

Supplementary Information

A facile mixed-complexing synthesis for perovskite oxides toward electrocatalytic oxygen reduction

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1. Synthesis of perovskite-type $\text{La}_{(0.5+x)}\text{Sr}_{(0.5-x)}\text{FeO}_{3-\delta}$ ($x = 0.00, 0.10, 0.20$) oxides

The perovskite-type $\text{La}_{(0.5+x)}\text{Sr}_{(0.5-x)}\text{FeO}_{3-\delta}$ ($x = 0.00, 0.10, 0.20$) oxide powders were synthesized by the facile reaction-EDTA/citric acid mixed complexing sol-gel method. Analytic grade $\text{La}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, SrCO_3 , $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, EDTA and citric acid were used as starting materials. Firstly, precisely weighed SrCO_3 powders were reacted with HNO_3 solution, and then the corresponding nitrate salts were also weighed carefully according to the nominal metal elemental compositions of $\text{La}_{(0.5+x)}\text{Sr}_{(0.5-x)}\text{FeO}_{3-\delta}$ ($x = 0.00, 0.10, 0.20$). Subsequently, the weighted nitrate salts were dissolved completely into the solution, and a certain amount of EDTA and citric acid (molar ratio: EDTA: citric acid: metal cations = 0.6:0.6:1.0) as complexing reagents, were added stirringly. Finally, a dark brown gel obtained was dried at 110-150 °C, and ignited at 300-350 °C for obtaining the original powders. The

as-synthesized precursors were then further calcinated in a muffle oven at different temperatures (850-950 °C) for 5 h to obtain the final perovskite-type powders.

2. Materials characterization

The crystalline structure of the as-prepared samples was determined by X-ray diffraction (XRD, D2 PHASER, Bruker, Germany). The oxide powders were also analyzed by a laser particles size analyzer (S3500, Microtrac BEL, Japan). The chemical states of elements were characterized by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, USA). The morphologies and microstructures of the materials were examined by a scanning electron microscopy (SEM, Sigma 500, Carl Zeiss, Germany) with Energy-dispersive X-ray (EDX) elemental mappings. Transmission electron microscope (TEM, Tecnai G2 FEI, USA), and high-resolution TEM (HRTEM, Tecnai G2 TF20, FEI, USA) were also examined, and further processed by the DigitalMicrograph software.

3. Electrochemical testings

The evaluation of ORR electrochemical activities were conducted on an electrochemical workstation (Solartron, S1 1287, UK) equipped with an RRDE-3A (ALS, Japan). The three-electrode electrolyte cell consists of a 3-mm glassy carbon working electrode (GCE), an Hg/HgO electrode as the reference electrode and a platinum wire as the counter electrode (CE). 3.0 mg of catalyst was dissolved in the mixture of 50 μ L Nafion solution (5 wt%) and 950 μ L ethanol, and then was ultrasonicated for 25 min. to obtain the catalyst slurry. The catalyst ink was dropped onto the working electrode and dried naturally to obtain film electrode at room temperature. For the electrochemical ORR experiments, the linear sweep voltammetry (LSV) was performed in an O₂-saturated 0.1 M KOH electrolyte, the rotating speed is 400-2500 rpm, and scan rate is 5 mV s⁻¹. The Hg/HgO potential was also converted to the RHE scale as $E_{(RHE)} = E_{(Hg/HgO)} + 0.0591 \times pH + 0.098 + iR$. The ohmic resistances were also measured by electrochemical imped spectroscopy (EIS) for iR compensation in the electrolyte cells.

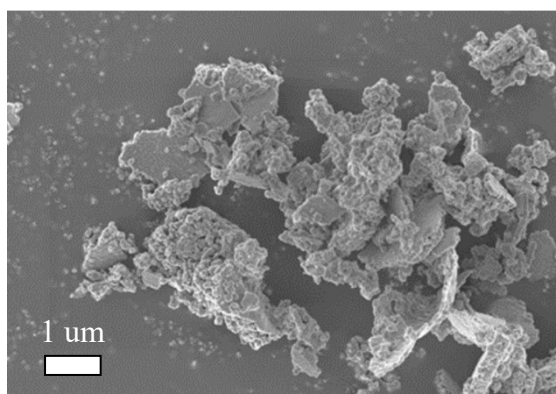


Fig. S1. SEM micrograph of the as-synthesized $\text{La}_{(0.5+x)}\text{Sr}_{(0.5-x)}\text{FeO}_{3-\delta}$ ($x = 0.10$) perovskite-type oxide powders.

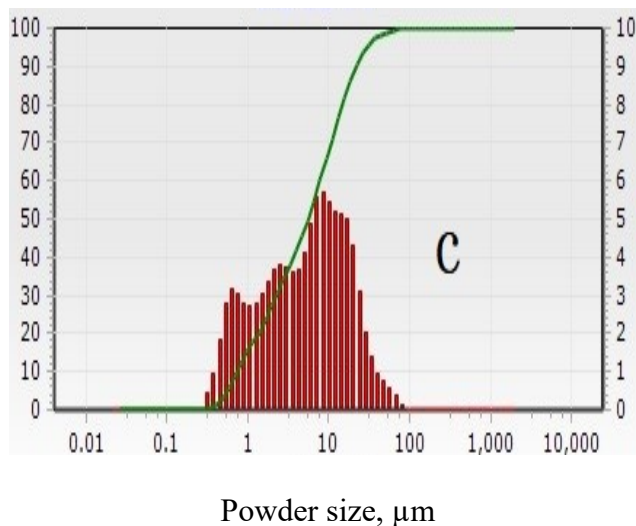
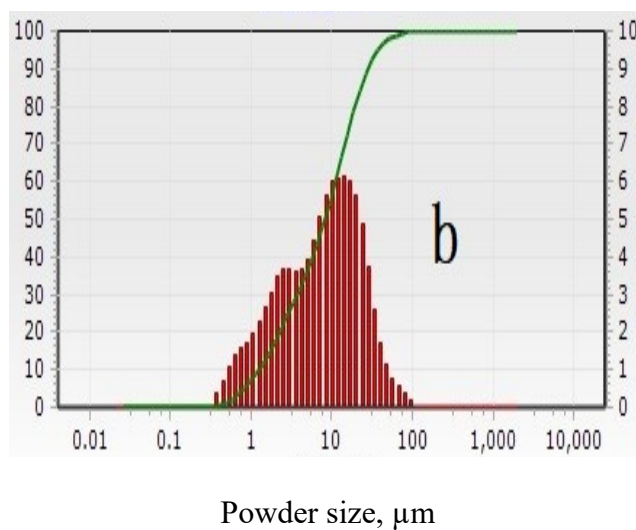
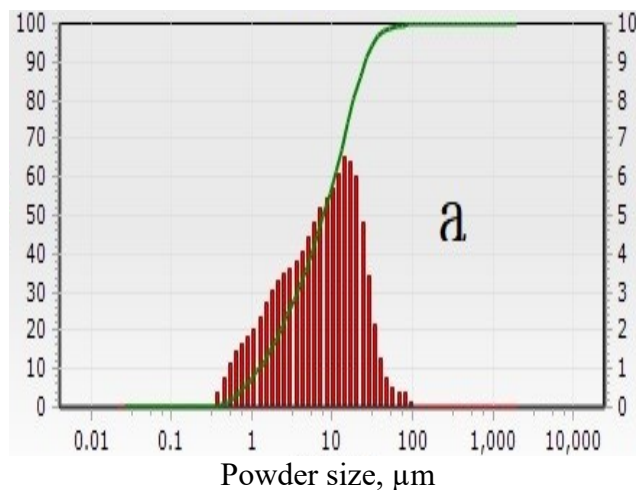


Fig. S2. Powders size distribution (by laser particle size analysis, LPSA) of the as-synthesized $\text{La}_{(0.5+x)}\text{Sr}_{(0.5-x)}\text{FeO}_{3-\delta}$ ($x = 0.00, 0.10, 0.20$) perovskite-type oxide powders (a-0.00; b-0.10; c-0.20) calcinated at 950 °C.

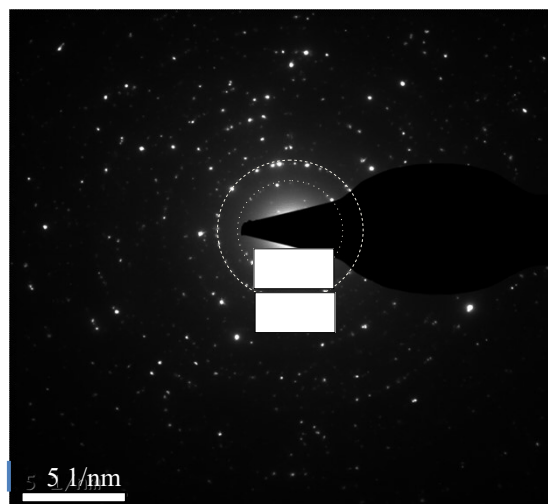


Fig. S3. SAED of the perovskite-type $\text{La}_{(0.5+x)}\text{Sr}_{(0.5-x)}\text{FeO}_{3-\delta}$ ($x = 0.10$) oxide polycrystal.

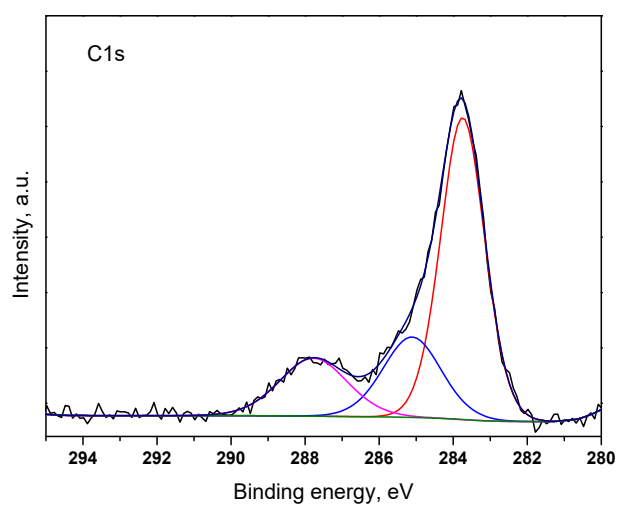


Fig. S4. XPS C1s spectra of the perovskite-type $\text{La}_{(0.5+x)}\text{Sr}_{(0.5-x)}\text{FeO}_{3-\delta}$ ($x = 0.10$) oxide powder.

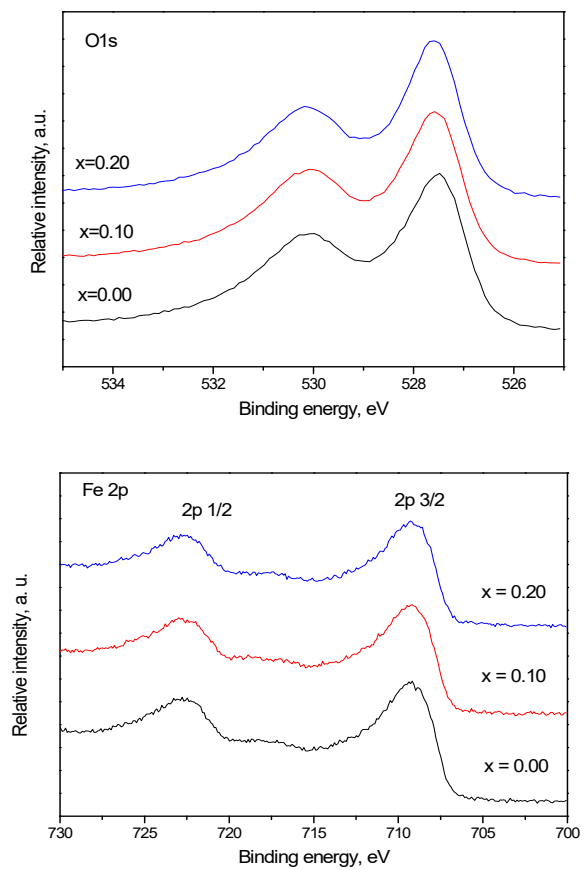


Fig. S5. High-resolution XPS O 1s and Fe 2p spectra of the perovskite-type $\text{La}_{(0.5+x)}\text{Sr}_{(0.5-x)}\text{FeO}_{3-\delta}$ ($x = 0.00, 0.10, 0.20$) oxide powders.

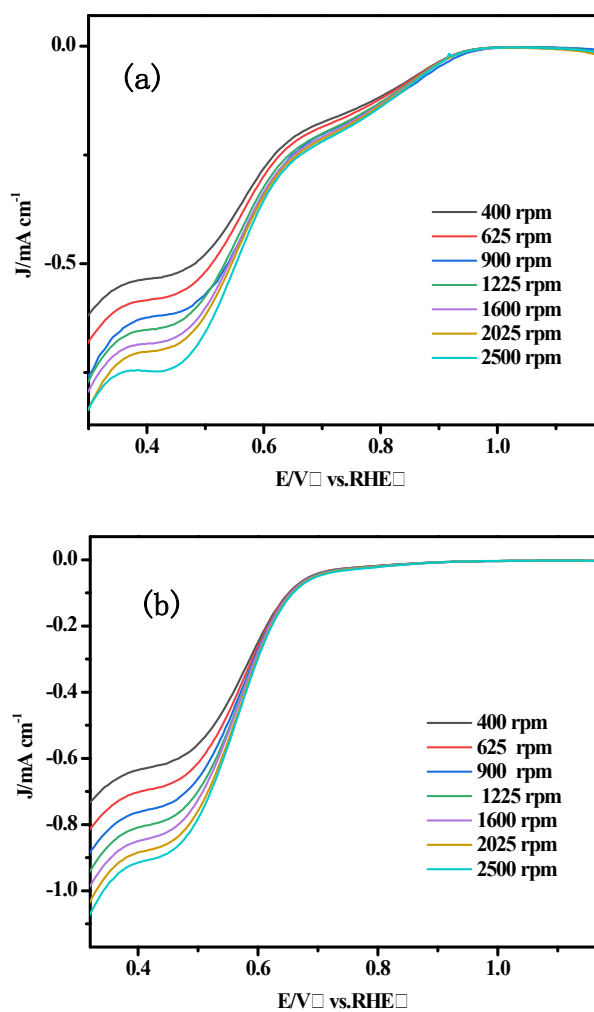


Fig. S6. The electrochemical LSV curves towards ORR of the $\text{La}_{(0.5+x)}\text{Sr}_{(0.5-x)}\text{FeO}_{3-\delta}$ ($x = 0.00$, 0.20) oxides in 0.1 M KOH solution. (a) $x = 0.00$, and (b) $x = 0.20$.