Supporting Information

Oxygen-vacancy-mediated $LaFe_{1-x}Mn_xO_{3-\delta}$ perovskite nanocatalysts for degradation of organic pollutants through enhanced surface ozone adsorption and metal doping effects

Shengzhe Wang[a,b], Peiwei Han[c], Ying Zhao[a], Wenjing Sun[a], Rui Wang[c], Xin Jiang[d], Chunyan Wu[d], Chenglin Sun[a*], Huangzhao Wei[a,b*]

a. Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P.R. China

b. University of Chinese Academy of Sciences, Beijing 100049, P.R. China

c. Beijing Key Laboratory of Fuels Cleaning and Advanced Catalytic Emission Reduction Technology/College of Chemical Engineering, Beijing Institute of Petrochemical Technology, Beijing 102617, Beijing, China

d. Beijing North Energy Conservation Environment Protection Co. Ltd., Beijing 100070, China

Corresponding Authors: Chenglin Sun (clsun@dicp.ac.cn); Huangzhao Wei (whzhdicpwtg@dicp.ac.cn)

There was 15 pages in this SI file, including 1 text, 6 tables and 13 figures.

Text S1. Iodometric titration method

Iodometric titration was carried out to investigate the content of oxygen vacancy of the perovskite-based catalysts [1-2]. Briefly, 20 mg of $LaFe_{1-x}Mn_xO_{3-\delta}$ catalyst was dissolved in 6mL of 4 M HCl followed by adding 10 mL of degassed deionized water for dilution in a sealed two-neck round-bottom flask under N_2 atmosphere. The mixture solution was kept stirred and degassed with N_2 for another 15 min. Then 8 mL of 1 M KI solution made in degassed deionized water was injected into the flask. The solution was then titrated with 0.01 M $Na_2S_2O_3$ solution.

It is assumed that the amount of La and Mn in the samples is in a stoichiometric 1:1 ratio, and that La has the oxidation state of La^{3+} and Mn can exist in the oxidation states of Mn^{2+}, $Mn^{3+}$and Mn^{4+}. Therefore, the chemical formula of $LaFe_{1-x}Mn_xO_{3-\delta}$ can be expressed as follows.

And Fe and Mn share the oxidation states of 2+, 3+ and 4+, where M represents the B site metals.

$$La^{3+}Mn^{3+}_{(1-\alpha-\beta)}Mn^{4+}_{\alpha}Mn^{2+}_{\beta}O_{3-\delta} \qquad \text{Eq. (S1)}$$

δ and $\alpha-\beta$ fulfill the following relationship to achieve the charge neutrality.

$$\delta=(0.5-\alpha+\beta)/2 \qquad \text{Eq. (S2)}$$

By dissolving in HCl solution and react with KI:

$$2Fe^{3+}/Mn^{3+}+2Cl^{-}\rightarrow Cl_2+2Fe^{2+}/Mn^{2+} \qquad \text{Eq. (S3)}$$

$$Mn^{4+}+2Cl^{-}\rightarrow Cl_2+Mn^{2+} \qquad \text{Eq. (S4)}$$

$$Cl_2+2I^{-}\rightarrow 2Cl^{-}+I_2 \qquad \text{Eq. (S5)}$$

The iodine was titrated with a standard solution of sodium thiosulphate according to the reaction below.

$$2S_2O_3^{2-}+I_2\rightarrow 2I^{-}+S_4O_6^{2-} \qquad \text{Eq. (S6)}$$

The amount of iodine (mol) formed in this reaction is

$$\begin{aligned}[I_2]&=0.5[Fe^{3+}/Mn^{3+}]+[Mn^{4+}]\\&=0.5(1-\alpha-\beta)m/M+\alpha m/M\end{aligned} \qquad \text{Eq. (S7)}$$

where [Fe^{3+}/Mn^{3+}] and [Mn^{4+}] in molar concentrations and M (g/mol) and m (g) are the molar weight and the mass of $LaFe_{1-x}Mn_xO_{3-\delta}$, respectively. In $LaFe_{1-x}Mn_xO_{3-\delta}$, M depends on the contents of oxygen as

$$M = M_0 - m_1\delta \qquad \text{Eq. (S8)}$$

where M_0=241.84-242.75 g/mol is the molar weight of $LaFe_{1-x}Mn_xO_{3-\delta}$ when all manganese is in the trivalent state, and m_l=15.9994 g/mol is the atomic weight of oxygen. The amount of Cl_2 formed during titration is

$$[I_2] = CV/2 \qquad \text{Eq. (S9)}$$

where C is the concentration (mol/mL) and V is the volume (mL) of the $Na_2S_2O_3$ solution. Substituting (6) and (7) in (5) we will get

$$\delta = (CVM_0 - m)/(CVm_1 - 0.75m) \qquad \text{Eq. (S10)}$$

Table S1. XRD Spectrum refined table of $LaFe_{1-x}Mn_xO_{3-\delta}$

Phase name		$LaMnO_{3-\delta}$	$LaFe_{0.26}Mn_{0.74}O_{3-\delta}$	$LaFe_{0.5}Mn_{0.5}O_{3-\delta}$	$LaFe_{0.74}Mn_{0.26}O_{3-\delta}$	$LaFeO_{3-\delta}$
Crystal system		Rhombohedral	Rhombohedral	Rhombohedral	Rhombohedral	Orthorhombic
Space Group		R-3c	R-3c:H	R-3c	R-3c	Pbnm
R-Values	Rexp	2.50%	2.39%	2.24%	2.22%	1.83%
	Rwp	3.35%	2.40%	2.26%	2.24%	1.95%
	Rp	2.28%	1.85%	1.74%	1.70%	1.54%
	GOF	1.34	1.00	1.01	1.01	1.06
Cell parameters	a (Å)	5.439（6）	5.519（5）	5.531（7）	5.537（6）	5.586（6）
	b (Å)	5.439（6）	5.519（5）	5.531（7）	5.537（6）	5.515（6）
	c (Å)	13.13（6）	13.36（9）	13.41（5）	13.45（3）	7.859（8）
	α(°)	90	90	90	90	90
	β(°)	90	90	90	90	90
	γ(°)	120	120	120	120	90
	Volume($Å^3$)	336.4	352.6	355.4	357.1	242.1
	Density (g/cm^3)	7.163	6.841	6.793	6.766	6.661

Table S2. Comparison of refined and theoretical results of $LaFe_{1-x}Mn_xO_{3-\delta}$

Theoretical phase	$LaMnO_{3-\delta}$	$LaFe_{0.26}Mn0_{.74}O_{3-\delta}$	$LaFe_{0.5}Mn_{0.5}O_{3-\delta}$	$LaFe_{0.74}Mn_{0.26}O_{3-\delta}$	$LaFeO_{3-\delta}$
Actual phase	$LaMnO_{3-\delta}$	$LaFe_{0.2546}Mn_{0.7454}O_{3-\delta}$	$LaFe_{0.4836}Mn_{0.5164}O_{3-\delta}$	$LaFe_{0.7285}Mn_{0.2715}O_{3-\delta}$	$LaFeO_{3-\delta}$

Sample	La (wt.%)	Fe (wt.%)	Mn (wt.%)	O Calculated (wt.%)	O Theory (wt.%)
$LaMnO_{3-\delta}$	58.60	-	22.25	19.16	19.84
$LaFe_{0.26}Mn_{0.74}O_{3-\delta}$	53.95	7.76	16.30	22.00	19.83
$LaFe_{0.5}Mn_{0.5}O_{3-\delta}$	53.86	15.25	12.67	18.23	19.85
$LaFe_{0.74}Mn_{0.26}O_{3-\delta}$	48.54	23.23	6.93	21.31	19.79
$LaFeO_{3-\delta}$	44.95	39.03	-	16.03	9.77

Table S3. Element content of $LaFe_{1-x}Mn_xO_{3-\delta}$

Table S4. $LaFe_{1-x}Mn_xO_{3-\delta}$ XPS-Fe

Sample	**Fe ions based XPS studies**		
	Fe^{2+} (at. %)	**Fe^{3+} (at. %)**	**Fe^{2+}/Fe^{3+}**
$LaFe_{0.26}Mn_{0.74}O_{3-\delta}$	69.44	30.56	2.27
$LaFe_{0.5}Mn_{0.5}O_{3-\delta}$	65.36	34.64	1.89
$LaFe_{0.74}Mn_{0.26}O_{3-\delta}$	63.29	36.71	1.72
$LaFeO_{3-\delta}$	62.50	37.50	1.67

Table S5. $LaFe_{1-x}Mn_xO_{3-\delta}$ XPS-Mn

Sample	Mn ions based XPS studies			
	Mn^{3+} (at. %)	Mn^{4+} (at. %)	Satellite (at. %)	Mn^{3+}/Mn^{4+}
$LaMnO_{3-\delta}$	66.67	24.67	8.67	2.70
$LaFe_{0.26}Mn_{0.74}O_{3-\delta}$	61.71	29.93	8.64	2.08
$LaFe_{0.5}Mn_{0.5}O_{3-\delta}$	53.76	30.11	16.13	1.78
$LaFe_{0.74}Mn_{0.26}O_{3-\delta}$	51.28	37.95	10.77	1.35

Table S6. $LaFe_{1-x}Mn_xO_{3-\delta}$ XPS-O

Sample	O based XPS studies			
	Lattice oxygen (at. %)	Oxidative oxygen species (at. %)	Oxygen vacancies (at. %)	Adsorption water (at. %)
$LaMnO_{3-\delta}$	51.81	9.84	33.16	5.18
$LaFe_{0.26}Mn_{0.74}O_{3-\delta}$	34.13	18.25	39.68	7.94
$LaFe_{0.5}Mn_{0.5}O_{3-\delta}$	47.17	5.19	33.96	13.68
$LaFe_{0.74}Mn_{0.26}O_{3-\delta}$	55.25	7.18	32.04	5.52
$LaFeO_{3-\delta}$	46.95	14.08	27.23	11.74

Figure S1. XRD Spectrum refined diagram of $LaFe_{1-x}Mn_xO_{3-\delta}$

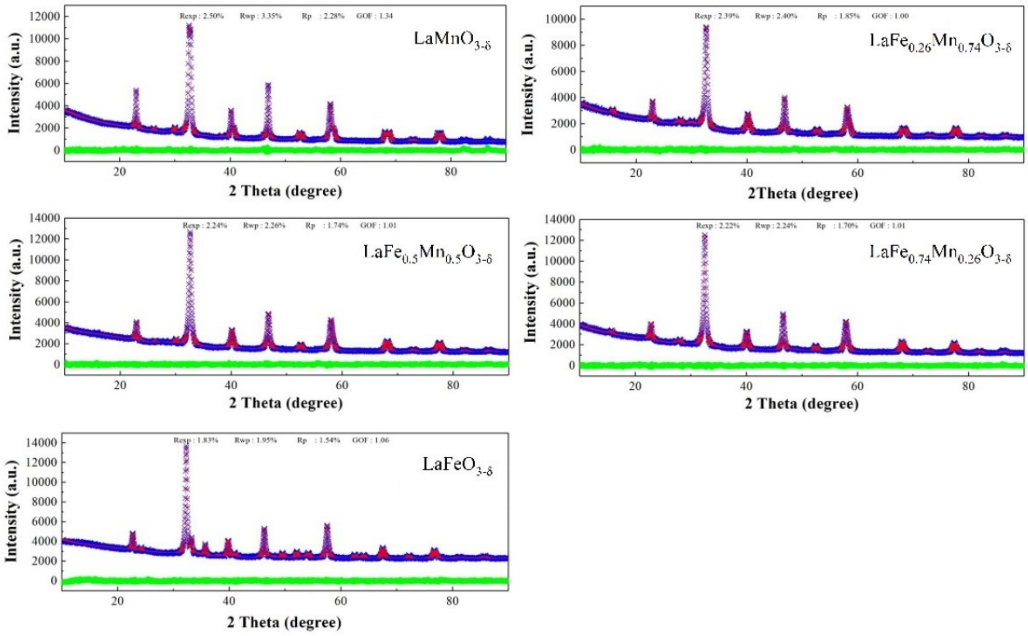


Figure S2. Nitrogen sorption isotherms of $LaFe_{1-x}Mn_xO_{3-\delta}$

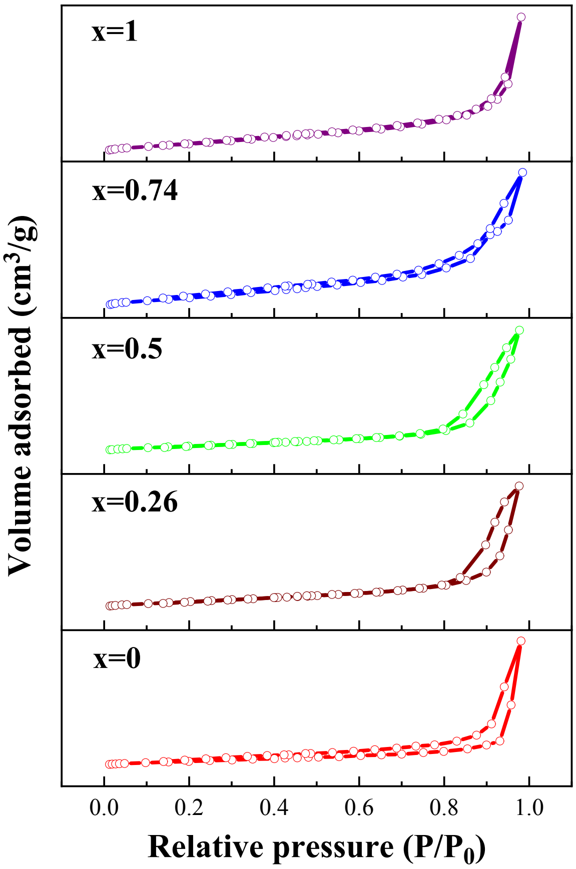


Figure S3. Pore size distribution of $LaFe_{1-x}Mn_xO_{3-\delta}$

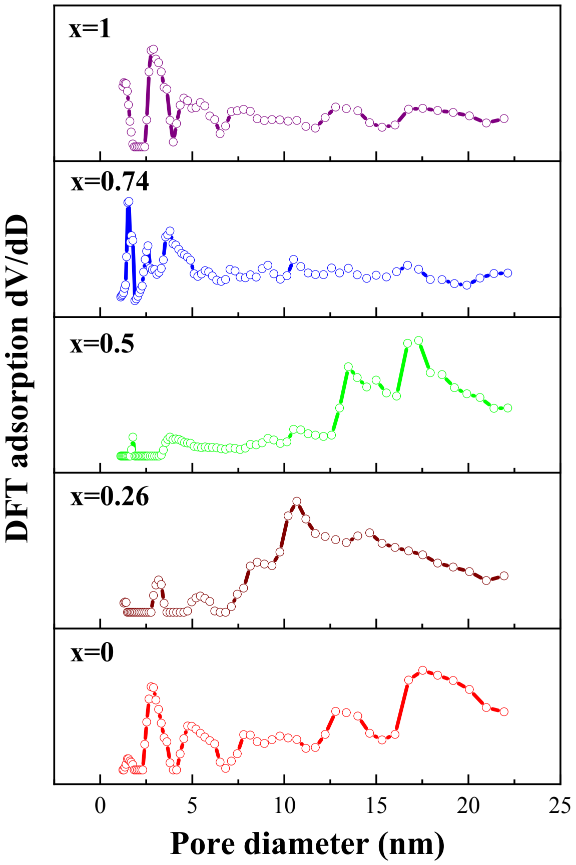


Figure S4. m-Cresol conversion on different catalysts

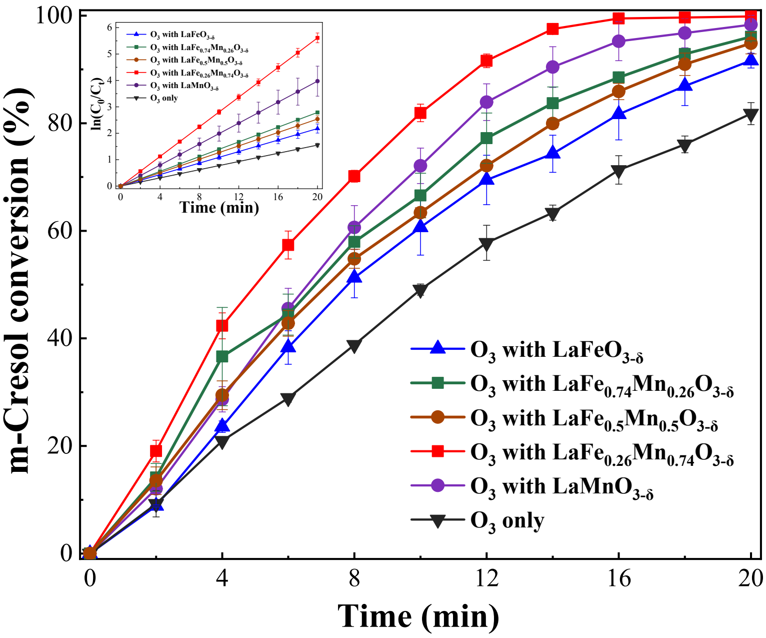
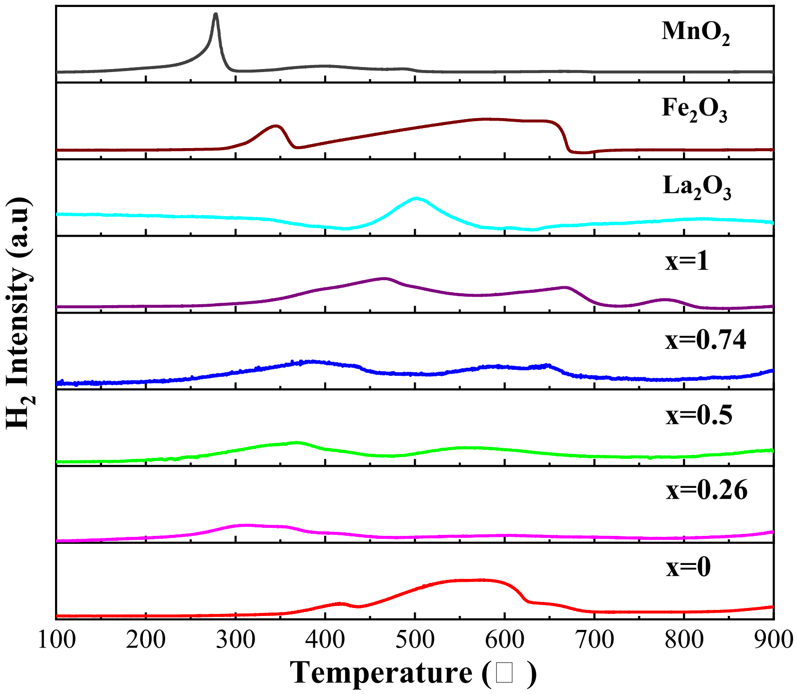


Figure S5. H_2-TPR of $LaFe_{1-x}Mn_xO_{3-\delta}$



The reduction behaviors of the catalysts were examined by H_2-TPD experiments. It can be obtained that the reduction of MnO_2 mainly has four stages: reduction from MnO_2 to Mn_2O_3 at 280°C, reduction from Mn_2O_3 to Mn_3O_4 at 410°C, reduction from Mn_3O_4 to MnO at 480°C and reduced from MnO to Mn at 690°C [3]. There are three main stages in the reduction of Fe_2O_3, reduction from Fe_2O_3 to Fe_3O_4 at 360°C, reduction from Fe_3O_4 to FeO at 580°C, and reduction from FeO to Fe at 670°C [4-5]. The reduction of La_2O_3 mainly occurs at about 400-600°C. There are obvious reduction peaks in the H_2-TPR reduction curve of $LaFe_{1-x}Mn_xO_{3-\delta}$ catalysts. It can be proved that the synthesized material has good surface reducibility, so it can be inferred that the catalyst has good catalytic activity in the redox reaction.

Figure S6. GC-MS

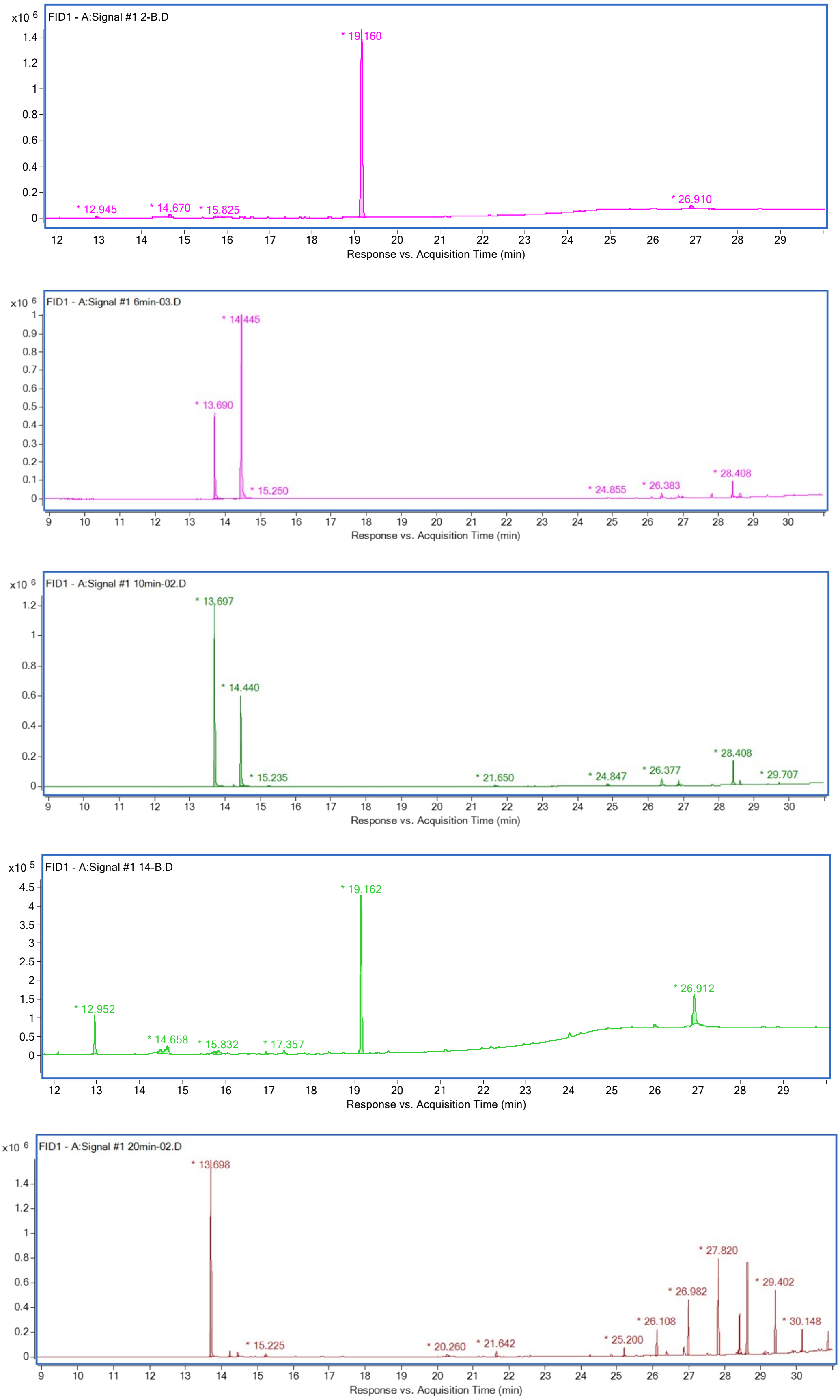


Figure S7. HPLC-MS

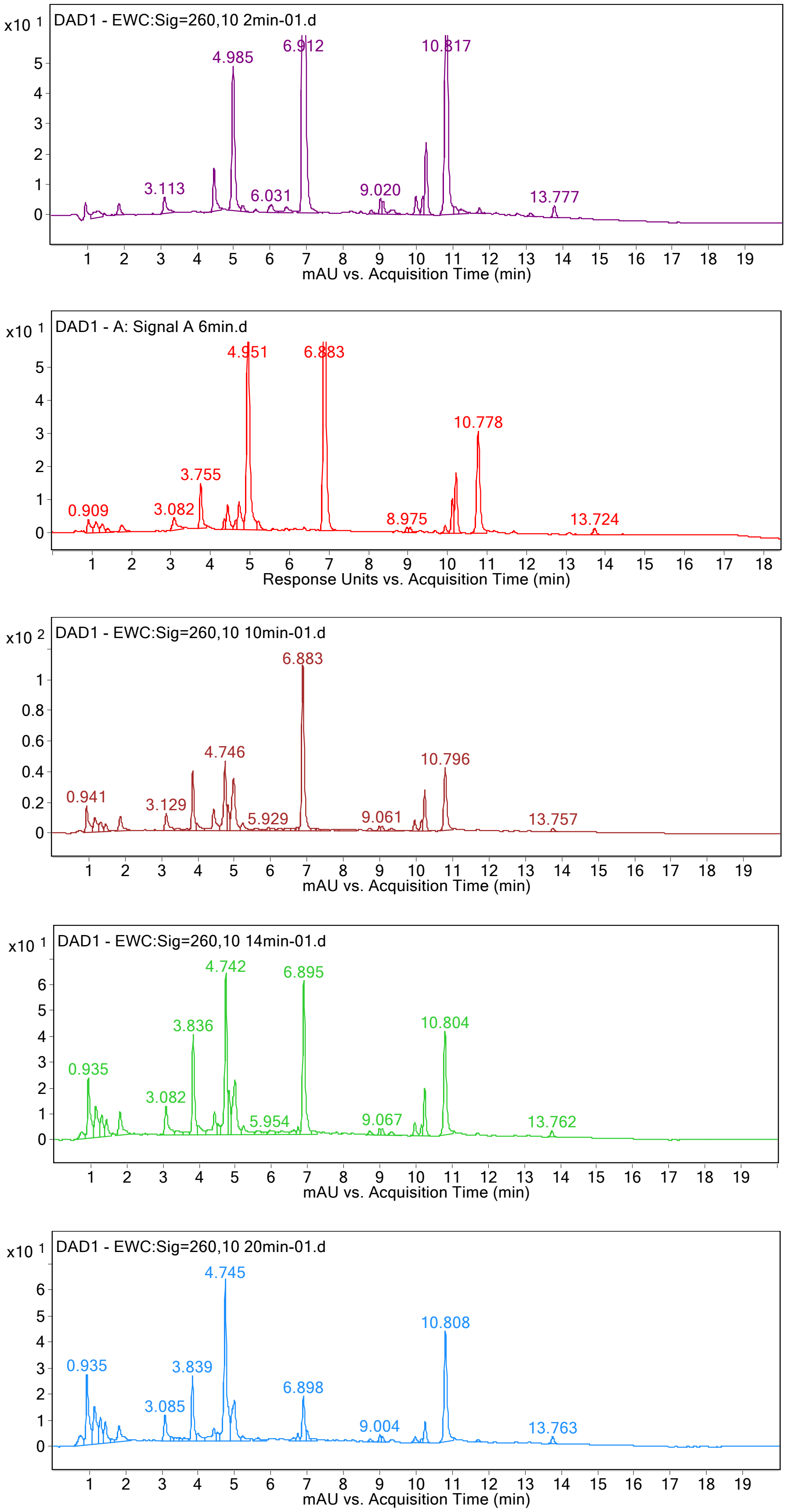


Figure S8. $LaFe_{0.26}Mn_{0.74}O_{3-\delta}$, Fe/ZSM-5 catalytic activity comparison

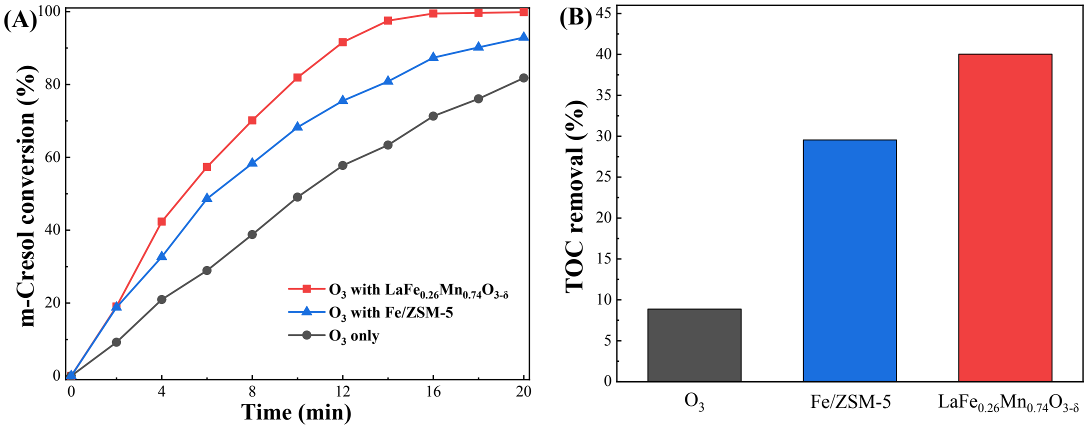


Figure S9. SEM of $LaFe_{0.26}Mn_{0.74}O_{3-\delta}$ after continuous reaction

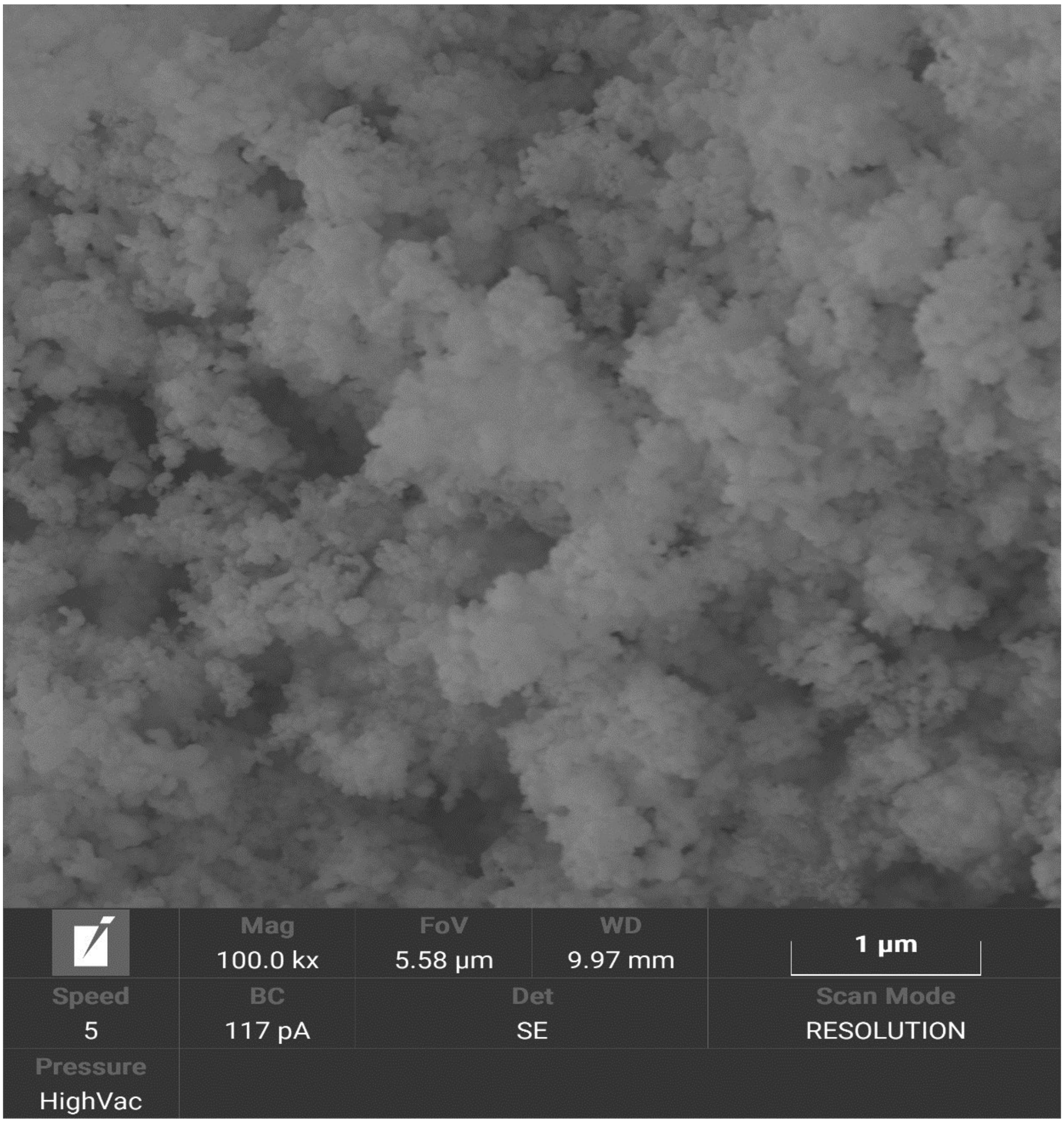


Figure S10. TEM of $LaFe_{0.26}Mn_{0.74}O_{3-\delta}$ after continuous reaction

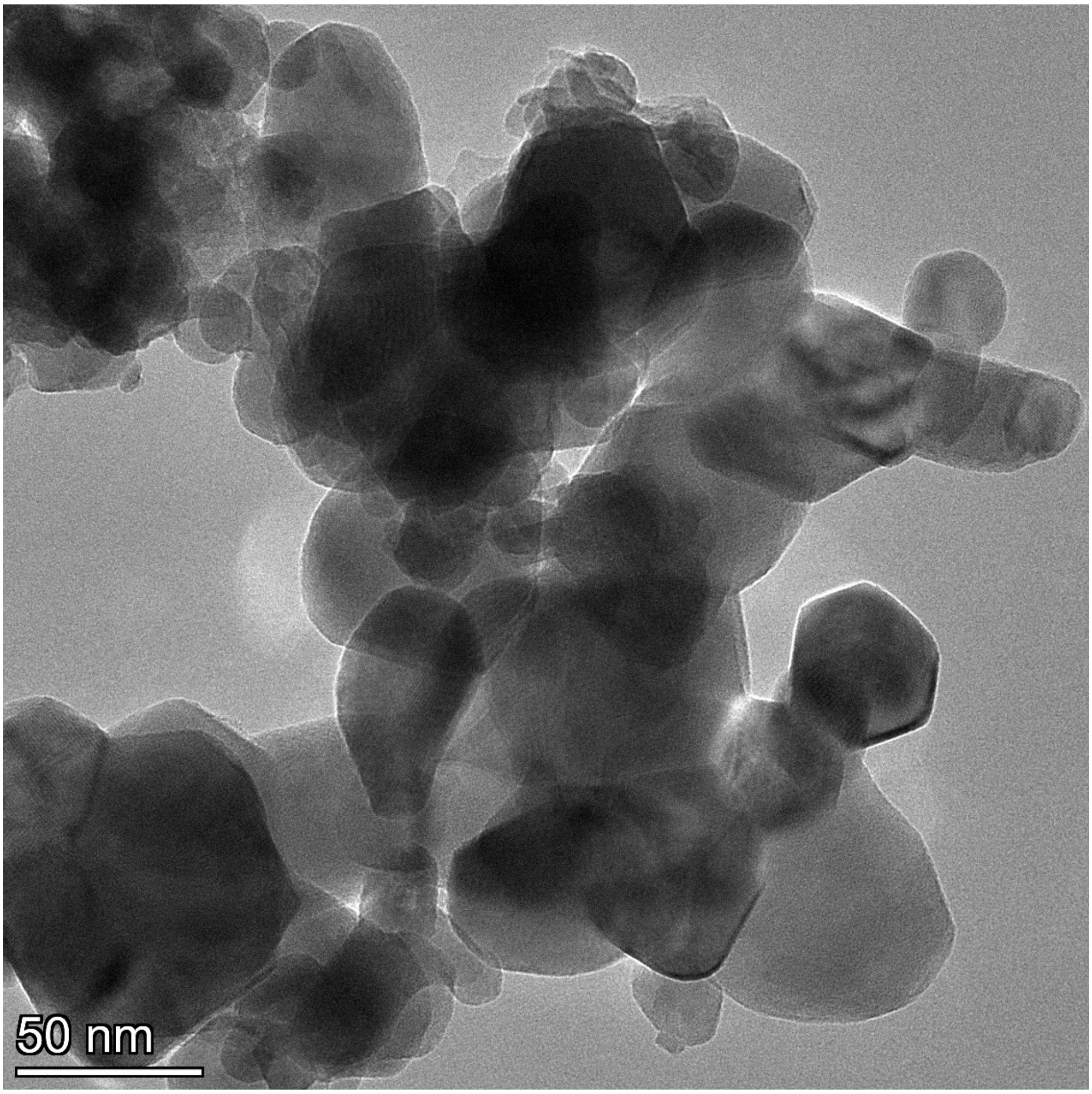


Figure S11. HRTEM of $LaFe_{0.26}Mn_{0.74}O_{3-\delta}$ after continuous reaction

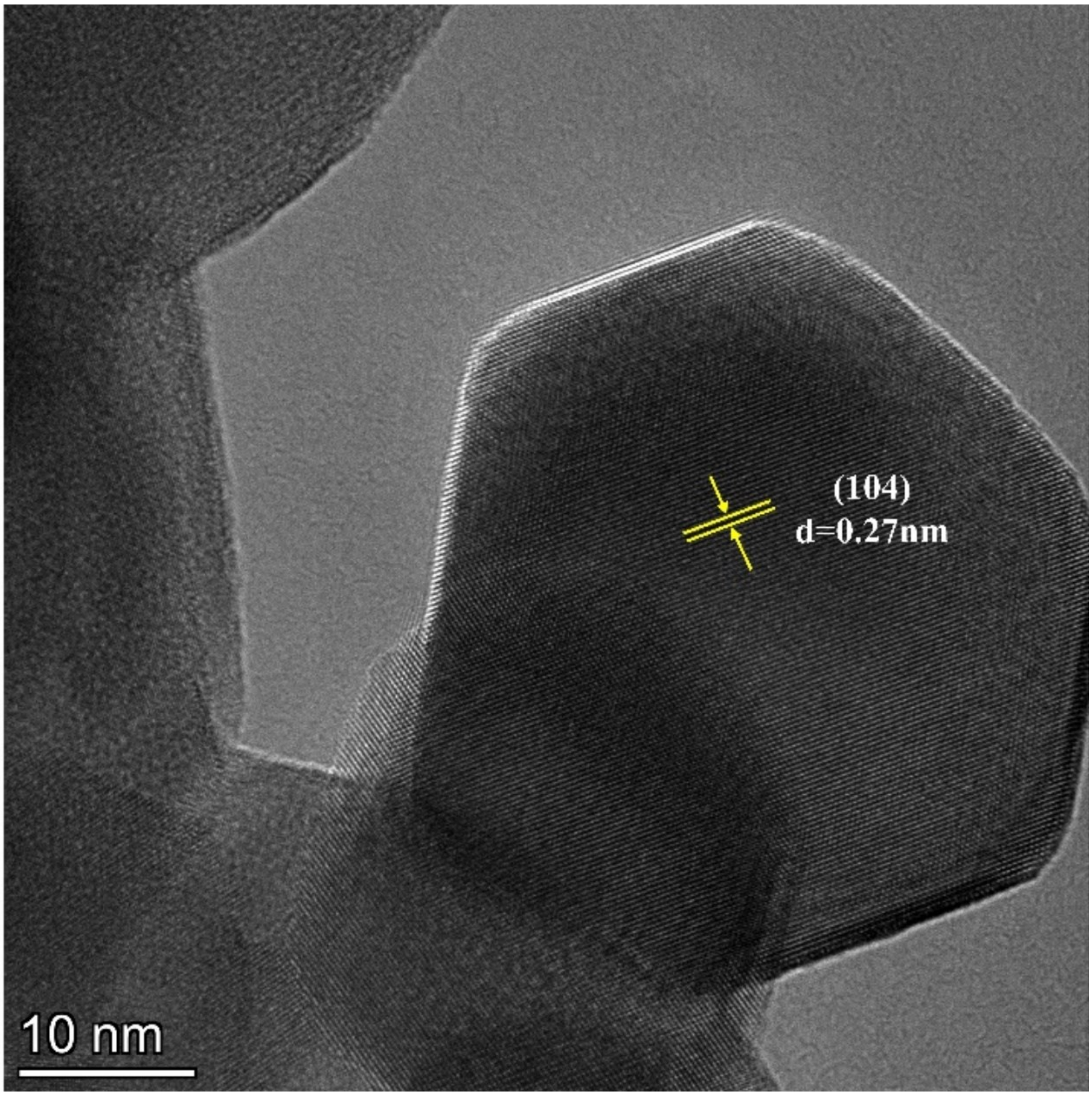


Figure S12. EDS mapping of $LaFe_{0.26}Mn_{0.74}O_{3-\delta}$ after continuous reaction

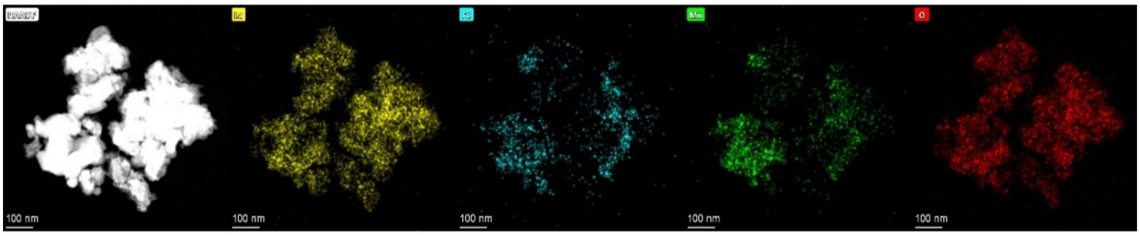
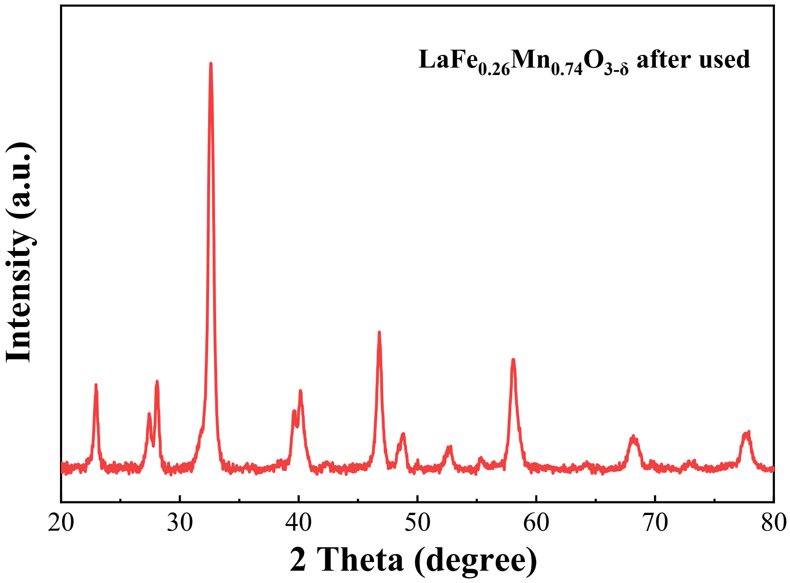


Figure S13. XRD of $LaFe_{0.26}Mn_{0.74}O_{3-\delta}$ after continuous reaction



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