

Supporting information

High-content atomically distributed W(V,VI) on FeCo layered  
double hydroxide with high oxygen evolution reaction activity

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## Experimental Section

*Materials.* Cobalt (II) chloride hexahydrate ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , 98%), iron (III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 98%), tungsten (VI) chloride ( $\text{WCl}_6$ , 99%), Triethylamine (TEA), N,N-dimethylformamide (DMF), ethanol (99.5 %) and potassium hydroxide (KOH, 95%) were purchased from Beijing Chemical Works (Beijing, China). Acetylene black was provided from KJ Group (Hefei, China). Commercial  $\text{RuO}_2$  and Pt/C (20 wt%) were purchased from Alfa Aesar. High purity  $\text{O}_2$  and  $\text{N}_2$  were provided by Longhuijingcheng company (Beijing, China). All reagents were used without further treatment. The deionized water was used in all experiments.

*Preparation of SAC W-FeCo LDH and FeCo LDH.* The SAC W-FeCo LDH sample is synthesized via a one-step coprecipitation method. Specifically,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.6 mmol),  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (0.06 mmol) and  $\text{WCl}_6$  (0.06 mmol) were dissolved into 35 mL of mixed solvent ( $V_{\text{DMF}}: V_{\text{water}}: V_{\text{ethanol}} = 15: 1: 1$ ) in plastic centrifuge tube under stirring to form a clear solution, followed by 0.5 mL of triethanolamine (TEA) fast addition. The mixture was stirred for 30 min and ultrasonicated for 8 h airtight at room temperature. The obtained viscous colloidal suspensions were separated by centrifuging at 3500 rpm and washed by dimethylformamide and ethanol three times to thoroughly remove the TEA. The obtained SAC W-FeCo LDH was dried at room temperature.

*Materials Characterizations.* X-ray diffraction patterns (XRD) were collected on a D/MAX 2200pc X-Ray diffractometer (Rigaku, Japan) with X-ray source of Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). High-resolution TEM (HRTEM) images were acquired by using FEI Tecnai F20 (200 kV). High angle annular dark field (HAADF) images were acquired by using scanning-TEM (STEM) of JEOL JEM ARM200F with Cs-corrected (probe) at 200 kV. The samples were prepared by dispersing the ground material powder in ethanol and adding a few drops onto the lacey carbon film. Energy-dispersive X-ray (EDX) analysis data were obtained using Oxford X-max 100TLE system. X-ray photoelectron spectroscopy (XPS) were performed on PHI Quantera II (Ulvac-Phi Inc., Japan) with

Al K $\alpha$  radiation. All the spectra were corrected using aliphatic carbon C 1s at binding energy of 284.6 eV as reference. N<sub>2</sub> adsorption-desorption isotherms were collected using a Micromeritics ASAP 2010 analyzer at 77 K. All samples were degassed in vacuum at 200 °C. X-ray absorption fine structure spectra (W L-edge) were collected at a 1W1B station in Beijing Synchrotron Radiation Facility (BSRF).

*Electrochemical Measurements.* The electrochemical tests, including cyclic voltammetry (CV) and linear scan voltammograms (LSVs), were performed at 25 °C using a standard three-electrode configuration (Pine Research Instruments, USA) on a workstation (WaveDriver 2000, USA). The saturated Hg/HgO electrode and graphite rod were used as reference and counter electrode, respectively. The reversible hydrogen electrode (RHE) potential can be calculated based on the following equation:  $E(\text{RHE}) = E(\text{Hg}/\text{HgO}) + 0.098 + 0.059 \times \text{pH}$ . Before the test, the electrolyte (1 M KOH) was saturated with O<sub>2</sub> by bubbling high-pure O<sub>2</sub>. And the O<sub>2</sub> flow was maintained throughout the experiments. When preparing working electrode, ten milligrams of ground catalysts were dispersed in 1 mL of mixed ethanol and 0.04 mL of Nafion solution under sonication for 60 min. Glassy carbon disk electrode (surface area: 0.196 cm<sup>2</sup> for RDE, 0.247 cm<sup>2</sup> for RRDE) was polished using alumina suspensions (0.3 and 0.05  $\mu\text{m}$ ) and rinsed with deionized water and ethanol, successively, before catalysts loading. Four microliters of catalyst ink were casted onto a pretreated glassy carbon electrode and dried at room temperature (loading: 0.2 mg<sub>cat.</sub> cm<sup>-2</sup>).

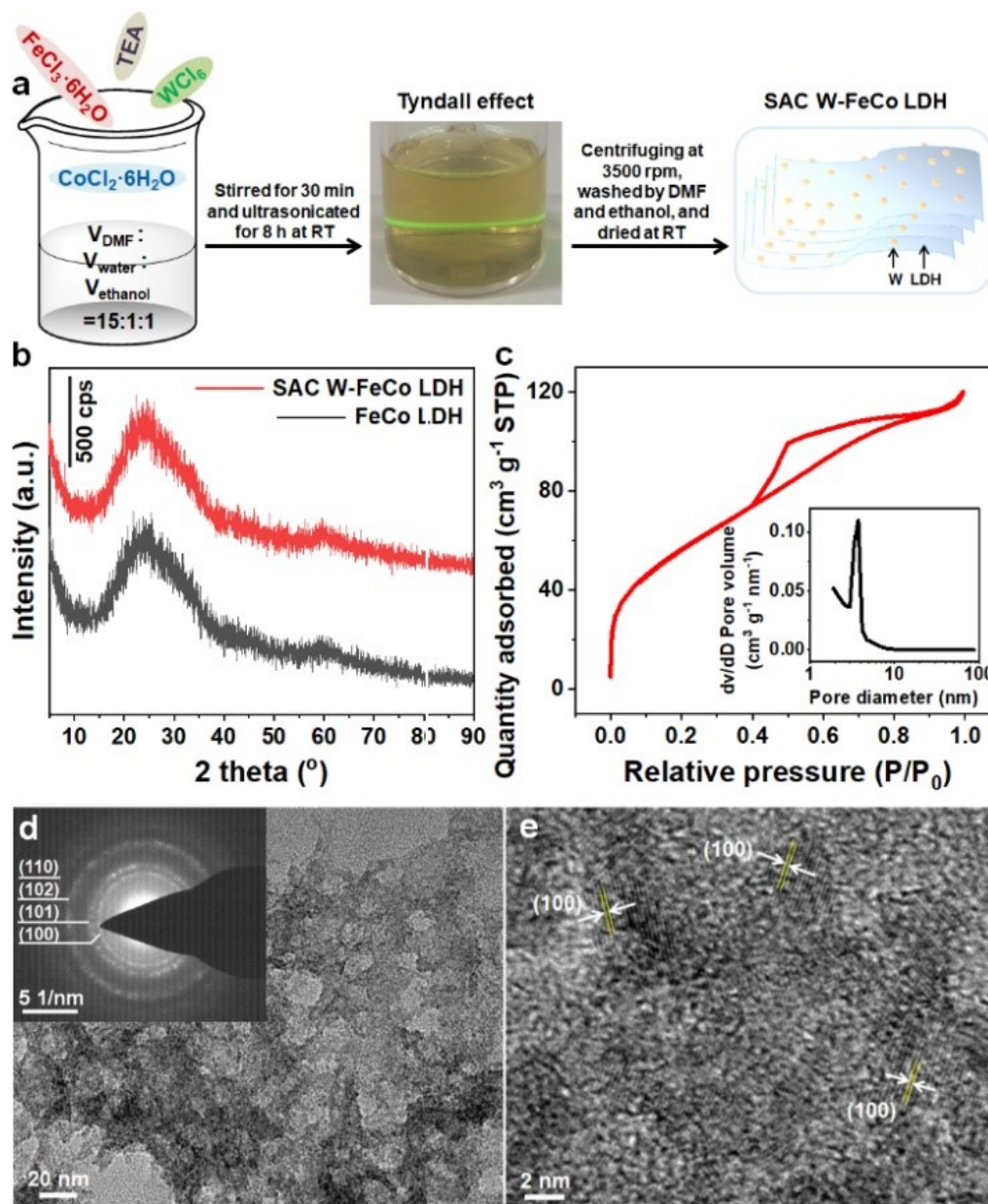
Before each test, the working electrode was scanned by CV until the signals were stabilized. The LSV curves were measured at a scan rate of 5 mV s<sup>-1</sup>. All potential values were *iR*-corrected to compensate for the effect of the solution resistance, which was calculated by the following equation:  $E_{iR\text{-corrected}} = E - iR$ , where *i* is the current and *R* is the uncompensated ohmic electrolyte resistance measured *via* the high-frequency AC impedance in O<sub>2</sub>-saturated 1.0 M KOH (*R* = 6  $\Omega$ ). The LSV curves used to calculate Tafel slopes were recorded at a scan rate of 1 mV s<sup>-1</sup>. And the Tafel slopes

were derived from LSV curves based on  $\eta = a + b \lg j$ , where  $\eta$  is the overpotential ( $\eta = E - 1.23$  V),  $a$  is the exchange current density,  $b$  is the Tafel slope and  $j$  is the measured current density. The long-term durability was evaluated via Galvan-static measurement at a constant current density of 10 mA cm<sup>-2</sup>. The electrochemical active surface area (ECSA) of all samples were estimated *via* CV at different scanning rates (2-10 mV s<sup>-1</sup>) within the non-Faradic potential regions.

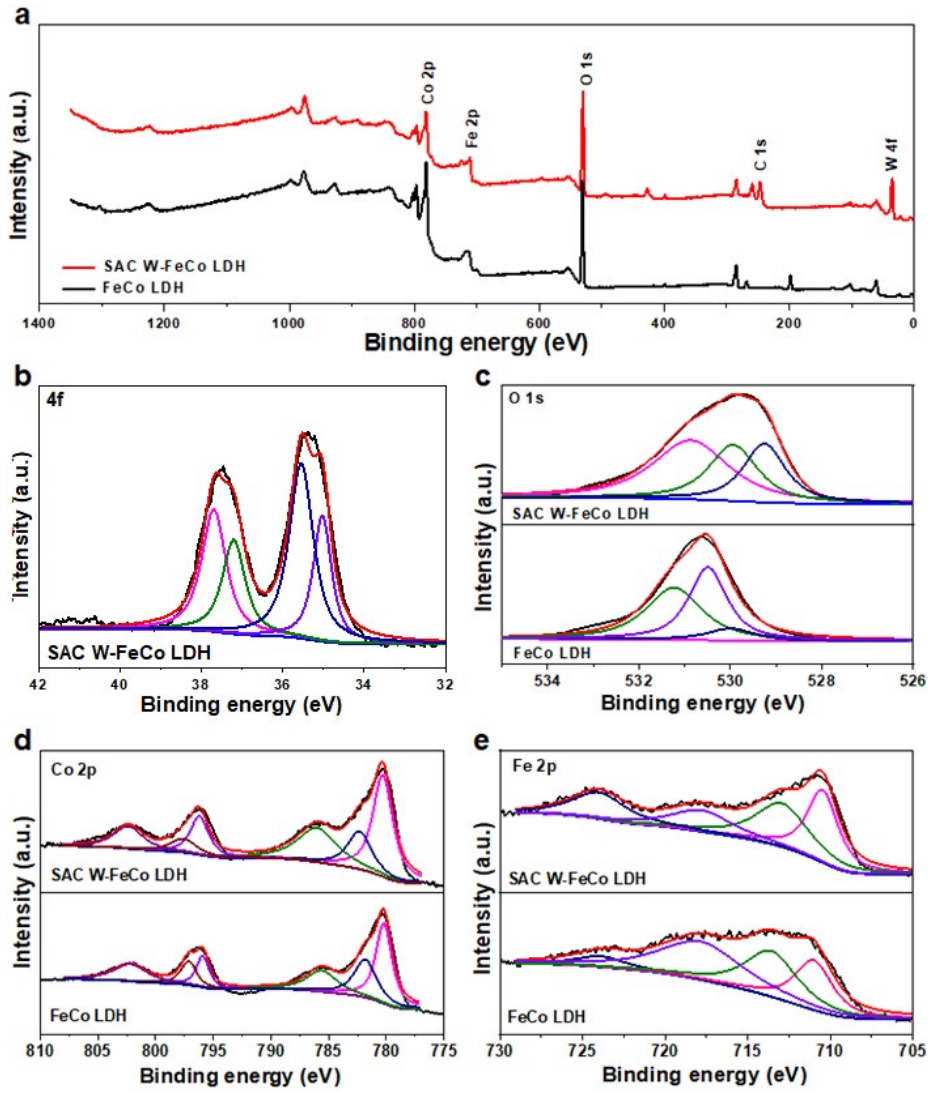
Turnover frequency (TOF) was calculated *via* the equation:

$$\text{TOF} = (J_K \times N_e) / (\omega_W \times m_{\text{cat}} \times (N_A / M_W))$$

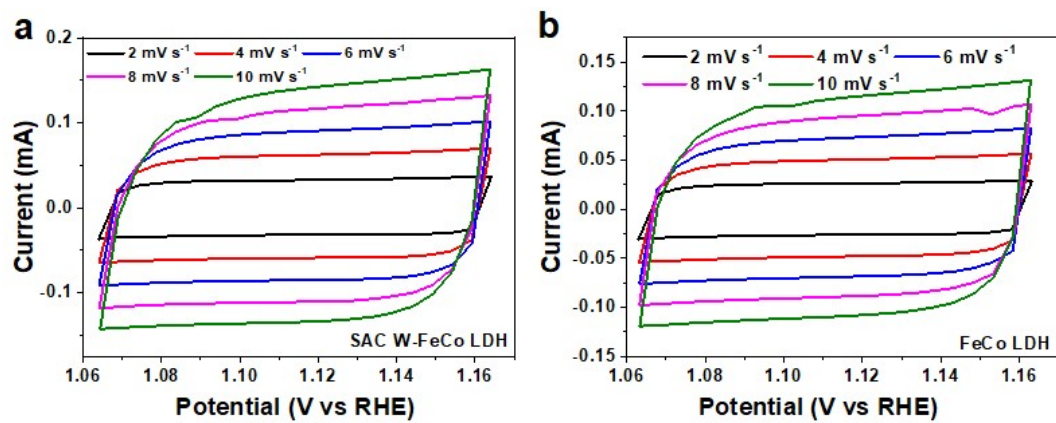
where,  $J_K$  is the kinetic current density (A cm<sup>-2</sup>),  $N_e$  is electron number per Coulomb ( $6.24 \times 10^{18}$ ),  $\omega_W$  is the W element content in the catalyst,  $m_{\text{cat}}$  is the catalyst mass loading on the electrode (g cm<sup>-2</sup>),  $N_A$  is Avogadro constant ( $6.022 \times 10^{23}$ ), and  $M_W$  is molar mass of W element (183.8 g mol<sup>-1</sup>). When just considering the contribution of single-atom W in SAC W-FoCo LDH, the  $J_K$  is the difference value of sample SAC W-FeCo LDH and FeCo LDH at 1.45 V, *i.e.*,  $J_K = J_K (\text{SAC W-FeCo LDH}) - J_K (\text{FeCo LDH})$ .



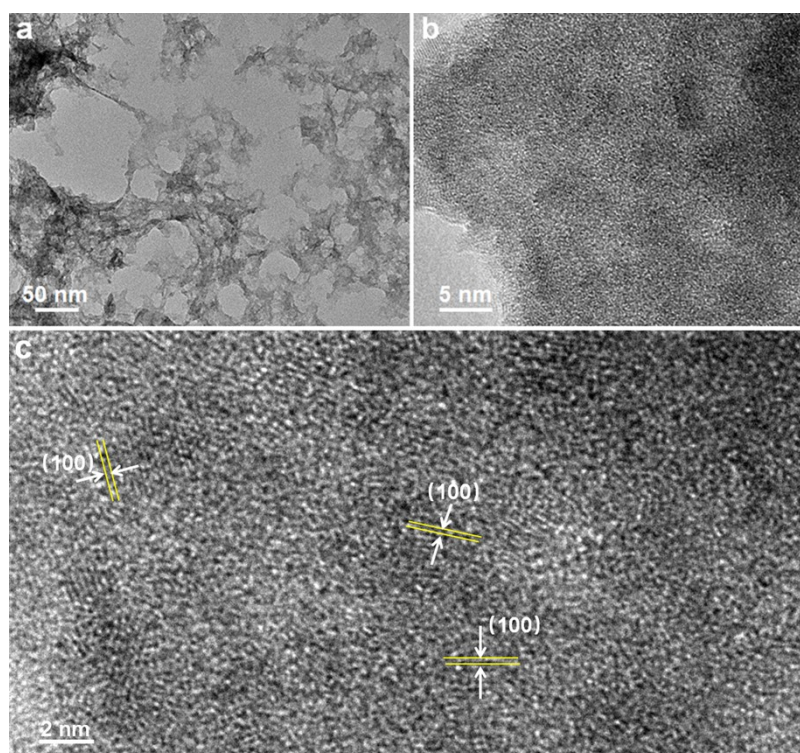
**Figure S1.** (a) Scheme of the preparation process. (b) XRD patterns of SAC W-FeCo LDH and FeCo LDH. (c)  $\text{N}_2$  sorption isotherms with the pore size distribution, (d) TEM and (e) HRTEM image with insert in (d) of SAED pattern of SAC W-FeCo LDH.



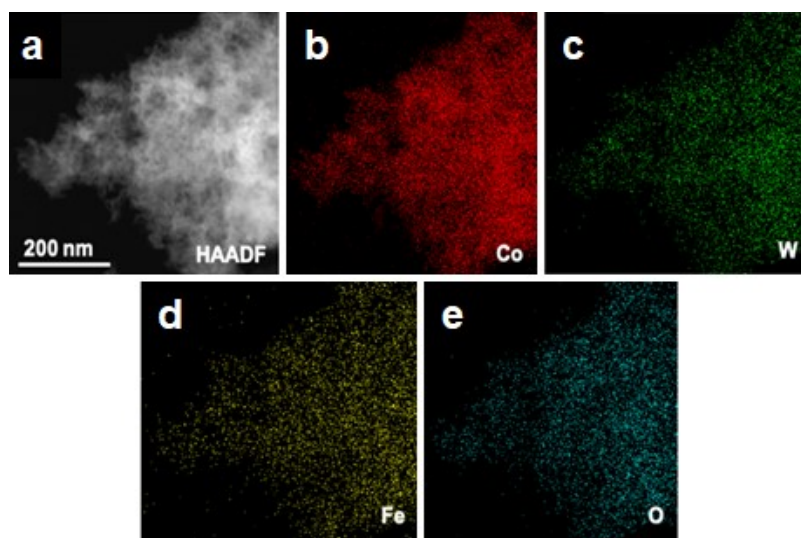
**Figure S2.** (a) Full survey and high-resolution (b) W 4f, (c) O 1s, (d) Co 2p and (e) Fe 2p XPS spectra of SAC W-FeCo LDH and/or FeCo LDH.



**Figure S3.** CV curves of (a) SAC W-FeCo LDH and (b) FeCo LDH under various scan rates.

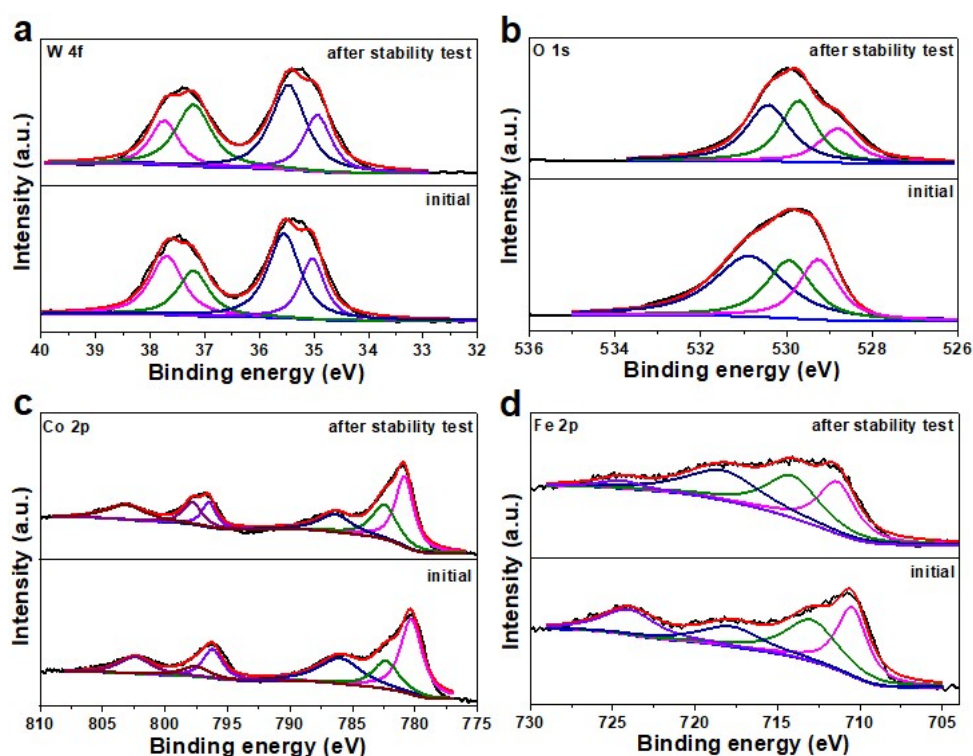


**Figure S4.** (a) TEM and (b,c) HRTEM images of SAC W-FeCo LDH after the long-time OER process.



**Figure S5.** (a) STEM image and (b-e) the related elemental mappings of the SAC W-FeCo LDH after the long-time OER process. The hardly changed images and elemental mappings indicate the excellent stable OER catalytic character of SAC W-FeCo LDH.





**Figure S6.** High-resolution (a) W 4f, (b) O 1s, (c) Co 2p and (d) Fe 2p XPS spectra of the initial SAC W-FeCo LDH and the sample after the long-time OER process.

Based on the full survey XPS analysis, the content of W (5.97 at.%), Fe (10.31 at.%) and Co (12.89 at.%) decreased a little, while the content of O (70.83 at.%) increased after the long-time OER process, which are unfavorable for the electrocatalytic activity. The decreased  $W^{6+}/W^{5+}$  ratio and increased  $Co^{3+}/Co^{2+}$  and  $Fe^{3+}/Fe^{2+}$  ratios after the long-time OER process suggest the W was reduced and Co/Fe were oxidized in some extent during the OER catalytic process, compared with those of the initial SAC W-FeCo LDH. The three components with the O 1s XPS peaks at 529.2, 529.9 and 530.9 eV for the initial sample shifted toward a little lower energy (528.8, 529.3 and 530.4 eV) after the long-time OER process, which are helpful for the fast charge transfer in the OER process.