

Electronic Supplementary Information

Three-Dimensional Ordered Macroporous $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3$ with High Stability for Efficiency NO Oxidation and Sulfur Resistance

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Experimental Section

1. Materials

Methyl methacrylate (MMA), Shanghai Macklin Biochemical Technology Co., LTD; 50% manganese nitrate solution ($\text{Mn}(\text{NO}_3)_2$), Sinopharm Chemical Reagent Co., LTD; lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), Shanghai Aladdin Biochemical Technology Co., LTD.; ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), Shanghai Aladdin Biochemical Technology Co., LTD.; potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), Shanghai Aladdin Biochemical Technology Co., LTD.; methanol (CH_3OH), Tianjin Jindong Tianzheng Fine Chemical Reagent Factory and ethylene glycol (CH_2OH)₂, Tianjin Jindong Tianzheng Fine Chemical Reagent Factory were obtained.

2. Samples preparation

2.1 Synthesis of PMMA microspheres

A four-mouth round bottom flask was regarded as the reaction device which was linked with spherical condensing tube and nitrogen interface at rate of 30 mL/min. 120 ml methyl methacrylate and 440 ml deionized water were added before the reaction, Stiring at the rate of 300 r/min and waiting the temperature to 80 °C. Meanwhile, 0.6 g potassium persulfate was dissolved in 50 mL deionized water as the initiator and heated to 80 °C. When the solution both reached to 80 °C, the initiator solution was added into the flask and stirred for 2 h. After stirring for 2h, the reaction was stopped and the product was filtered with a microporous membrane while still hot. Resulting emulsion was centrifuged at 3000 r/min for 12 h. Pour out the supernatant and the PMMA microspheres were dried at 60 °C. Finally, the arranged orderly PMMA hard template with green fluorescence was obtained.

2.2 Synthesis of the order macroporous $\text{LaFe}_{1-x}\text{MnxO}_3$ catalysts

The ordered macroporous catalysts were obtained by impregnation method with PMMA hard template. Amounts of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 50% $\text{Mn}(\text{NO}_3)_2$ solution were displayed in a 100 mL beaker, which was dissolved by 30 mL mixture solution of methanol and ethylene glycol at a volume ratio of 1:4. Heat to 40 °C and stir when the metal salts dissolved completely. Change the different molar ratio of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 50% $\text{Mn}(\text{NO}_3)_2$ and get a series of catalysts, namely LFM1(iron-manganese ration 9:1), LFM3(iron-manganese ration 7:3), LFM5(iron-manganese ration 1:1), LFM7(iron-manganese ration 3:7), LFM8(iron-manganese ration 2:8), LFM9(iron-manganese ration 1:9).

At the first, PMMA hard template is impregnated in a solution where the metal salts have been dissolved completely and putted into the vacuum drying oven at the room temperature. After impregnating for 12 h, the product is filtered by Brinell funnel and dried in an oven at 60 °C for 24 h. The dried samples were calcinated in a vertical tubular furnace by temperature gradient method. The dried samples and alumina pellets are alternately packed into the quartz tube. The PMMA hard template was removed from 30 to 300 °C at a rate of 1 °C/min for 3 h in the air atmosphere and then product was heated to 650 °C at rate of 1 °C/min for 4 h. The three-dimensional ordered macroporous catalysts were obtained after the tubular furnace cooled down to room temperature.

For comparison, the pure lanthanide iron perovskite LaFeO_3 and the pure lanthanide manganese perovskite LaMnO_3 were synthesized by same method, named as LF and LM respectively.

3. Material characterization and catalytic performance

The catalyst activity performance was tested in a fix-bed reactor which the length is 500 mm and the diameter is 30 mm. 0.1 g catalyst was put into a quartz tube and heated by the reactor. Before the NO-TPO tests, 40 mL/min nitrogen was fed into the gas path to remove the effects of other gases. After clearing the background, 5 mL/min NO and 2.8 mL/min O₂ were injected into gas path. It was heated from 50 to 100 °C in 5 minutes and heated to 500 °C at a rate of 2 °C/min. The space velocity of NO oxidation reaction is 30000 h⁻¹.

NO conversion rate is defined as follows:

$$\text{NO conversion rate} = ([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}) / [\text{NO}]_{\text{in}} \times 100\%$$

Soot-TPO was tested in a fix-bed reactor which the length is 500 mm and the diameter is 30 mm. The 0.1 g catalyst and 0.01 g soot were put into the quartz tube. And the mixture mode is in a loose contact. Inject 25 mL/min nitrogen, 19 mL/min nitrogen oxide and 2.5 mL/min oxygen into the gas path during the reaction. It was heated from 30 to 120 °C in 12 minutes and heated to 550 °C at a rate of 2 °C/min.

CO₂ selectivity is defined as follows:

$$\text{CO}_2 \text{ selectivity} = [\text{CO}_2] / ([\text{CO}_2] + [\text{CO}]) \times 100\%.$$

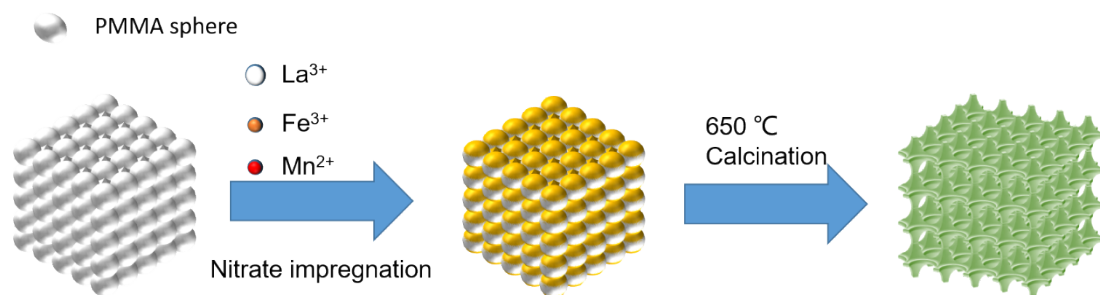
During the hydrogen programmed temperature reduction test (H₂-TPR), H₂-TPR test was reacted in a U-shaped fluidized bed reactor. 100 mg catalysts were pretreated in 30 mL/min nitrogen at 350 °C and cooled for calibration at 50 °C in a 30 mL/min hydrogen atmosphere. Catalysts were reduced at 10 °C/min ranged from 50 °C to 850 °C and hydrogen consumption was detected by a thermal conductivity detector (TCD).

During the nitric oxidation programmed temperature desorption test (NO-TPD), 50 mg catalysts were pretreated in 30 mL/min argon at 500 °C and cooled for calibration at 30 °C in a

30 mL/min nitric oxide atmosphere. Replace the nitric oxide with the argon. Catalysts were adsorbed and desorbed at 10 °C/min ranged from 30 °C to 500 °C.

The surface area of the catalysts was tested by BSD-660M A3M analyzer based on N₂ adsorption-desorption at 200 °C and degassing for 4 h.

In situ diffuse infrared Fourier transform (DRIFT) spectroscopy was tested by the IRTracer-100 infrared spectrometer at Shimadzu Manufacturing in Japan. Firstly, the adsorbed impurities were purged under the nitrogen with a rate of 46.1 mL/min at 300 °C for 30 minutes. Under the same nitrogen flow, the background was collected from 450 °C and background was collected for every 50 °C. Then, NO was adsorbed under the mixture flow of NO and nitrogen for 30 minutes and NO was oxidized under the mixture flow of NO, nitrogen and oxygen for 30 minutes respectively. Finally, temperature rises from 50 °C and corresponding infrared spectra are collected for every 50 °C.



Scheme S1 Synthesis strategy of the perovskite catalysts with a three-dimensional ordered macroporous structure.

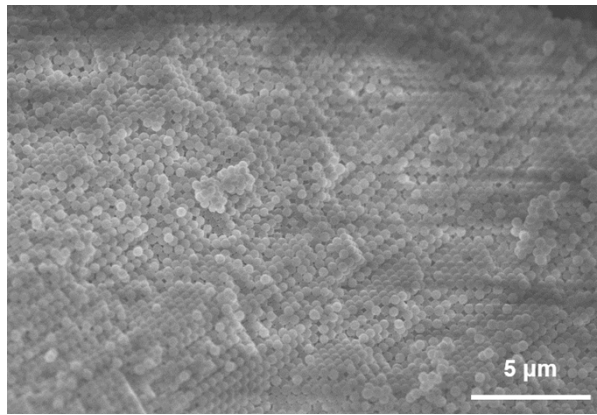


Fig. S1. PMMA microsphere.

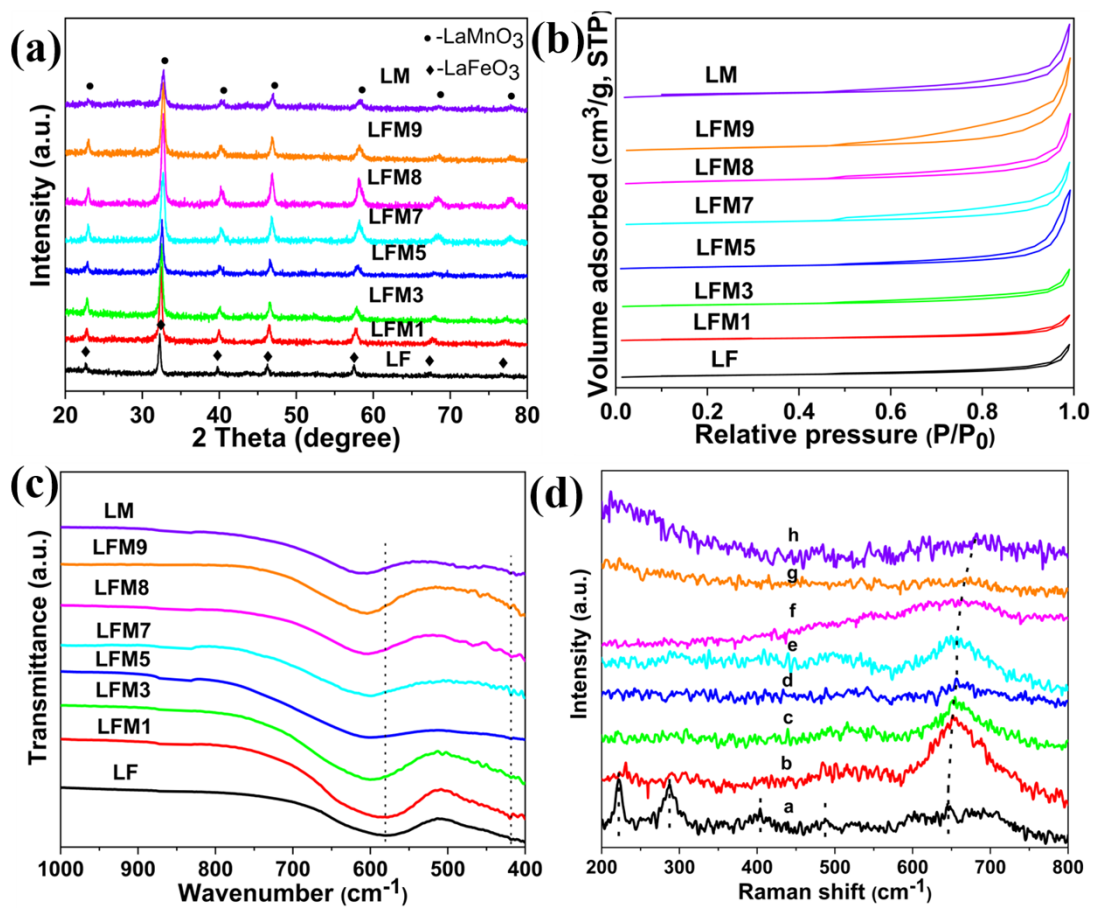


Fig. S2 (a) X-ray diffraction of a series perovskite catalysts. (b) Adsorption and desorption isotherm of perovskite catalysts. (c) FTIR of a series of catalysts. (d) Raman spectra of catalysts, a. LF, b. LFM1, c. LFM3, d. LFM5, e. LFM7, f. LFM8, g. LFM9, h. LM.

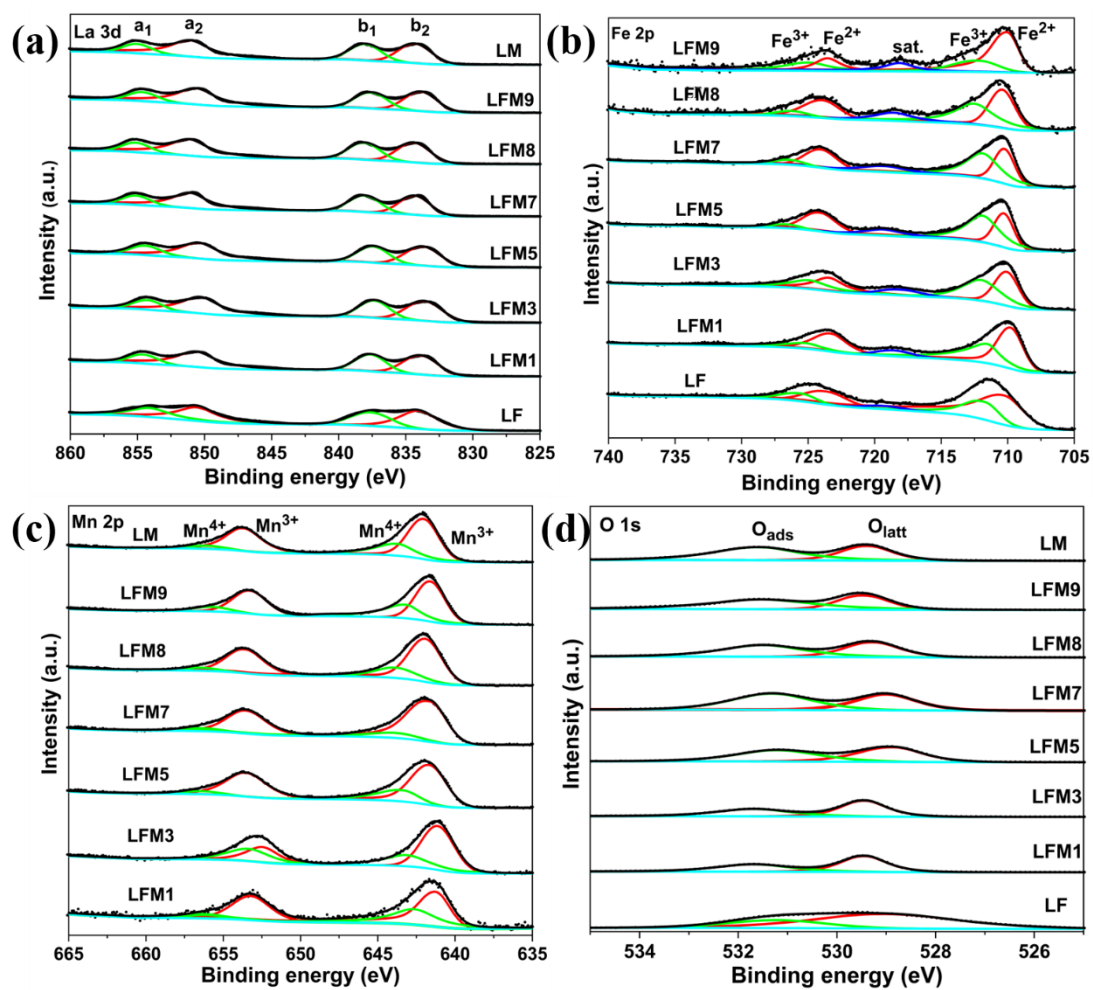


Fig. S3 XPS spectra of samples (a) La 3d, (b) Fe 2p, (c) Mn 2P and (d) O 1s.

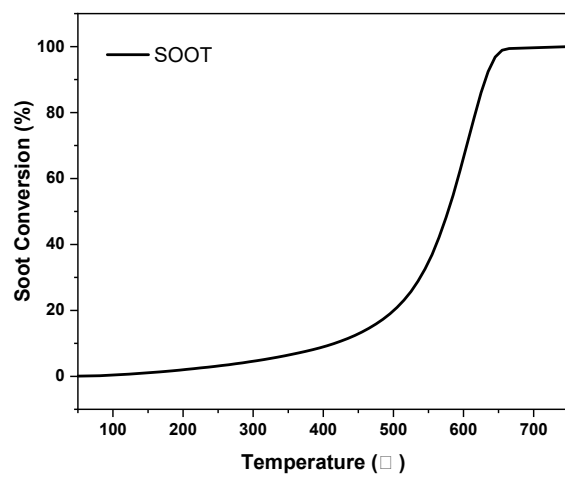


Fig. S4 Soot-TPO without catalysts.

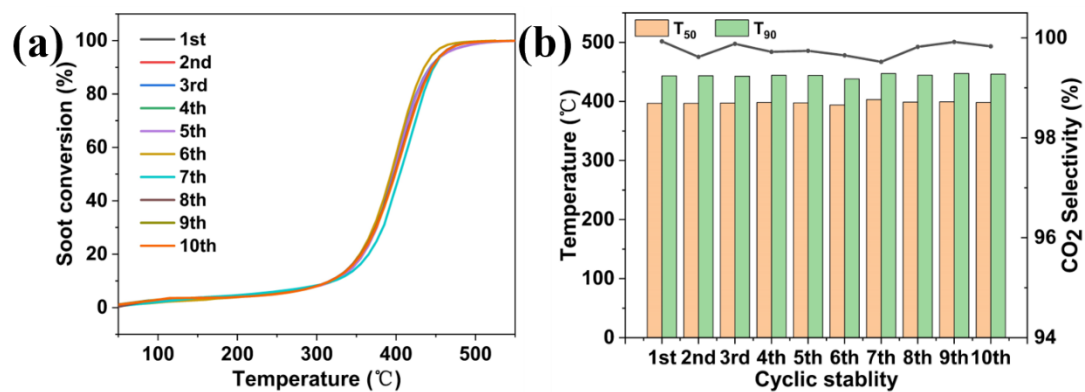


Fig. S5 (a) Soot combustion stability tests of LFM9 catalyst for 10 times. (b) Special soot combustion temperatures of T₅₀ and T₉₀ and CO₂ selectivity for LFM9 by 10 times.

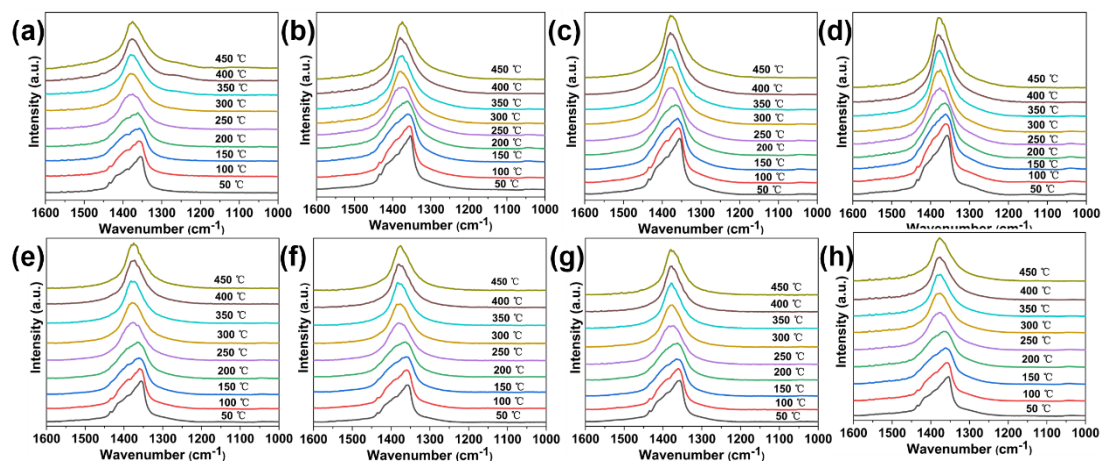


Fig. S6 DRIFT spectra: (a) LF, (b) LFM1, (c) LFM3, (d) LFM5, (e) LFM7, (f) LFM8, (g) LFM9, (h) LM.

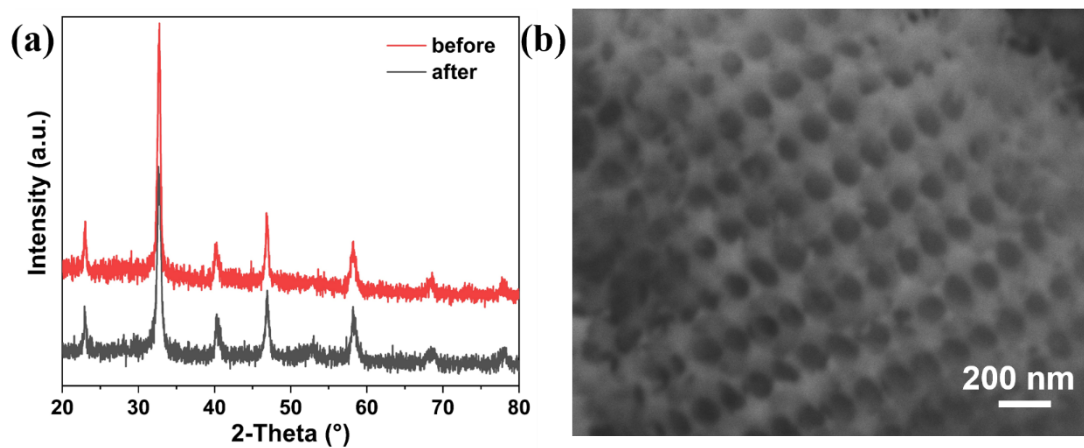


Fig. S7 (a) XRD of LFM9 after activity testing. (b) SEM of LFM9 after activity testing.

Table S1. Mapping element content of LFM9.

element	Lanthanum	Iron	Manganese
atom (%)	50.44	44.02	5.54

Table S2. Specific surface area, pore volume and mesoporous aperture of catalysts.

Catalysts	Surface area (m ² /g)	Total pore volume (cm ³ /g)
LF	22.57	0.09
LFM1	22.60	0.17
LFM3	23.65	0.10
LFM5	28.90	0.19
LFM7	36.41	0.17
LFM8	32.31	0.17
LFM9	42.63	0.23
LM	37.49	0.19

Table S3. Compositions of catalyst surfaces.

Catalysts	Fe ²⁺ (%)	Mn ³⁺ (%)	O _{ads} /O _{latt}
LF	53.5	0	0.91
LFM1	54.3	62.5	1.08
LFM3	55.0	63.4	1.10
LFM5	58.8	65.6	1.27
LFM7	61.1	69.6	1.59
LFM8	61.2	67.8	1.31
LFM9	66.9	82.6	1.79
LM	0	74.4	1.65

Table S4. Specific combustion temperatures of a series of catalysts.

Catalysts	T ₁₀ (°C)	T ₅₀ (°C)	T ₉₀ (°C)
LF	373.7	446.4	489.8
LFM1	366.3	436.5	474.1
LFM3	350.3	430.2	471.9
LFM5	351.5	414.5	459.5
LFM7	339.3	415.4	460.4
LFM8	339.0	422.4	472.4
LFM9	320.9	397.0	443.5
LM	328.4	402.6	452.3
Soot	416.0	580.0	666.0

Table S5. Different cycles of specific combustion temperatures of LFM9.

Catalysts	T ₁₀ (°C)	T ₅₀ (°C)	T ₉₀ (°C)	S _{CO₂} (%)
1st	320.9	397.0	443.5	99.93
2nd	321.0	396.9	443.6	99.62
3rd	320.4	397.4	442.9	99.88
4th	320.8	398.4	444.4	99.72
5th	321.7	397.8	444.0	99.74
6th	319.6	394.0	438.1	99.65
7th	322.9	403.2	447.4	99.52
8th	316.9	398.9	444.5	99.82
9th	318.7	399.5	447.3	99.92
10th	319.1	398.3	446.2	99.83