

Supporting for

Synthesis of shape-controlled $\text{La}_2\text{NiO}_{4+\delta}$ nanostructures and their anisotropic properties for oxygen diffusion

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1. Experimental section

1.1 Material synthesis

All chemicals were used as commercially received without further purification. The LNO precursor complex was prepared using a reverse microemulsion method. In a typical synthesis using NaOH as the precipitating agent, two separate reverse-microemulsions were first prepared in round glass flasks, with each containing a quaternary reverse-microemulsion system consisting of cetyltrimethylammonium bromide (CTAB)/water/hexane/n-Butanol. One microemulsion was formed by adding the aqueous solution of 1.734 g of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.999%, Sigma Aldrich) and 0.594 g of $\text{Ni}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (98%, Alpha Aesar) dissolved in deionized water, and the other one had 0.825 g NaOH (ACS grade, Fisher) in deionized water. In each microemulsion, the amounts of CTAB, hexane, and n-butanol were fixed at 11.25 g, 56.0 mL, and 11.3 ml, respectively. The amount of water in the hydroxide ion containing reverse microemulsion solution was fixed at 7.0 g, while the amount of water in the metal cation reverse microemulsion solution was varied to obtain a CTAB to H_2O mass ratio ranging from 1.6 to 14.0. After the microemulsion systems were well-mixed, the microemulsion solution containing the base was added to the one containing the metal salts under stirring (1200 rpm). The system was maintained under the same conditions for 4 hours to form the gel suspension containing the metal hydroxide precursor complex. The solid gel was collected via centrifuging (600 rpm, 3 min), was washed two times using ethanol, and rinsed three times with deionized water. This was followed by drying under static air at 80 °C for 12 hours. A similar procedure was used for the synthesis of metal carbonate precursor complex, except that Na_2CO_3 was used as the precipitating agent, and the CTAB/ H_2O mass ratio in the metal cation reverse microemulsion solution was fixed at 14.0.

The dried precursor complex was then subjected to thermal treatment to obtain the oxide crystals. Calcination of the metal hydroxide precursors was performed at 825 °C (2°C/min ramp from room temperature) under flowing argon (350 sccm) for 2 hours. In the case of the metal carbonate complex, successful calcination could only be achieved when the samples were heated at 2°C/min to 1025 °C under static air for 2 hours.

1.2 Characterization

An X-ray diffractometer (XRD, Smartlab, Rigaku Inc., Japan) was employed to determine the crystal structure of the samples. The equipment uses a Cu K α radiation ($\lambda = 0.15418$ nm). XRD pattern of each LNO sample was recorded over 2θ values of 20° to 80° at a rate of 4° / min.

A field-emission scanning electron microscopy (FE-SEM, JSM 7600, JEOL Inc., Japan) was used to inspect the morphology of the samples, with the instrument operating at 15 kV. Transmission electron microscopy (TEM) analysis of the samples was carried out on a JEOL 2010F electron microscope (JEOL Inc., Japan) at an accelerating voltage of 200 kV in the Electron Microbeam Analysis Laboratory at the University of Michigan.

1.3 Oxygen uptake/release measurement

Thermal gravimetric analysis (TGA) was employed to study the oxygen uptake/release of different LNO nanostructures. In these experiments, the weight of the LNO sample was monitored as it was exposed to air and argon (Ar) sequentially. The variation in the weight of the material was associated to the oxygen uptake/release during exposure to air and Ar, respectively. Initially, the sample (~50 mg) was heated under air to 500 °C and maintained at this temperature for 60 min to remove any impurities, and then purged with Ar for 90 min to remove the excess oxygen in the sample. This was followed by switching the feed gas to air and measuring the weight-gain due to the oxygen uptake. After a defined delay time of 60 min, the feed gas was switched back to Ar, and the weight loss of the sample was measured. These measurements were repeated for three different to determine the reversibility of oxygen uptake/release.

For each measurement, the oxygen storage capacity was calculated as the amount of oxygen accumulated (or released) per gram of catalysts. Oxygen diffusion rate in each experiment was defined as the amount of oxygen released per minute, per gram of the catalyst. This value was determined through polynomial regression of the plot of weight loss versus time, and calculation of the first derivative of the regression function at the initial time of oxygen release.

2. Supplementary figures

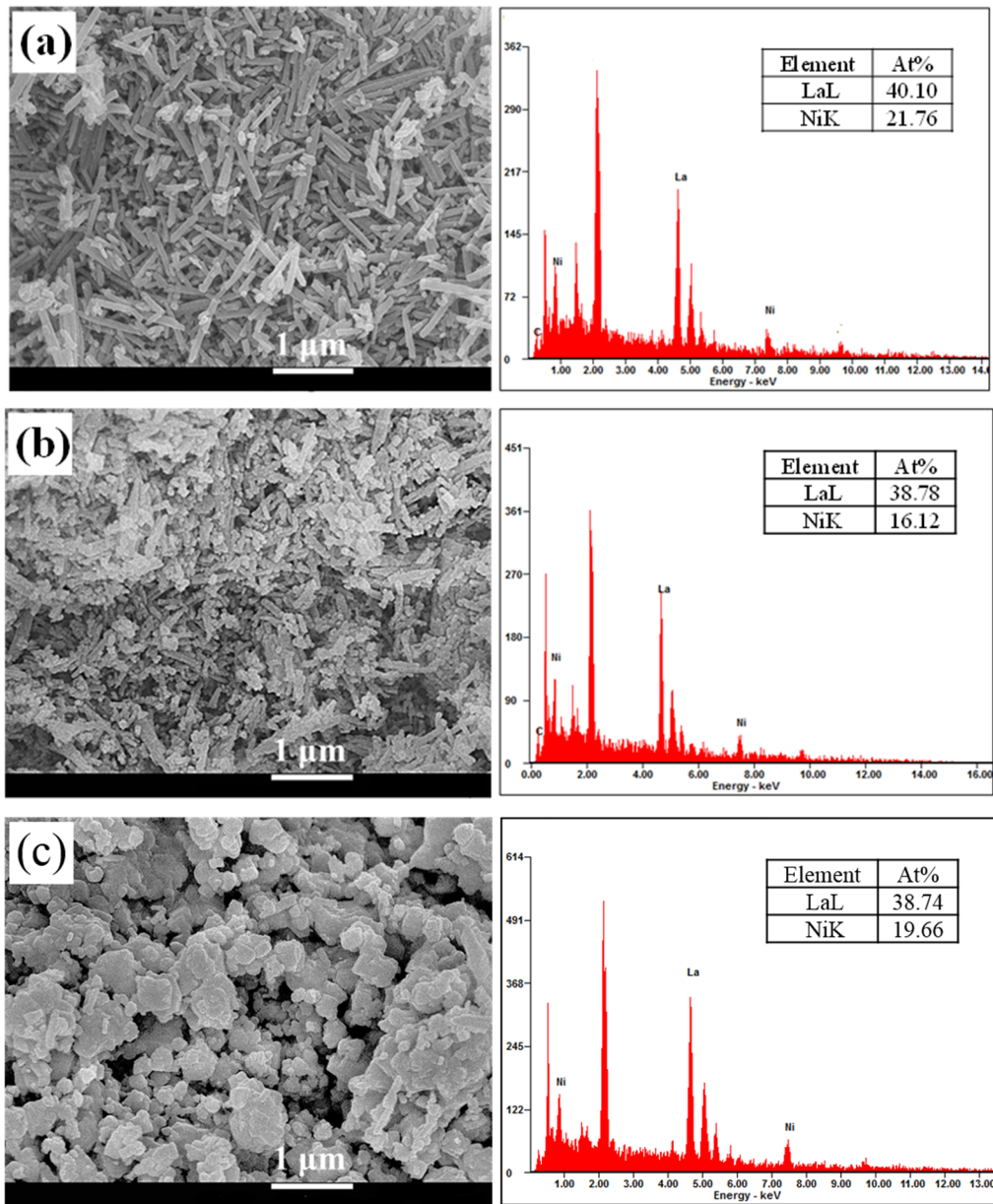


Fig. S1 EDS spectra of nanostructured LNO prepared at different CTAB to H₂O mass ratio (W_0) used for the synthesis of hydroxide precursor complex. (a) $W_0=1.6$, (b) $W_0=6.0$, (c) $W_0=14.0$.

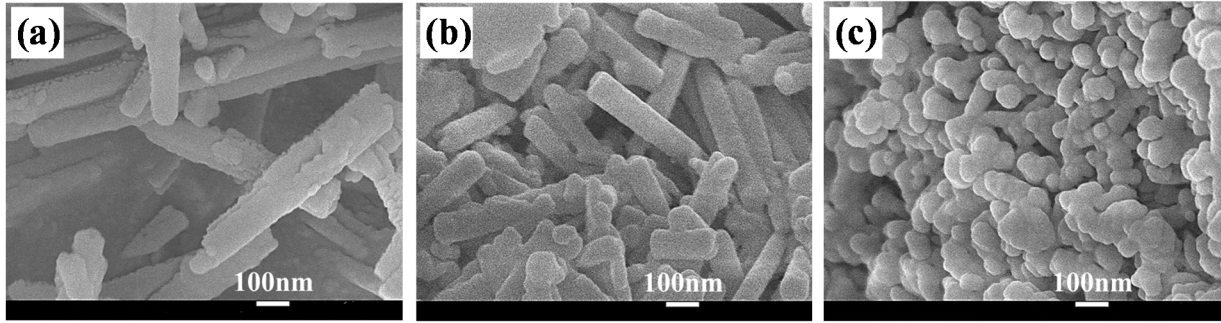


Fig. S2 SEM images of LNO hydroxide precursor complex prepared at different CTAB to H₂O mass ratio (W_0) in the metal cations reverse microemulsion. (a) $W_0=1.6$, (b) $W_0=6.0$, (c) $W_0=14.0$.

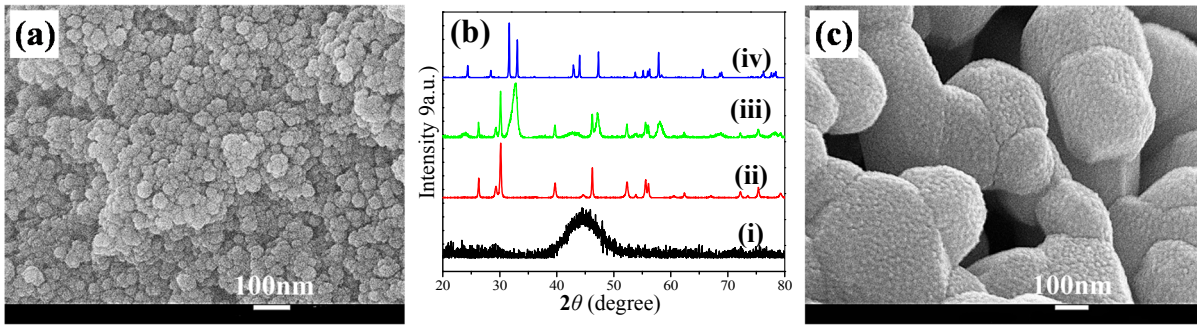


Fig. S3 (a) SEM image of metal carbonate precursor complex. (b) XRD spectra of (i) metal carbonate precursor complex, (ii) metal carbonate precursor complex calcined at 835°C under flowing Ar, (iii) metal carbonate precursor complex calcined at 835°C under static air, and (iv) metal carbonate precursor complex calcined at 1025°C under static air. (c) SEM image of LNO obtained by calcination of metal carbonate precursor complex at 1025°C under static air.

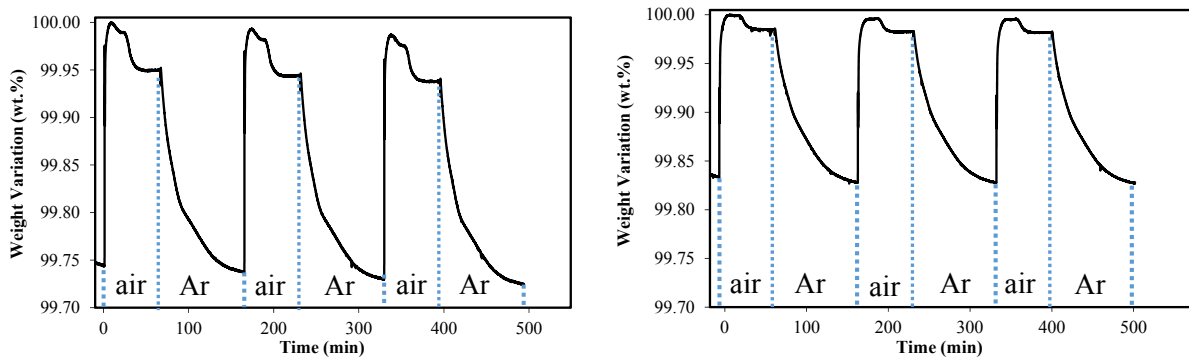


Fig. S4 Weight variation pattern of LNO under air/Ar cycling at 773 K. Similar patterns were observed for the measurement under other temperatures ranging from 723 K to 923 K.