Electronic Supporting Information

High Surface Area Mesoporous $LaFe_xCo_{1-x}O_3$ Oxides: Synthesis and Electrocatalytic Property for Oxygen Reduction

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Synthesis of silica template and ordered mesoporous $LaFe_xCo_{1-x}O_3$

Mesoporous silica KIT-6 with *Ia3d* symmetry was prepared following the procedure reported by R. Ryoo et al. [27]. Typically, 6 g of surfactant P_{123} and 6 g of n-butanol was dissolved in a solution of 217 g distilled water and 11.4 g concd HCl (37 wt%). To this homogeneous solution, 12.9 g of tetraethylorthosilicate (TEOS) was added under stirring at 311 K and continuously stirred at 311 k for additional 24 h. Themixture was heated for 24 h at 373 K under static conditions for the hydrothermal treatment followed by filtration, washing, drying at 353 K in air, and calcination at 823 K for 5 h to remove the organic template.

The as-prepared mesoporous KIT-6 was then used as a hard template for the preparation of mesoporous $LaFe_xCo_{1-x}O_3$ ($0 \leq x \leq 1.0$) oxides. The typical synthesis procedure is as follows: 4 mmol lanthanum nitrate ($La(NO_3)_3\ nH_2O$), 4(1-x) mmol cobaltous nitrate ($Co(NO_3)_2\ 6H_2O$) and 4x mmol ferric nitrate ($Fe(NO_3)_3\ 9H_2O$) were dissolved in solvent (ethanol : deionized water = 3 : 1) Citric acid was added into the nitrate precursors as the chelating agent, and the molar ratio of the citric acid and metal ions was 1:1. The above mixed solution was co-casted into 0.5 g as-prepared KIT-6 by a wetness impregnation technique. After the solvent evaporated, the lanthanum and cobaltous precursors@silica composite was calcined at 543 K for 2 h firstly and then at 973 K for 6 h. The silica template was finally removed by treating in a 2 M NaOH solution for three times. This template-free oxide was collected by centrifugation and washed with distilled water and ethanol, and then dried at 353 K. The synthesis process of the mesoporous $LaFe_xCo_{1-x}O_3$ oxide was shown in Fig. 1. The obtained mesoporous samples were named as mesoporous $LaFe_xCo_{1-x}O_3$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0) oxides. The acetylene black mixed mesoporous $LaFe_xCo_{1-x}O_3$ oxides were prepared as follows: mesoporous $LaFe_xCo_{1-x}O_3$ oxides (0.1 g) prepared as above was dispersed in ethanol by ultrasonic treatment and acetylene black (0.01 g) was added under continuous ultrasonication for 30 min. After the ethanol was evaporated gradually at 313 K, the obtained composites were named as mesostructured $LaFe_xCo_{1-x}O_3/C$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0) composites.

Electrochemical experiments

Electrochemical experiments were performed on CHI 660A electrochemical workstation (CH Instrument, Inc.) with a standard three-electrode cell. Glassy carbon disks of 6 mm diameter (0.283 cm^2) served as substrate for the catalyst materials.

Catalyst ink with 5 mg mL^{-1} (ethanol :water = 1 : 1, volume scale) and 25 μL Nafion solution (5%) was dispersed ultrasonically, and 20 μL aliqot was transferred onto the glassy carbon substrate, yielding a catalyst loading level of 0.35 mg cm^{-2}. A platinum wire and Ag/AgCl (3 M KCl) were used as counter and reference electrodes, respectively. 0.5 M H_2SO_4 solution was used as electrolyte for electrochemical measurements and methanol electro-oxidation studies, respectively. High purity O_2 was used prior to the measurements to deaerate the electrolyte. The catalysts were characterized by cyclic voltammetry (CV) test at room temperature.

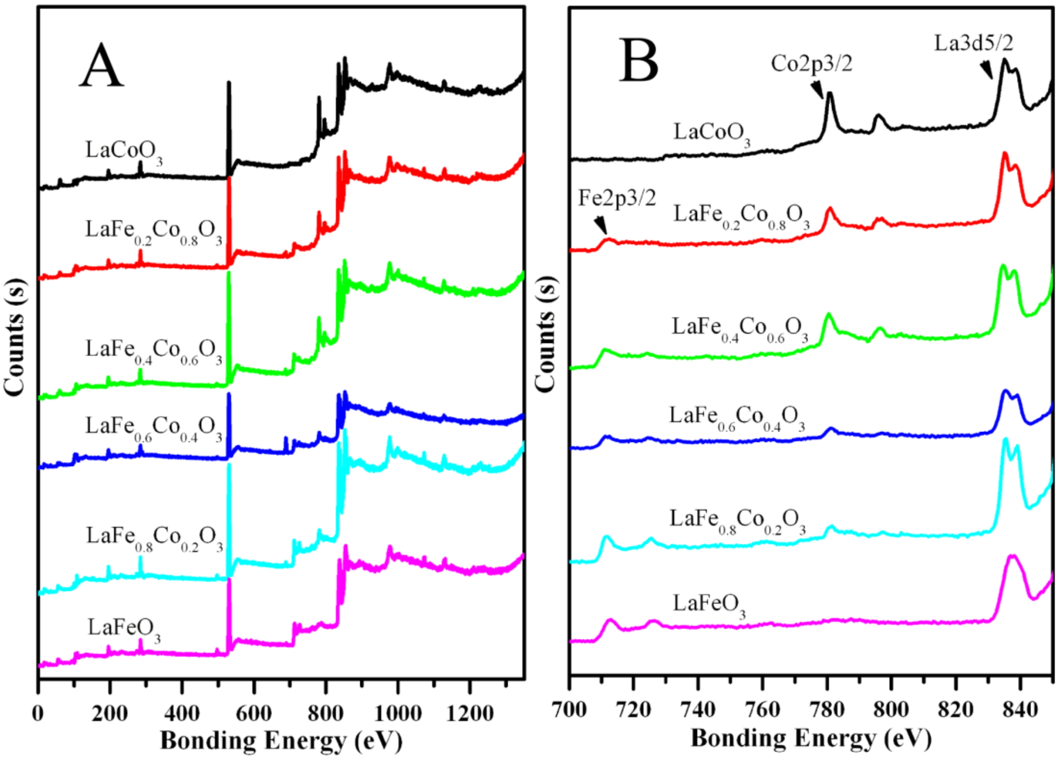

Fig. S1 XPS spectra of the mesoporous $LaFe_xCo_{1-x}O_3$ oxides.

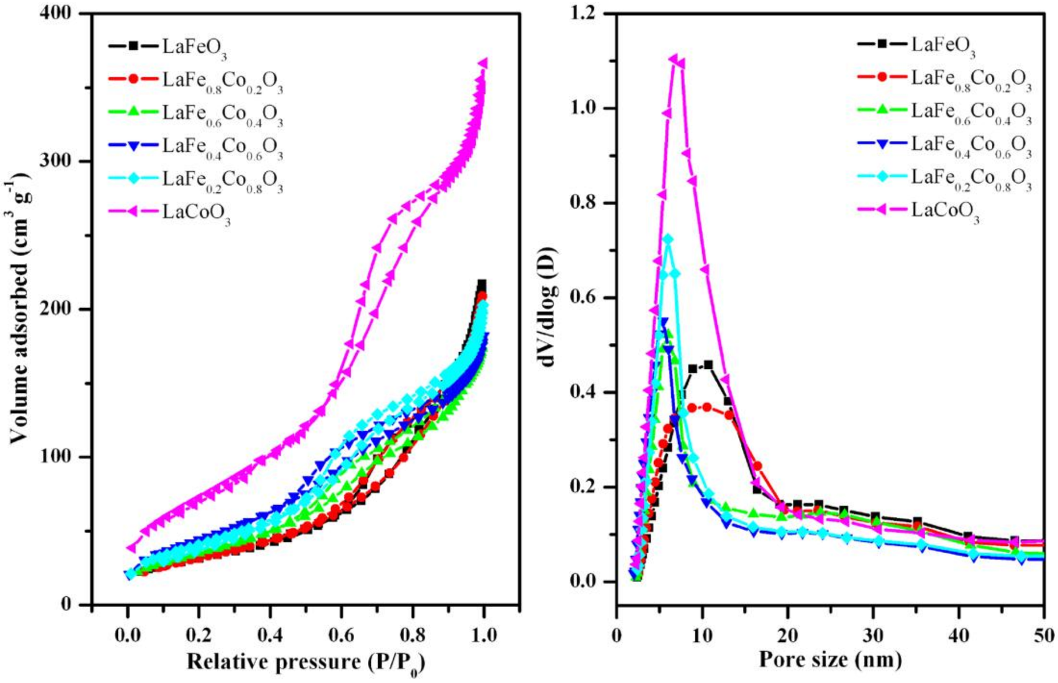

Fig. S2 N_2 sorption isotherms and pore size distributions of the mesoporous $LaFe_xCo_{1-x}O_3$ oxides.

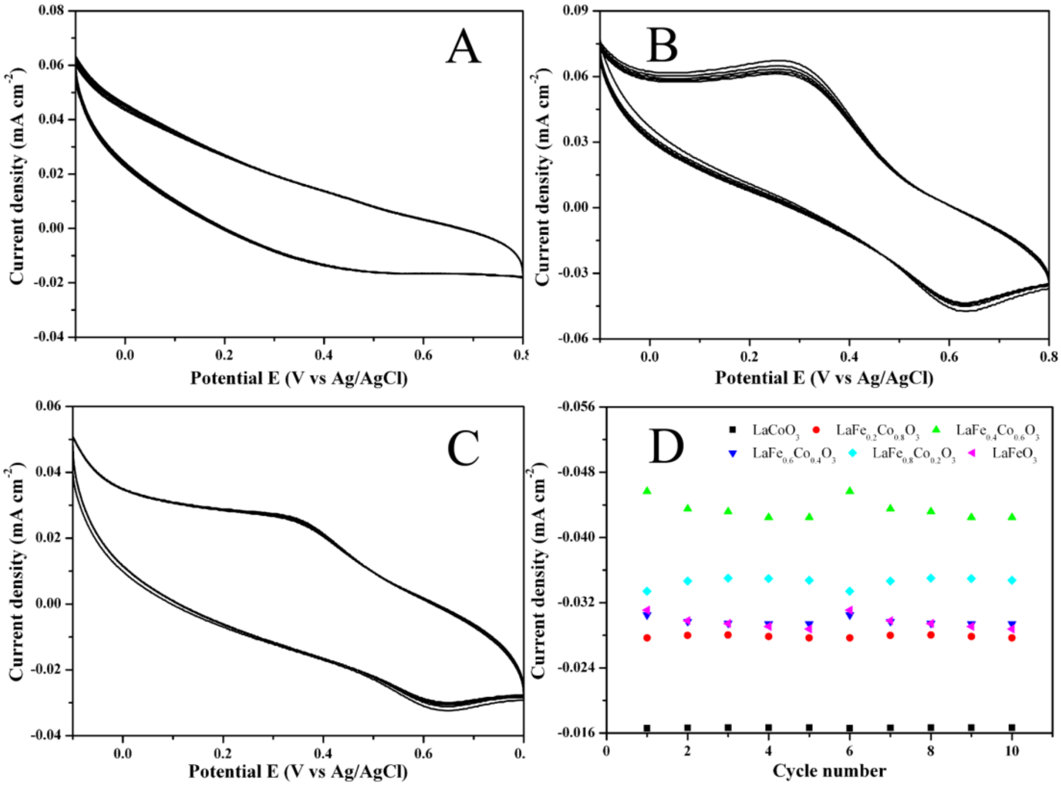

Fig. S3 Stability of the catalytic properties for oxygen reduction of the mesoporous $LaFe_xCo_{1-x}O_3$ oxides in O_2-staturated 0.5 M H_2SO_4 electrolyte solution at a scan rate of 50 mV s^{-1} (10 cycles): (A) x = 0, (B) x = 0.4, (C) x = 1.0. (D) The current density of the mesoporous oxides *vs* the cycle number (potential E = 0.6 V).

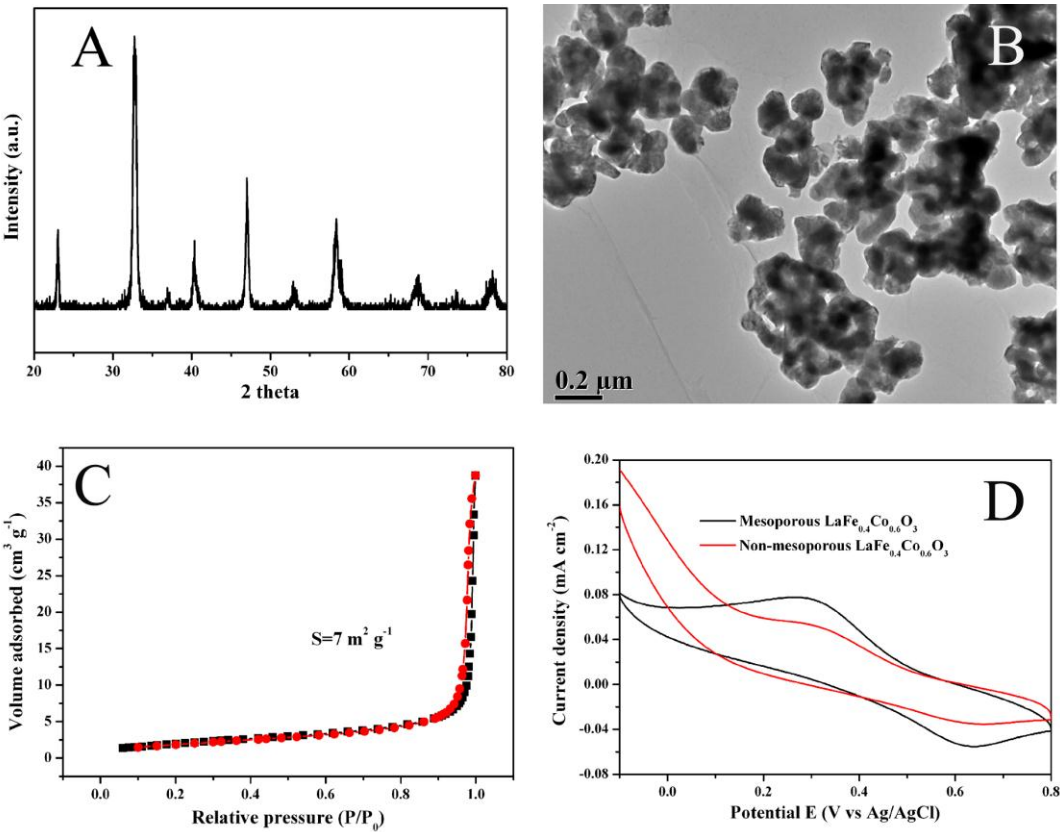

Fig. S4 A: XRD pattern of the non-mesoporous $LaFe_{0.4}Co_{0.6}O_3$ oxide prepared by conventional method; B and C: TEM image and N_2 sorption isotherm of the non-mesoporous $LaFe_{0.4}Co_{0.6}O_3$ oxide; D: the CV curves of the mesoporous and non-mesoporous $LaFe_{0.4}Co_{0.6}O_3$ oxides in O_2-staturated 0.5 M aqueous H_2SO_4 electrolyte solution at a scan rate of 50 mV s^{-1}.

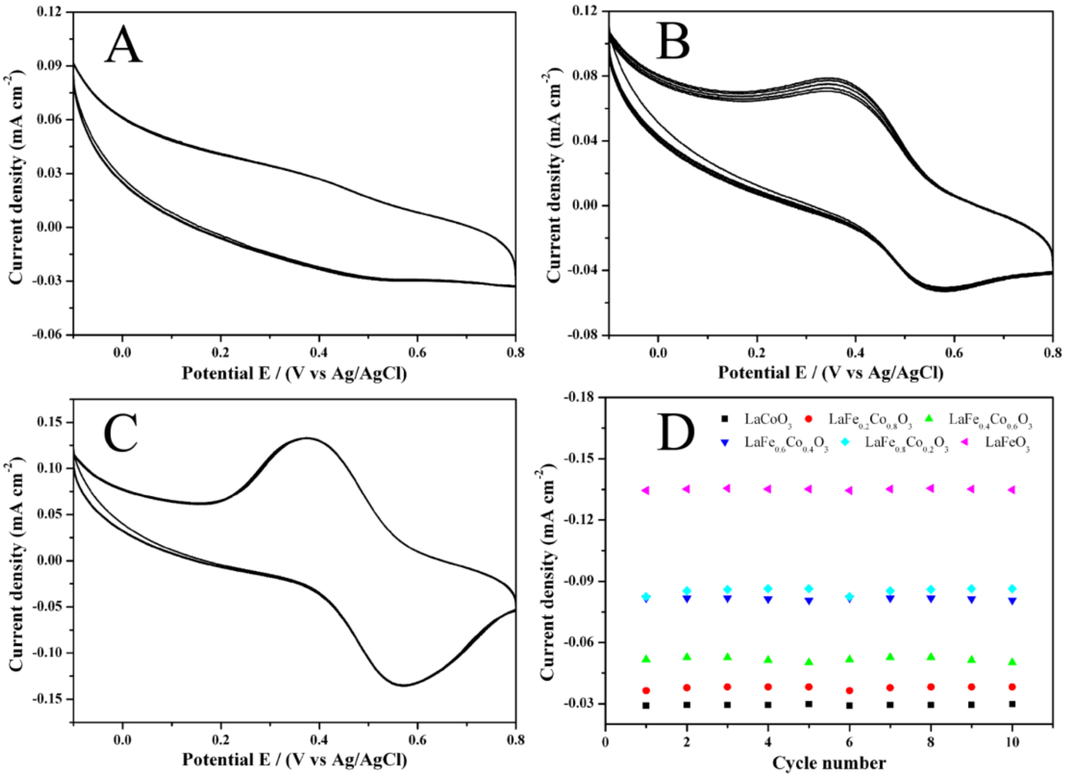

Fig. S5 Stability of the catalytic properties for ORR of the mesoporous $LaFe_xCo_{1-x}O_3$/C composite in O_2-staturated 0.5 M H_2SO_4 electrolyte solution at a scan rate of 50 mV s^{-1} (10 cycles): (A) x = 0, (B) x = 0.4, (C) x = 1.0. (D) Current density of the mesoporous oxides *vs* the cycle number (potential E=0.57 V).

Table S1 The electrical resistance and conductivity of the as prepared mesoporous $LaFe_xCo_{1-x}O_3$ oxides and mesostructured $LaFe_xCo_{1-x}O_3$/C composites

Sample	LFC (x = 0)	LFC (x = 0.2)	LFC (x = 0.4)	LFC (x = 0.6)	LFC (x = 0.8)	LFC (x = 1.0)
R (MΩ)	127	89	84.1	66	45	10.4
σ (10^{-7} S m^{-1})	0.669	0.954	1.01	1.29	1.89	8.17
Sample	LFC/C (x = 0)	LFC/C (x = 0.2)	LFC/C (x = 0.4)	LFC/C (x = 0.6)	LFC/C (x = 0.8)	LFC/C (x = 1.0)
R (KΩ)	0.39	0.47	0.42	0.48	0.51	0.45
σ (10^{-3} S m^{-1})	9.98	8.28	9.27	8.11	7.63	8.65

LFC: mesoporous $LaFe_xCo_{1-x}O_3$ oxides; LFC/C: mesostructured $LaFe_xCo_{1-x}O_3$/C composites.