalytic performance of CoOx/FeOx/CNTs with various reported non-precious electrocatalysts in alkaline media.

| Electrocatalyst | OER (η (mV) at j=10 mA $cm^{-2}$) | Tafel (mV $dec._{-1}$) | Reference |
|---|---|---|---|
| Fe/Co-N/S-Cs | 285 | / | [29] |
| Fe-Co-S/N-C | 329 | 63.2 | [30] |
| $Co_3O_4/Fe_2O_3$ NC | 310 | 67 | [31] |
| NiCo/PFC | 400 | 106 | [32] |
| CoOx / $Fe_2O_3$ /CC | 316 | 56 | [11] |
| $Co_3Fe_{1.5}$-O | 284 | 60 | [33] |
| $Fe_{0.4}Co_{0.6}$ | 383 | / | [34] |
| $Fe_1Co_2$-P/C | 362 | 50.1 | [35] |
| $Co_3O_4$/NPGC | 450 | / | [36] |
| Co-N-CNTs | 460 | / | [37] |
| SS-Fe-0.5 | 440 | 68 | [38] |
| **CoOx/FeOx/CNTs** | **308** | **43** | **This work** |

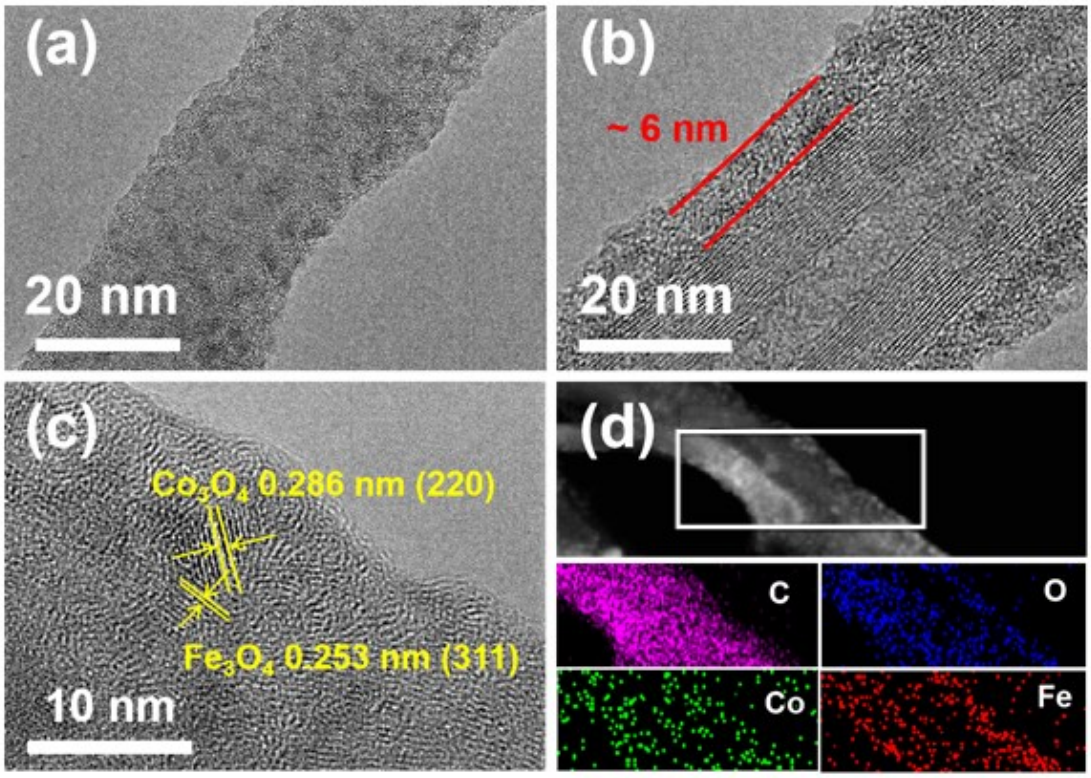


**Fig. S3**. (a and b) TEM images of the CoOx/FeOx/CNTs electrocatalyst after electrochemical test; (c) HRTEM image; (d) TEM-mapping of elements.

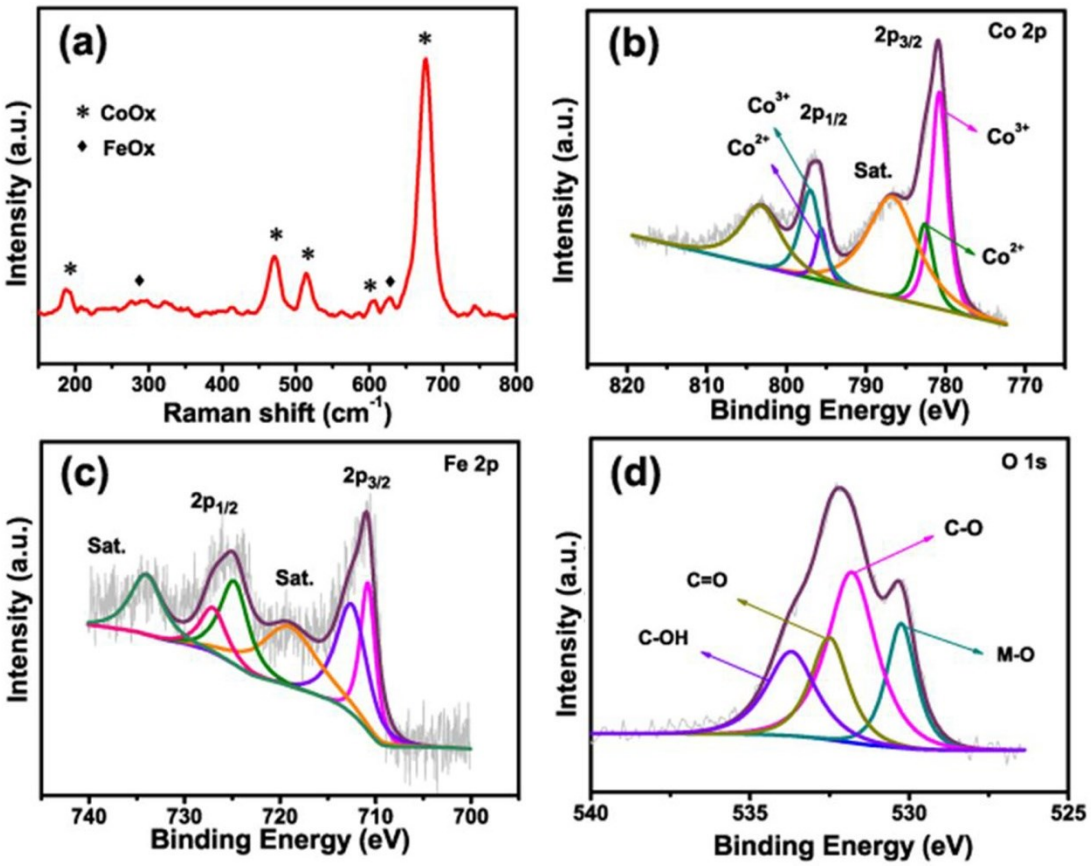


**Fig. S4**. (a ) Raman spectrum and (b) Co 2p; (c) Fe 2p; and (d) O 1s XPS spectra of CoOx/FeOx/CNTs after test.

**Computational Methods**

First-principles calculations were performed using Vienna Ab-Initio Simulation Package.[1,2] Exchange-correlation energy was described using the spin-polarized Perdew-Burke-Ernzerhof functional with a energy cutoff of 500 eV. Van der Waals correction was adopted using the Grimme scheme (D2).[3-5] Due to the strong electronic correlations in the localized 3*d* orbitals of Co and Fe ions, an on-site Coulomb interaction respectively with an effective parameter of U – J = 3.3 and 4.0 eV was applied.[6] The lattice constants of bulk $Co_3O_4$ and $Fe_3O_4$ (space group FD–3M) in were calculated to be 8.09 and 8.28 Å, respectively, in good agreement with previous studies.[7,8] The $Co_3O_4/Fe_3O_4$ interface was built by matching an eight-layer slab of $Co_3O_4(110)$ to an eight-layer slab of $Fe_3O_4(311)$ (see Figure S1) according to the experimental observations. The average value of their constants was adopted and kept fixed in the hybrid system, resulting in 1.15% lattice mismatch. The $Co_3O_4$ surface was modeled by the most energetically favorable $Co_3O_4(110)$.[9,10] Specifically, $Co_4O_4$-terminated plane was selected because it was found to be more stable for $Co_3O_4(110)$ surface.[11] A eight-layer slab with a vacuum spacing of at least 20 Å was used. The upper four layers including the adsorbates were optimized until the residual forces are less than 0.01 eV/Å. A dipole correction[12] was applied due to the asymmetric layer arrangement.

**References**:


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**Table S2.** Thermodynamic data of molecular species. For liquid $H_2O$, the entropy was calculated at p = 0.035 atm through $TS = TS^0 + k_B T \ln (p^0/p)$ because gas-phase $H_2O$ is in equilibrium with liquid water at 298.15 K under this pressure.

| Molecule | Total energy (eV) | ZEP (eV) | TS (eV) |
|---|---|---|---|
| $H_2(g)$ | –6.77 | 0.34 | 0.40 |
| $H_2O(l)$ | –14.22 | 0.58 | 0.67 |

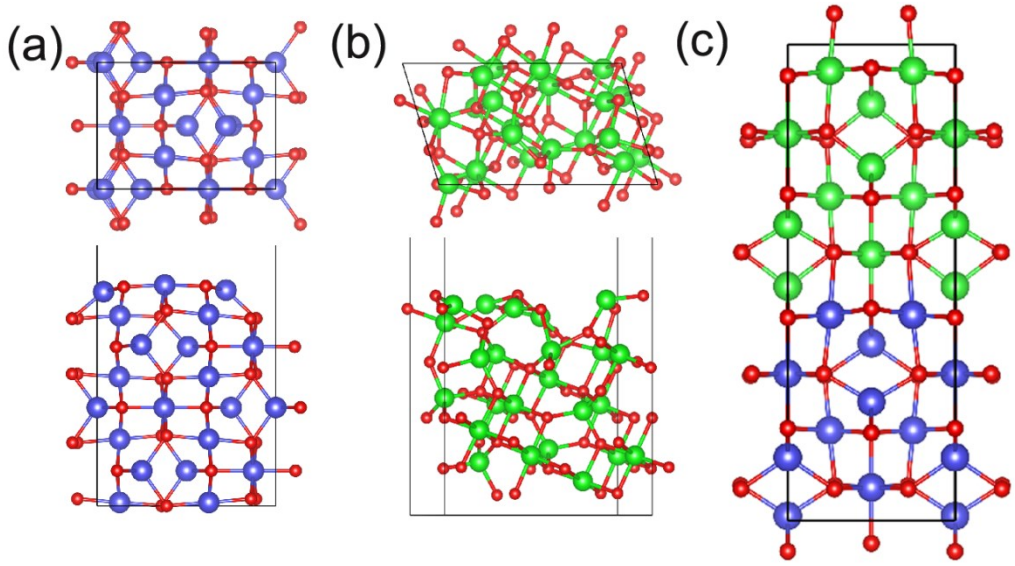


**Fig. S5.** (a) Top (upper panel) and side view (lower panel) of $Co_3O_4$(110) surface. Blue and red balls represent Co, Fe and O atoms, respectively. (b) Top (upper panel) and side view (lower panel) of $Fe_3O_4$ (311) surface. Green and red balls represent Co, and O atoms, respectively. (c) Side-view of the model structure of $Co_3O_4/Fe_3O_4$ hybrid system. Blue, green and red balls represent Co, Fe and O atoms, respectively.

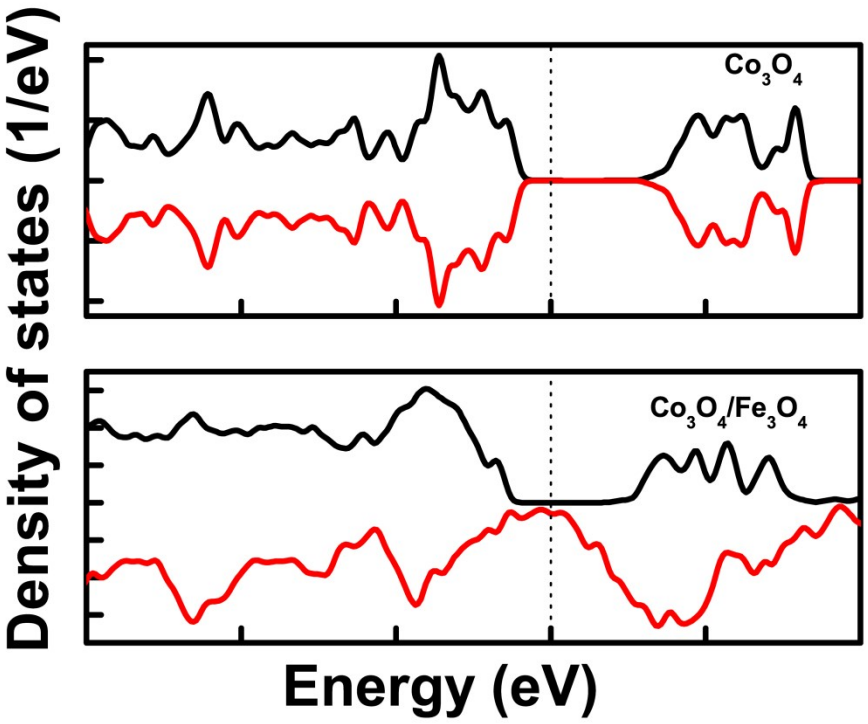


**Fig. S6.** The density of states (DOS) of $Co_3O_4$ and $Co_3O_4/Fe_3O_4$.