Vector Substrate Design for Grain Boundary Engineering: Boosting Oxygen Evolution Reaction Performance in $LaNiO_3$

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Experimental Section

Sample preparation: Epitaxial multilayer thin films were fabricated using a PLD technique. SAO and STO layers were sequentially deposited on the STO substrate at a temperature of 700 ℃. The growth oxygen pressure was set to 5×10^{-5} Torr for SAO and 1×10^{-1} Torr for STO. The as-grown sample was attached to PDMS and then immersed in deionized water to dissolve the SAO layer, obtaining a freestanding STO membrane that adhered to the PDMS. Then, the STO membrane was released from the PDMS by heating the as-sample at 100 °C for 10 minutes and transferred to another STO substrate with a different orientation. Then, the LNO layer was deposited on the modified substrate, with a temperature of 700 ℃ and a growth oxygen pressure of 1×10^{-1} Torr.

Characterizations: The crystal structure, surface morphology, and microstructure were characterized using XRD (Rigaku Smartlab), AFM (Asylum Research, MFP-3D Origin+), and TEM (JEM-2100Plus). XPS (PHI5000 VersaProbeIII) analyses were conducted using a non-monochromatized Al Kα X-ray source.

OER measurements: The OER performance was assessed using a standard three-electrode system with a CHI760E electrochemical workstation in 1 mol L^{-1} KOH solution. The carbon rod and Hg/HgO electrode served as the counter and reference electrodes, respectively. Additional experimental details can be found in the provided reference.[1] All potentials were converted to a reversible hydrogen electrode (RHE): E vs RHE=E vs Hg/HgO+0.098+0.059×pH. All potentials mentioned in this study are versus RHE.

Theoretical Calculations: All DFT computations were performed using the Vienna Ab-initio Simulation Package (VASP). Exchange-correlation effects were treated with the Perdew-Burke-Ernzerhof (PBE) functional in the generalized gradient approximation (GGA) method. Core-

valence interactions were handled using the projected augmented wave (PAW) method. A plane wave energy cutoff of 400 eV was applied. Structural optimization was achieved with energy and force convergence criteria set at 1.0×10^{-4} eV and 0.05 eV $Å^{-1}$, respectively. The Brillouin zone was sampled using a 3×3×1 K-point mesh. Dispersion interactions were modeled with Grimme's DFT-D3 approach.

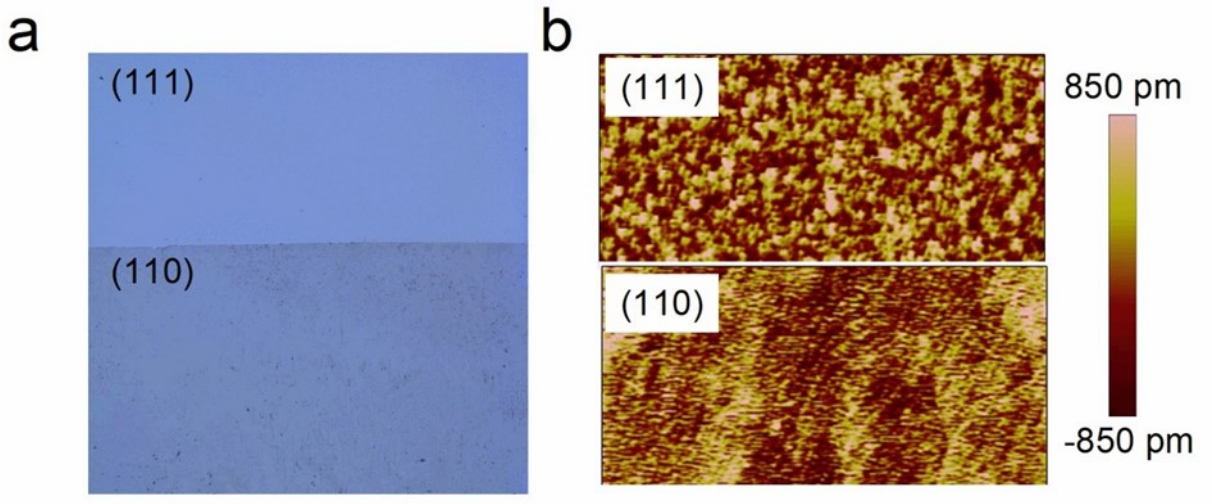

Fig. S1 Optical and AFM images of LNO (110/111).

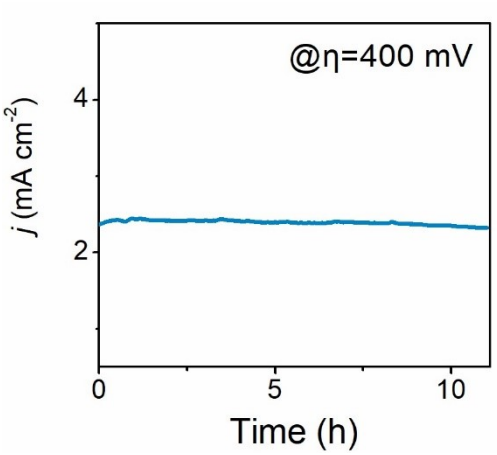

Fig. S2. Chronoamperometry curve at η=400 mV of the LNO (110/111).

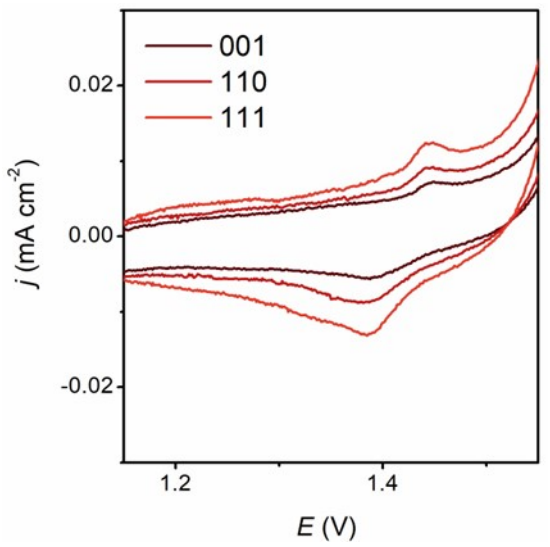

Fig. S3 CV curves of LNO (001), (110), and (111).

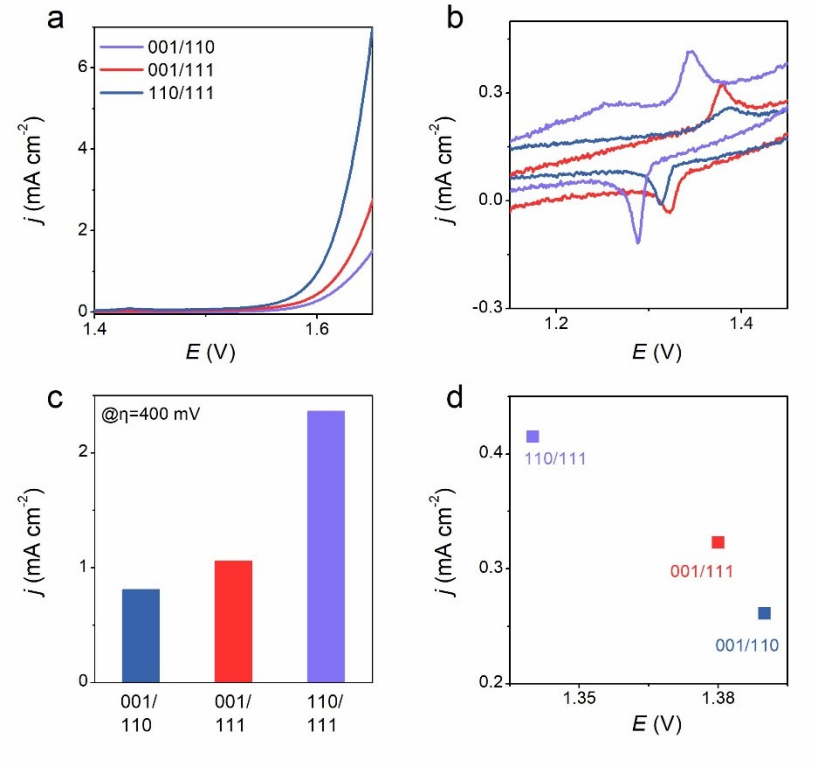

Fig. S4 (a) LSV and (b) CV curves of LNO (001/110), (001/111), and (110/111) grown on LAO substrates. The summarized (c) current density at η=400 mV and (d) oxidation peak positions.

References

1 H. Liu, B. He, Y. Han, J. Guo, J. Wang, H. Fang, J. Wang, W. Gao, Y. Zhang, Z. Wang, Z. Wang, S. Yan and W. Lü, *Appl. Catal. B-Environ. Energy*, 2024, **359**, 124495.