

Supporting Information

Tuning La_2O_3 to high ionic conductivity by Ni-doping

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Material and methods

1. Material preparation

NLO was prepared through a co-precipitation method. 0.01 mol $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aladdin LTD) and stoichiometric $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (Sinopharm Chemical Reagent Co. Ltd, Shanghai) were added into 50 ml deionized water to obtain a solution. EDTA (Sinopharm Chemical Reagent Co. Ltd, Shanghai) solution was prepared with molarity ratio $(\text{La}^{3+} + \text{Ni}^{2+}) : \text{EDTA}$ of 1:1.5. This was followed by adding it into the mixed solution under magnetic stirring at room temperature. The resulting solution was treated with an amount of 1 mol L^{-1} NaOH (Sinopharm Chemical Reagent Co. Ltd, Shanghai) solution then stirred at $70 \text{ }^\circ\text{C}$ for 5h. The precursors were centrifuged at 2500 rpm, then dried in an oven at $120 \text{ }^\circ\text{C}$ for 5h and ground into power. The obtained powers were calcinated at $800 \text{ }^\circ\text{C}$ in air atmosphere for 3 h to get final samples. To study the doping effect of NiO, the molar ration of Ni^{2+} to La^{3+} were set as 5%, 10% and 15%, which were donated as 5NLO, 10NLO and 15NLO.

2. Fuel cell fabrication

The NCAL powder was purchased from Tianjin Xinli Science &Technology Joint Stock Ltd., China. Ethanol and terpineol in 1:1 volume ratio were added into NCAL to get slurry, which was brushed on one side of nickel foam. Then the nickel foam with NCAL was dried in oven at $80 \text{ }^\circ\text{C}$ for 1 h to get NCAL electrode. Fuel cells with Ni-NCAL/NLO(La_2O_3)/NCAL-Ni configuration were fabricated by one step pressing under 6 MPa uniaxial pressure for 60 s to obtain the pellet. The obtained fuel cell had a thickness of 1 mm and an active area of 0.64 cm^2 .

3. Electrochemical measurement

The impedance spectroscopy (EIS) measurements were measured by CHI660E (Shanghai, China) at a frequency range of $0.1\text{--}10^6 \text{ Hz}$ in H_2/air atmosphere at $490\text{--}550 \text{ }^\circ\text{C}$. To further get the

performance of the cells, a fuel cell tester (ITECH DC ELECTRONIC LOAD, IT8511A+) was used to record electrical outputs under temperatures ranging from 550 °C to 490 °C. The flow rate of hydrogen and oxygen are 120 and 100 mL min⁻¹, respectively.

4. Characterization

The phase structure of pure La₂O₃ and NLO were characterized by Bruker D8 X-ray diffractometer with Cu K α radiation, from 20° to 80° at the rate of 10° min⁻¹. The morphology of the samples was investigated by SiGMA500, ZEISS Scanning Electron Microscope (SEM). Transmission electron microscopy (TEM) images and HR-TEM were measured by Titan G2 60-300, super X Transmission Electron Microscope. The X-ray photoelectron spectroscopy (XPS) was measured by AXI ultra DPD SHZMADZU. X-ray photoelectron spectra (XPS) were recorded on a Kratos Axis Ultra DLD spectrometer using Al KR radiation (1486.6 eV) as the excitation source. The analysis was performed at room temperature. Binding energies were calibrated by using the containment carbon (C 1s = 284.6 eV). Semiquantitative analysis of the atomic ratio was accomplished by determining the elemental peak areas. Ultraviolet-visible (UV-vis) diffuse reflectance spectra were performed under ambient conditions using a Nicolet Evolution 500 spectrophotometer equipped with an integrating sphere. BaSO₄ was used as a reference, and spectra were recorded in the range of 200-800 nm. Raman spectra were collected by a Renishaw RM1000 confocal microprobe under ambient conditions. The excitation wavelengths were 532 nm. The power of each laser line was kept at about 3 mW to prevent a local heating effect, and the resolution of the spectrometer was 1 cm⁻¹ with the diameter of the analyzed spot being ca. 1 μ m. The sample was always pretreated in N₂ at 500 °C for 1 h and then cooled down to room temperature under flowing N₂ before each measurement.

5. First principles calculation

To get the insight of Ni doping on the conductivity of 10NLO, first principle calculation was also performed in this work. The structure model of 10NLO was based on the La_2O_3 (P 63/mmc). The nuclei and core electrons were represented within the frozen-core projector-augmented wave approach using standard potentials for La (5s25p65d16s2), Ni (3p63d84s2) and regular O (2s22p4) from the VASP library, where the outer core/valence electrons shown in parentheses are self-consistently optimized. The generalized gradient approximation (GGA) method with the parameterization of Perdew-Burke-Ernzerhof revised for solids (PBEsol) was used for exchange and correlation functional. Each crystal structure was fully relaxed with the plane-wave energy cutoff of 560 eV under the conduction of residual force ≤ 0.01 eV/Å.

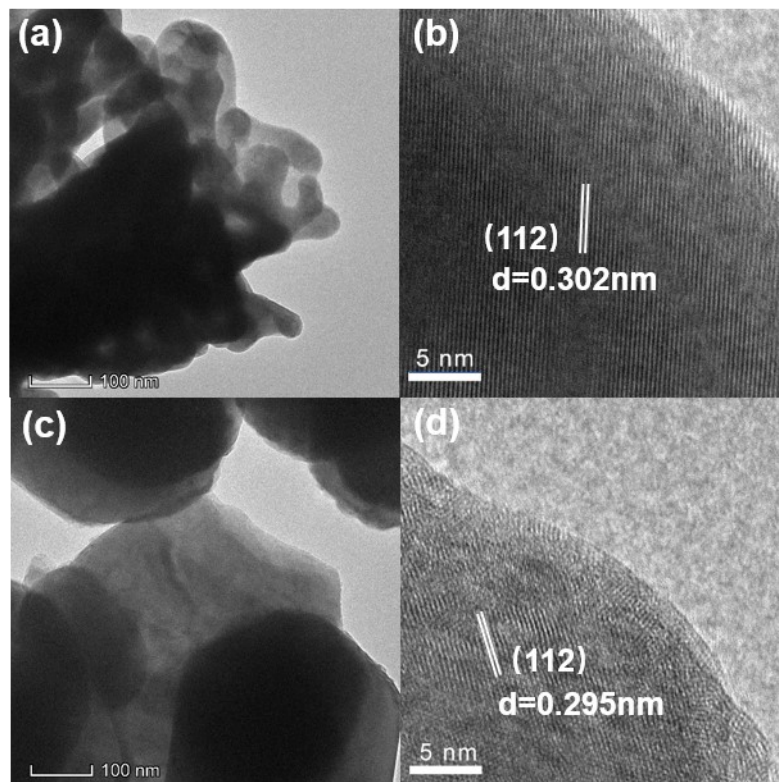


Figure S1 TEM and HRTEM images of (a-b) pure La_2O_3 and (c-d) 10NLO.

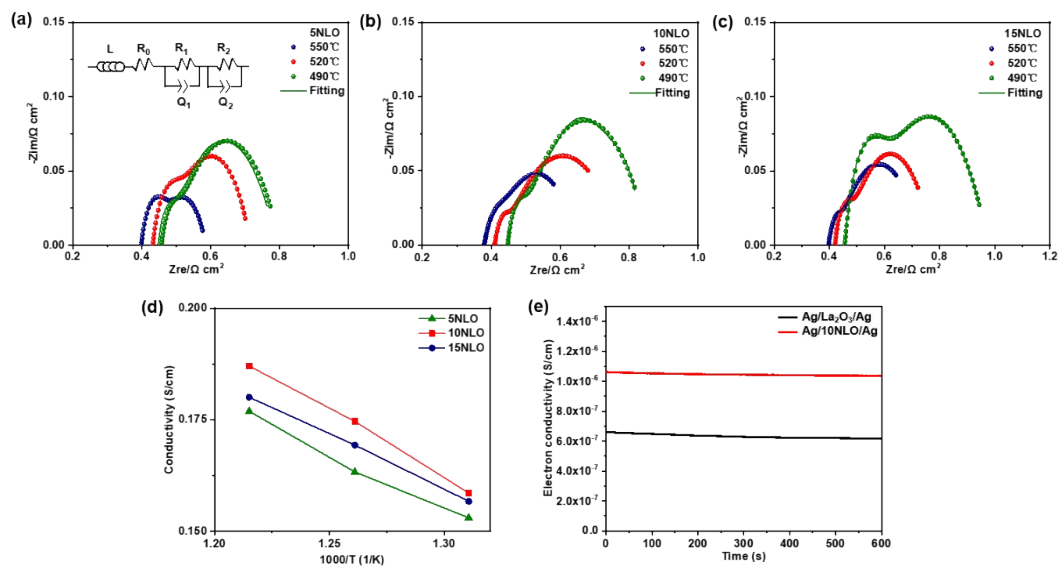


Figure S2 Impedance spectra measured in H_2/air at 490-550 °C of (a)5NLO, (b)10NLO and (c)15NLO. (d) Conductivity for three samples as a function of $1000/T$. (e) Electron conductivity as the function of time.

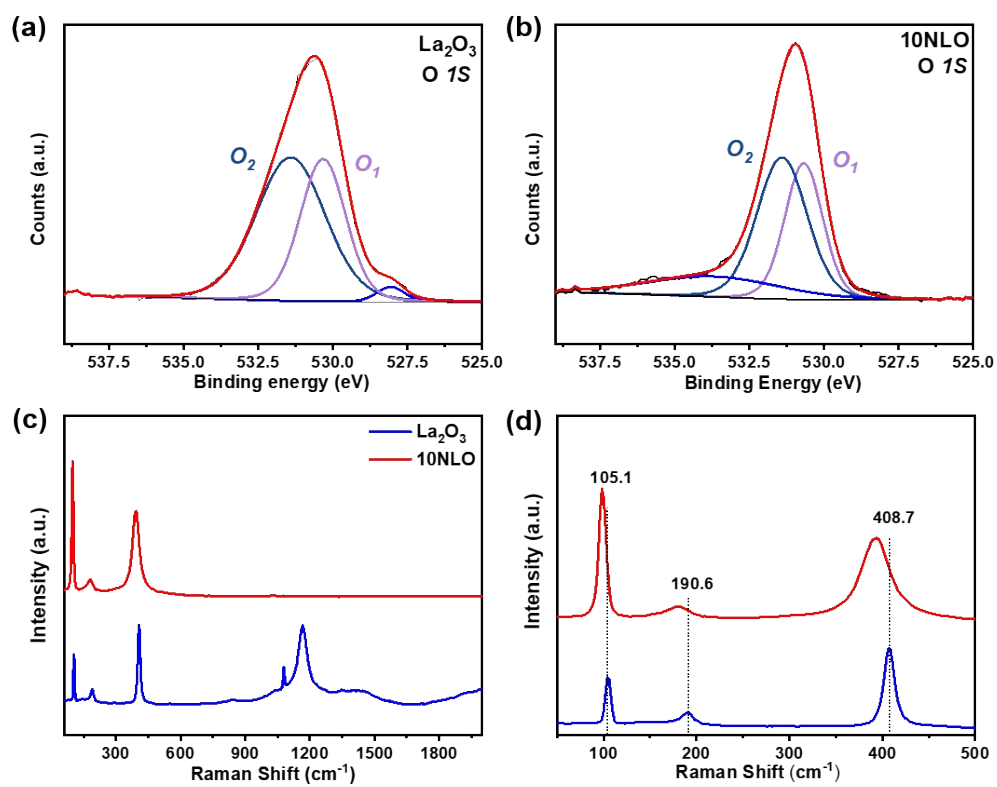


Figure S3 XPS results of O 1s for (a) La_2O_3 ; (b) 10NLO. Raman spectra for pure (c) La_2O_3 and (d) 10NLO.