Supporting Information

MXene-derived Ti$_3$C$_2$-Co-TiO$_2$ nanoparticle arrays via cation exchange for highly efficient and stable electrocatalytic oxygen evolution

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Fabrication of layered Ti₃C₂ MXene nanosheets (LM NS)

The synthesis of layered Ti_3C_2 MXene nanosheet is as reported in our previous work with minor modifications.[1] Briefly, 0.8 g of Ti_3AlC_2 MAX powder (≥99%, Kai Xi Ceramic Materials Co., Ltd.) was slowly added to 60 mL of concentrated HF (60%, Sinopharm Chemical Reagent Co., Ltd.), and the resulting solution was stirred at a low temperature (40 °C) for 72 h. The product was collected by centrifugation and washed several times with deionized water until the pH value was greater than 6. The collected wet powder was vacuum dried at 60 °C for 24 h.

Fabrication of layered Ti₃C₂-Na-TiO₂ MXene nanofibers (LM-Na-TO NF)

Dissolving NaOH (1.2 g, ≥96%, Sinopharm Chemical Reagent Co., Ltd.) in deionized water (30 mL), and adding LM NSs (0.1 g) with stirring.[2] After sonication for 15 min, the mixture was stirred for 96 h. The obtained product was collected by centrifugation, washed several times with deionized water, and dried in a vacuum oven at 60 °C for 24 h.

Fabrication of layered Ti₃C₂-Co-TiO₂ MXene nanoparticle arrays (LM-Co-TO NA)

First, preparing 30 mL of HCl diluted solution (2 M, 36.0~38.0%, Sinopharm Chemical Reagent Co., Ltd.), adding 0.1 g of LM-Na-TO NF, and stirring for 1 h. The resulting product was collected by centrifugation and washed several times with deionized water. Then, preparing 10 mL of $Co(NO_3)_2 \cdot 6H_2O$ solution (1 M, ≥98.5%, Sinopharm Chemical Reagent Co., Ltd.), and the above HCl-treated LM-Na-TO NF (LM-H-TO NP) was added to this solution. The mixed solution was stirred at 50 °C for

8 h, and the powder was collected by centrifugation, washed several times with deionized water, and vacuum dried at 60 °C for 24 h. Finally, the synthesized product (LM-H-Co-TO NA) was sealed in a tube furnace and heat-treated at 700 °C for 2 h under the protection of an N_2 atmosphere with a heating rate of 5 °C min^{-1}. The obtained powder was recorded as layered Ti_3C_2-Co-TiO_2 nanoparticle arrays (LM-Co-TO NA). For comparison, the LM-Na-TO NF without HCl treatment was also subjected to Co^{2+} loading and subsequent heat treatment, and the obtained product was marked as layered Ti_3C_2-Na-Co-TiO_2 MXene nanoparticles (LM-Na-Co-TO NP). In addition, the HCl concentration (1 M, 4 M) and heat-treatment temperature (600 °C, 800 °C) were also optimized to obtain excellent OER activity.

Materials characterization

The crystal phases of the catalysts were analyzed by X-ray diffraction (XRD) spectrometry (D8Advance, Bruker, Germany) with a Cu Kα radiation source (λ = 0.15406 nm, 40 kV, 30 mA). The microstructure and micromorphology of the products were observed by field-emission scanning electron microscope (FE-SEM, HITACHI SU8010) and transmission electron microscope (TEM, JEM-2100F, JEOL). Meanwhile, energy-dispersive X-ray spectroscopy (EDS) was also detected by the FE-SEM facility. Raman spectra were measured with a LabRAM HR800 (HORIBA) using a laser excitation wavelength of 532 nm. In addition, the bonding environment of elements in the catalyst was investigated by X-ray photoelectron spectroscopy (XPS, Thermo escalade 250Xi). The concentrations of metals in LM-Co-TO NA catalyst were measured by ICP-OES (Avio 500, PerkinElmer, USA).

Electrochemical measurement

The electrochemical performance of the catalysts was evaluated using a three-electrode system. The electrolyte, counter electrode, and reference electrode were 1 M KOH solution, graphite rod, and Ag/AgCl electrode, respectively. Electrocatalytic experiments were performed using a rotating ring-disk electrode (RRDE-3A, ALS Inc., Tokyo, Japan) connected to an electrochemical workstation (CHI 760E, Shanghai Huachen Instrument Co. Ltd., China). 4 mg of the catalyst was added to 1 mL Nafion solution (5 wt%) and sonicated for 6 h to obtain a catalyst ink, which was dropped on a glassy carbon rotating disk electrode (RDE) (3 mm in diameter) with a loading of 0.2 mg cm^{-2}. Commercial RuO$_2$ ink was also prepared using the same method. Cyclic voltammetry (CV) curves were performed at scan rates of 20~200 mV s^{-1}. The double-layer capacitance (C_{dl}) is the capacitance calculated from the CV curves in the non-faradaic region. Meanwhile, the electrochemical surface area (ECSA) was calculated using the following equation: ECSA = C_{dl}/C_s, where C_s is the specific capacitance of a flat surface of 0.04 mF cm^{-2}. The polarization curves were achieved from linear sweep voltammetry (LSV) curves at a scan rate of 5mV s^{-1}. Impedance spectroscopy (EIS) curves were tested in the frequency range of 0.01 Hz to 100 kHz under an AC voltage of 5 mV. The chronoamperometry test was conducted at a constant potential of 1.506 V (vs. RHE). All the potentials were converted to the reversible hydrogen electrode (RHE) according to the equation: $E_{(RHE)} = E_{(Ag/AgCl)} + 0.0591*pH + 0.197 = E_{Ag/AgCl} + 1.0244$ V.
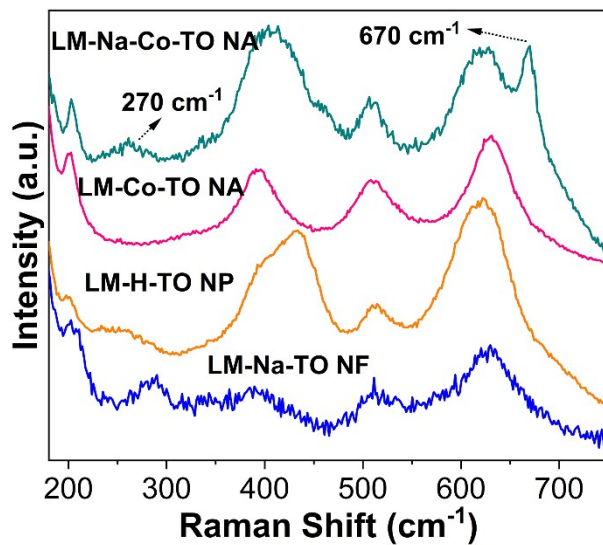
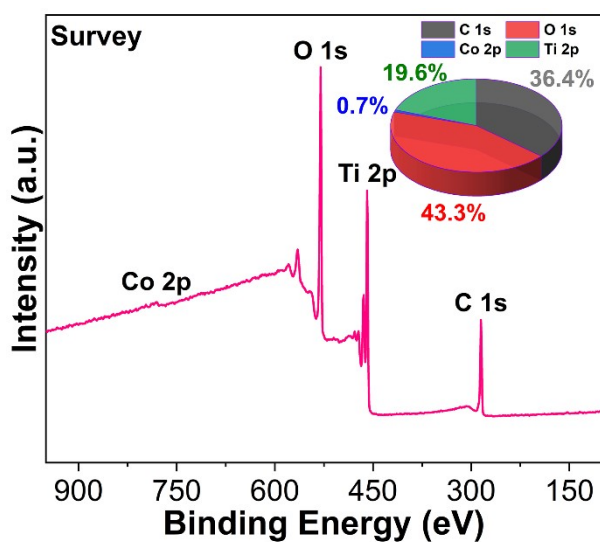**Figure S1.** Raman spectra of LM-Na-TO NF, LM-H-TO NP, LM-Co-TO NA, and LM-Na-Co-TO NA.
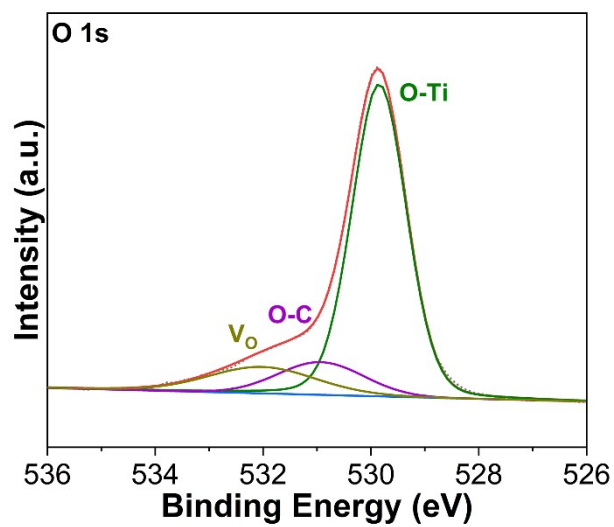

Figure S2. XPS survey spectra of LM-Co-TO NA.

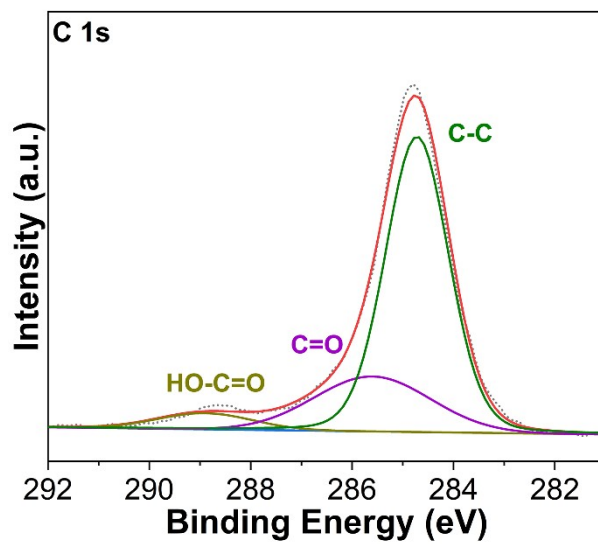**Figure S3.** XPS spectra of O 1s for LM-Co-TO NA.

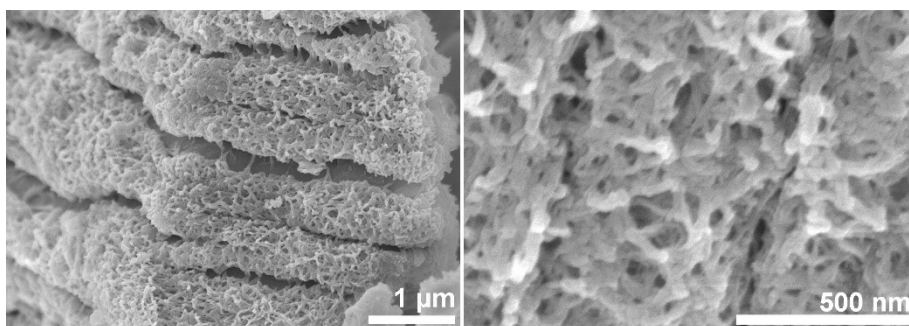**Figure S4.** XPS spectra of C 1s for LM-Co-TO NA.

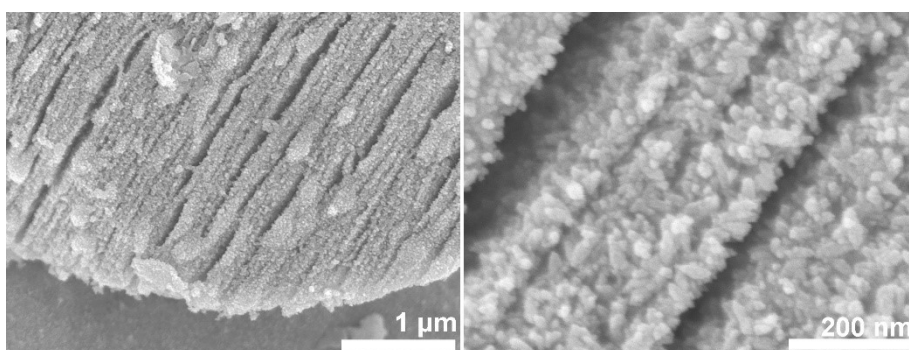**Figure S5.** SEM images of LM-Na-TO NF catalysts.
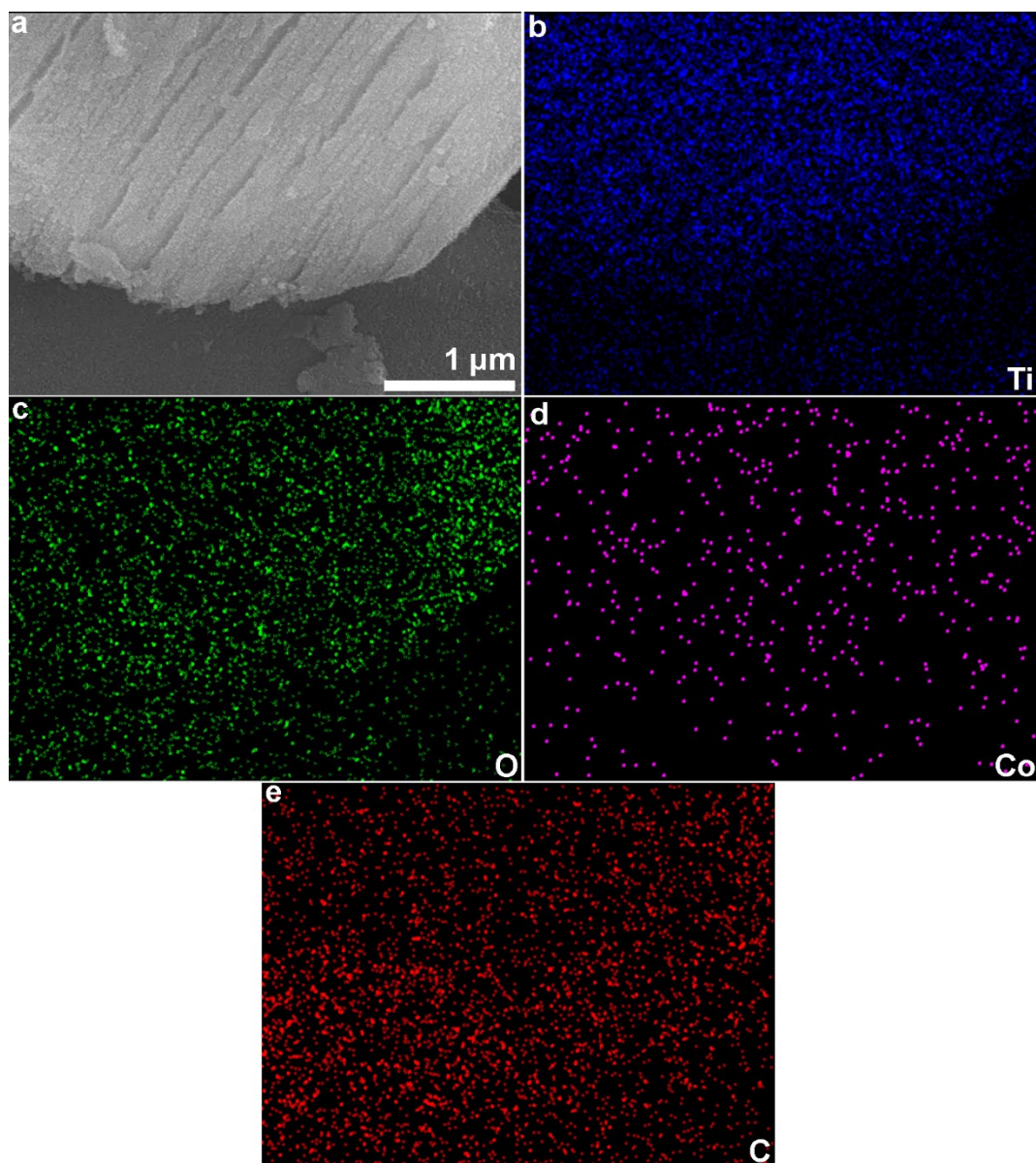

Figure S6. SEM images of LM-Co-TO NP catalysts.

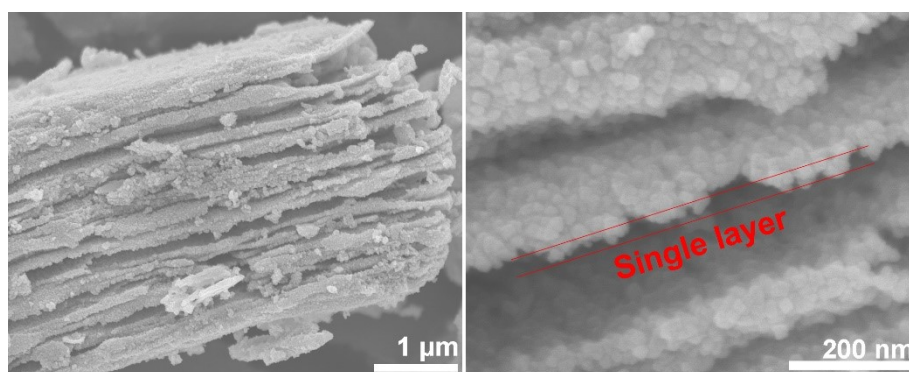**Figure S7.** Elemental mapping of Ti, O, Co, and C elements in LM-Co-TO NP catalysts.
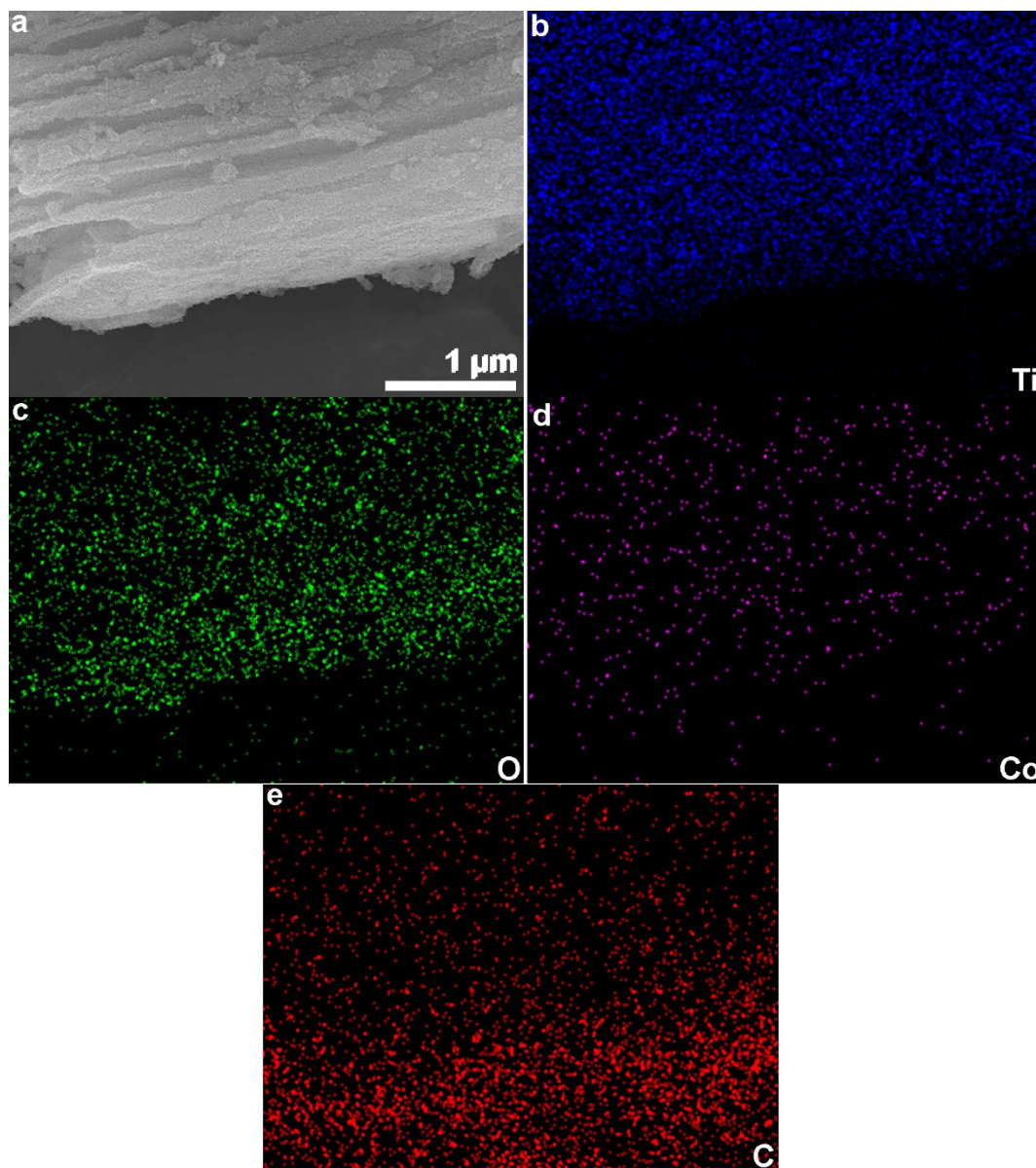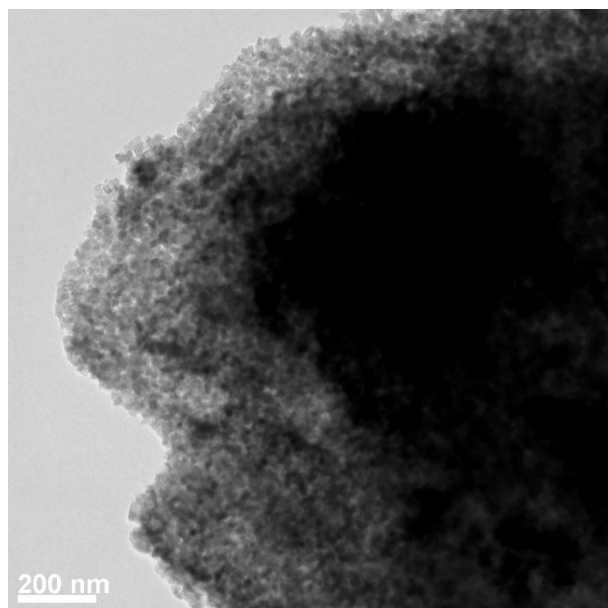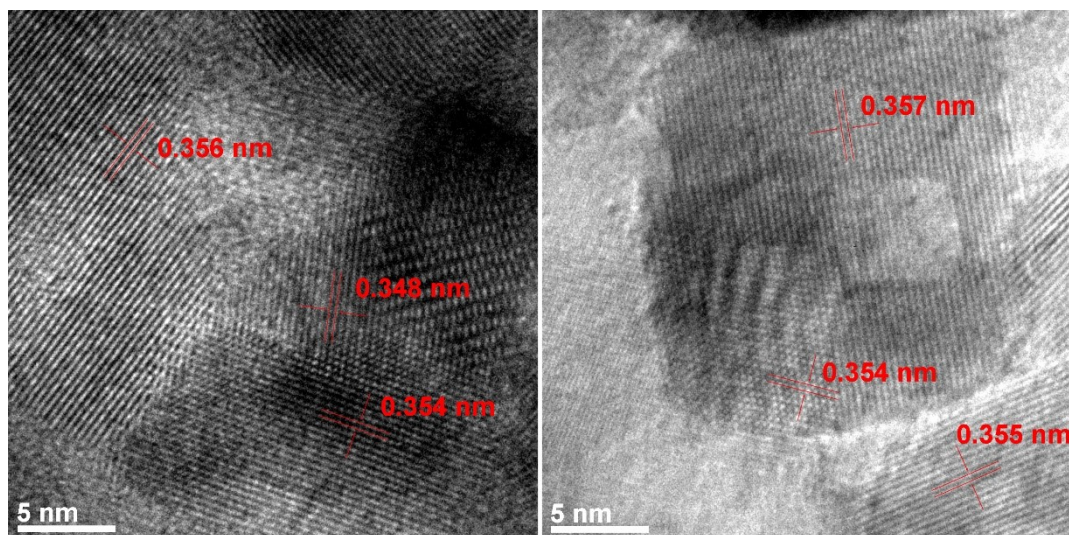
Figure S8. SEM images of LM-Co-TO NA catalysts.

Figure S9. Elemental mapping of Ti, O, Co, and C elements in LM-Co-TO NA catalysts.

Figure S10. TEM images of LM-Co-TO NA catalysts.
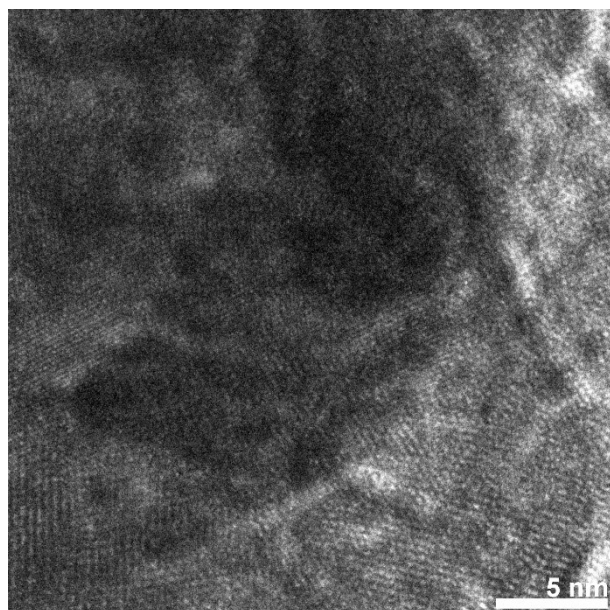

Figure S11. HRTEM images of LM-Co-TO NA catalysts.
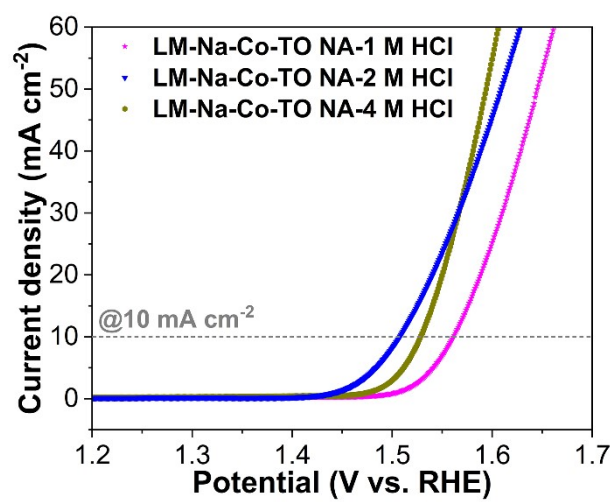
Figure S12. HRTEM images of LM-Co-TO NA catalysts.

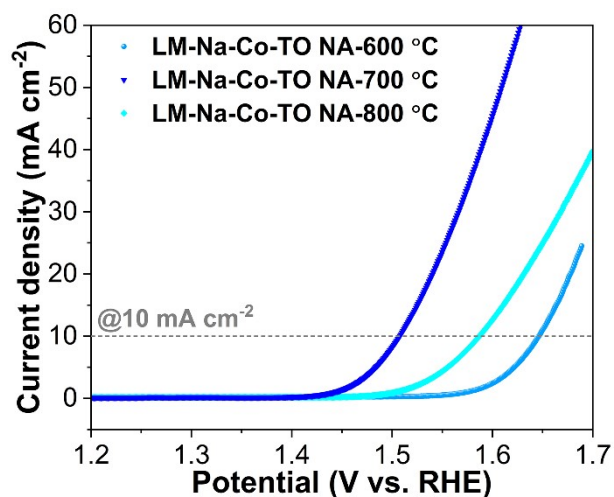**Figure S13.** OER LSV curves of LM-Co-TO NA electrocatalysts treated with different concentrations of HCl.

Figure S14. OER LSV curves of LM-Co-TO NA electrocatalysts pyrolyzed at different temperature.
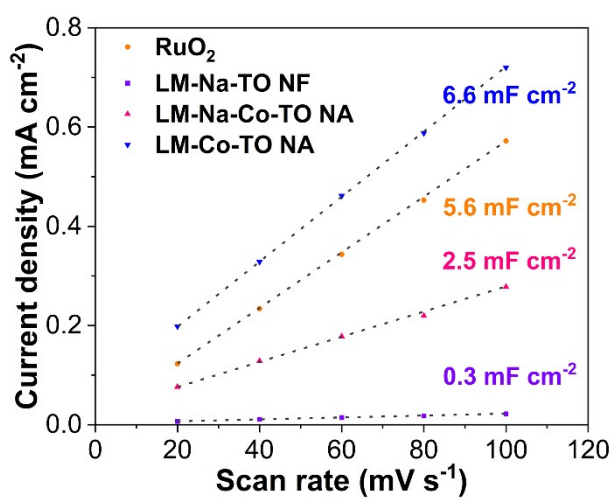

Figure S15. C_{dl} values of commercial RuO_2, LM-Na-TO NF, LM-Na-Co-TO NA, and LM-Co-TO NA electrocatalysts.
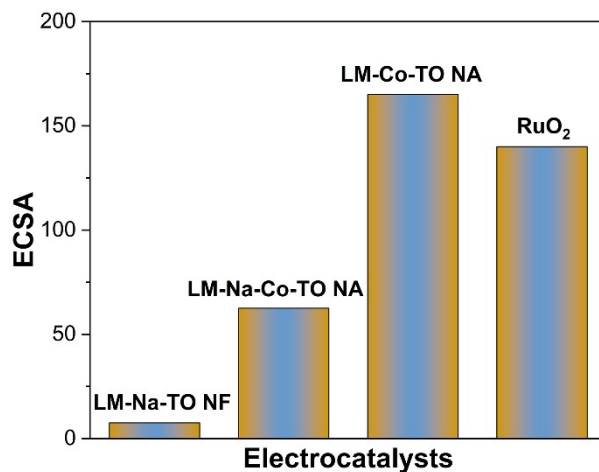
Figure S16. ECSA values of commercial RuO_2, LM-Na-TO NF, LM-Na-Co-TO NA, and LM-Co-TO NA electrocatalysts.
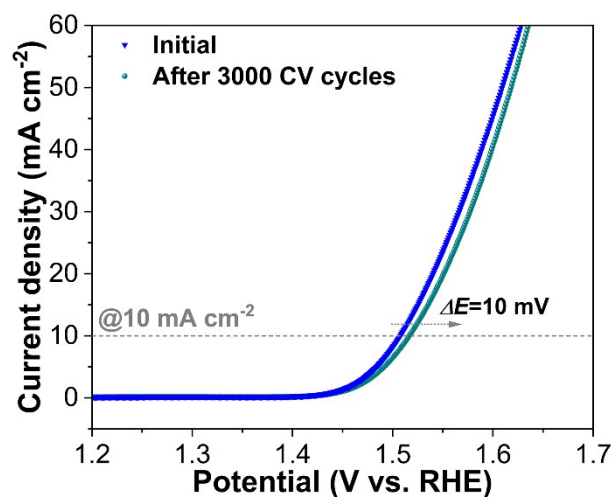

Figure S17. OER LSV curves of LM-Co-TO NA before and after 3000 CV cycles.
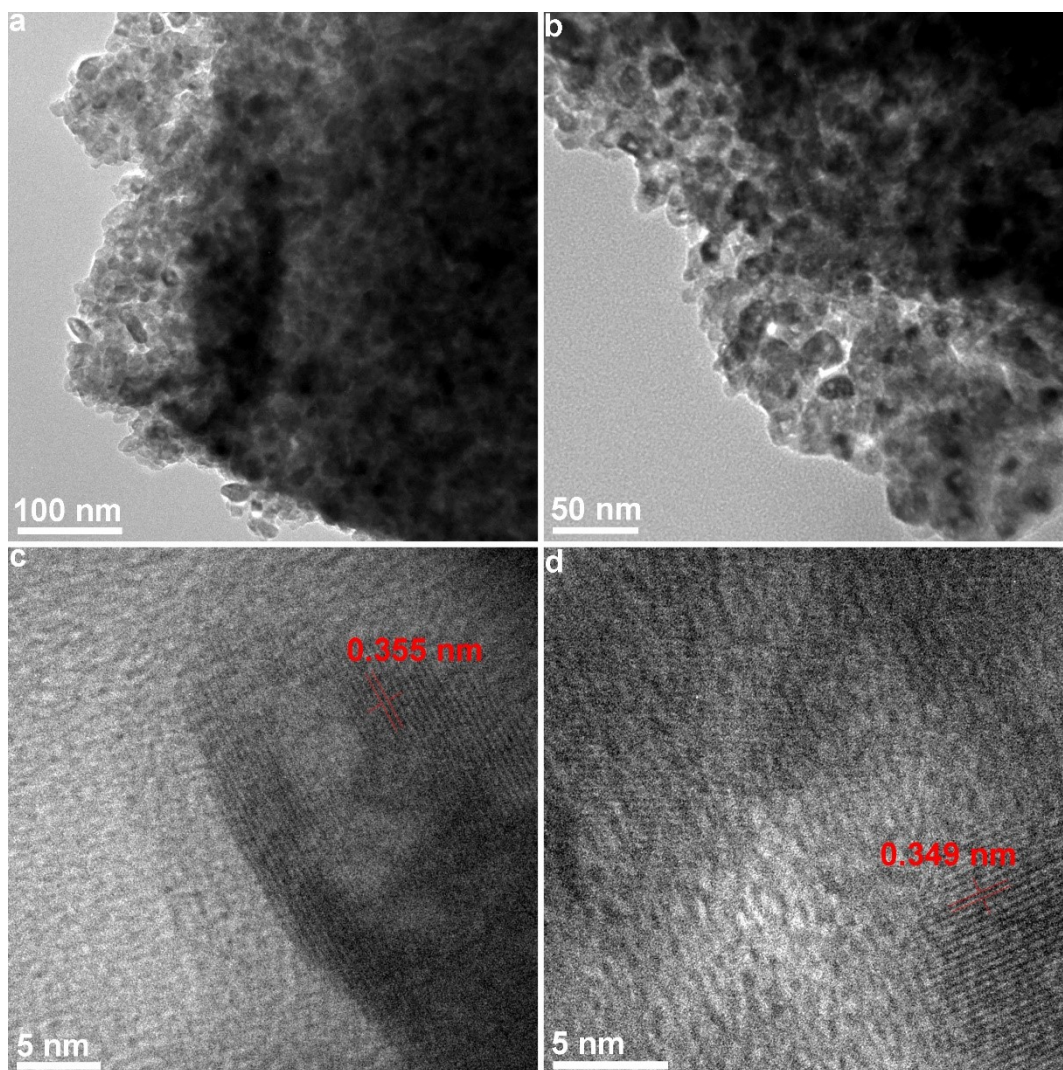
Figure S18. (a,b) TEM and (c,d) HRTEM images of LM-Co-TO NA after stability testing.

Table S1. Element content in LM-Co-TO NA detected by ICP-OES technique.

Name	wt%
Co	0.82
Na	0.02
Ti	52.94

Reference

[1] X. Zeng, D. Duan, X. Zhang, X. Li, K. Li, R. Yu and M. Moskovits, *J. Mater. Chem. C*, 2022, **10**, 4140.

[2] J. Huang, R. Meng, L. Zu, Z. Wang, N. Feng, Z. Yang, Y. Yu and J. Yang, *Nano Energy*, 2018, **46**, 20–28.