Supplementary Information

Porous manganese oxides synthesized with natural products at room temperature: A superior humidity-tolerant catalyst for ozone decomposition

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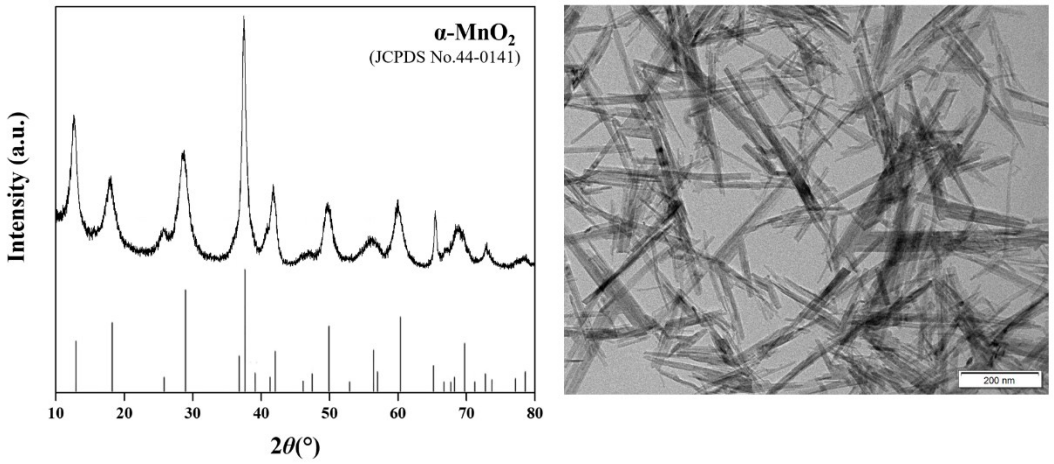

Fig. S1 The XRD pattern and TEM image of α-MnO_2 nanorods synthesized by hydrothermal method.

Table S1 The synthesis method, physical properties and catalytic performance for O_3 decomposition of reported manganese oxides.

Catalysts	Synthesis	Surface area (m^2/g)	Pore volume (cm^3/g)	Reaction conditions					O_3 conversion	Ref.
				Tempe-rature	Inlet O_3	Space velocity	Relative humidity	Duration		
Ce-MnO_x-2	Room-temperature reaction	294.4	0.77	25 °C 30 °C ~25 °C	100 ppm 40 ppm ~20000 ppm	540 L/g·h 840 L/ g·h 12 L/ g·h	RH 50% RH 65% RH 85%	10 h 6 h 8 h	100% 83% 100%	this study
MnO_x	Room-temperature reaction	299.7	0.65	25 °C	20 ppm	600 L/ g·h	RH 50%	10 h	100%	[22]
H-δ-MnO_2	Room-temperature reaction & Acid treatment	228	0.37	25 ℃	115 ppm	600 L/ g·h	RH 50%	10 h	55%	[23]
Ag-MnO_x	Room-temperature reaction & Calcination	32	-	30 °C	40 ppm	840 L/ g·h	RH 65%	6 h	81%	[24]
α-MnO_2	Hydrothermal method	80.7	-	25 °C	100 ppm	540 L/g·h	RH 50%	10 h	36%	[21]
W-MnO_2	Hydrothermal method	297.0	-	25 °C	120 ppm	660 L/ g·h	RH 65%	4 h	50%	[14]
Fe-MnO_x	Hydrothermal method	190.0	-	25 ℃	100 ppm	660 L/ g·h	RH 60%	6 h	73%	[25]
OMS-2	Hydrothermal method	83	-	30 °C	40 ppm	600 L/ g·h	RH 45%	6 h	100%	[20]
$MnFe_{0.5}O_x$	Hydrothermal method & Calcination	262	0.57	25 °C	10000 ppm	12 L/ g·h	RH 90%	8 h	90%	[16]
α-MnO_2	Hydrothermal method & Vacuum treatment	-	-	25 ℃	20 ppm	540 L/g·h	RH 50%	10 h	44%	[26]
Ce-γ-MnO_2	Hydrothermal method & Calcination	120	0.30	30 °C	40 ppm	840 L/ g·h	RH 65%	10 h	84%	[27]
N-MnO_2	Hydrothermal method & Ammonium-treatment	221	0.39	25 °C	115 ppm	600 L/ g·h	RH 50%	10 h	77%	[19]

Ce-MnO_x-2 in this study has been tested under different conditions to be compared with other reported manganese oxides. As shown in Table S1, it performed much better than other facilely synthesized catalysts (i.e. MnO_x [22], H-δ-MnO_2 [23] and Ag-MnO_x [24]) and exhibited very close activity to those best performing catalysts prepared by hydrothermal method (i.e. Ce-γ-MnO_2 [27]), which implies its excellent activity for O_3 decomposition in humid flow.

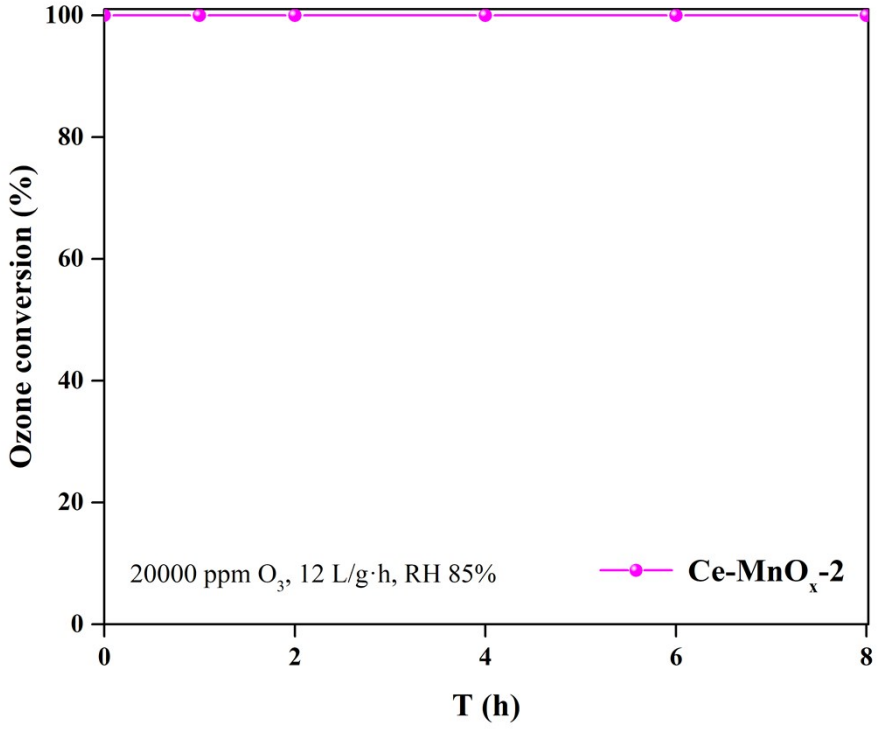

Fig. S2 The catalytic performance of Ce-MnO_x-2 for O_3 decomposition under high humidity and high concentration of O_3 (room temperature, 12 L/g_{cat}·h, RH 85%, O_3: 20000 ppm).

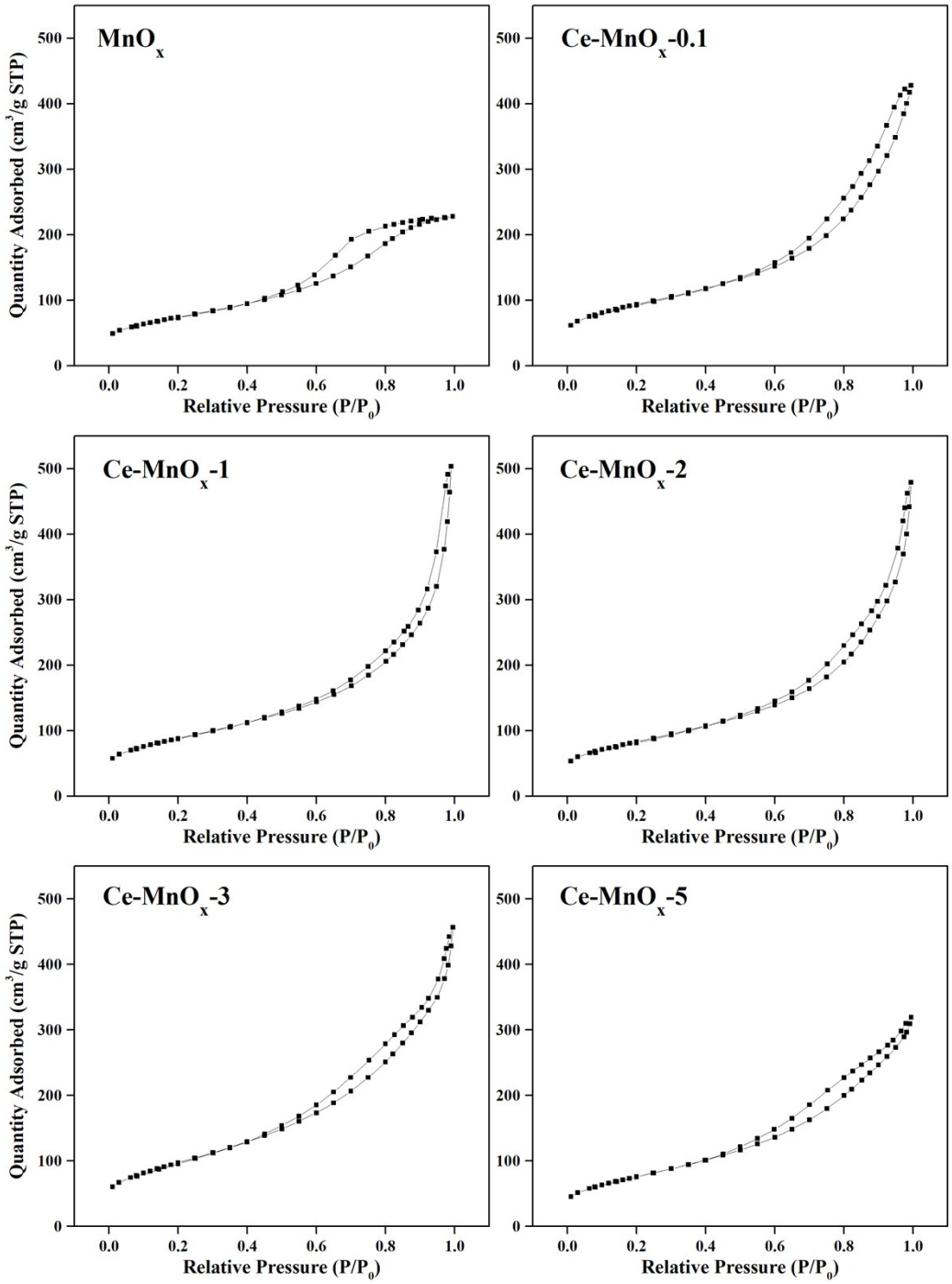

Fig. S3 N_2 adsorption-desorption isotherms of the undoped MnO_x and Ce-MnO_x.

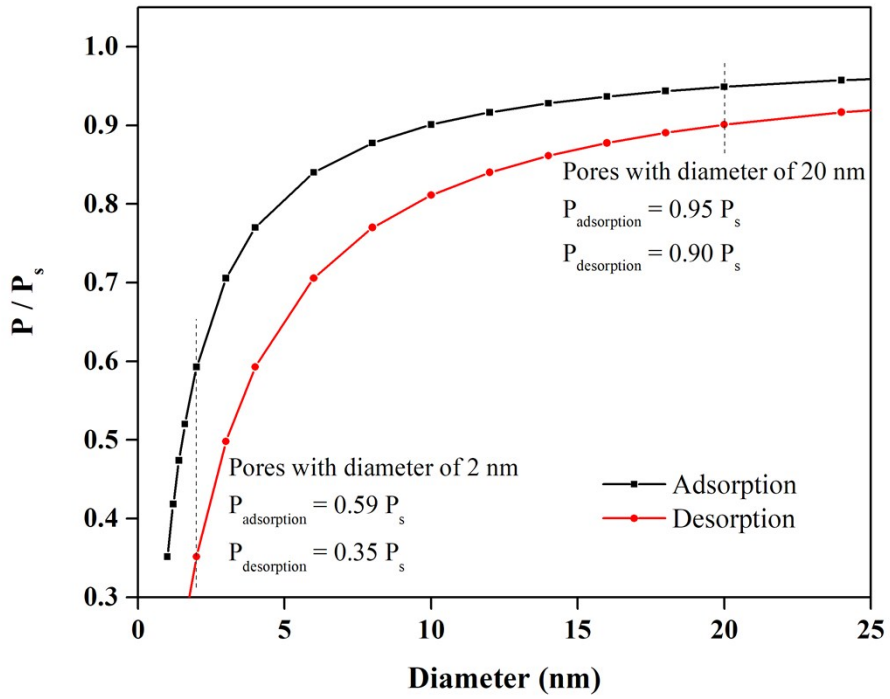

Fig. S4 The equilibrium pressures for water adsorption and desorption in the ideal cylindrical pores at 25 °C based on Kelvin equation (P_s: the saturation vapor pressure of water on a plane surface at 25 °C).

The equilibrium pressures on the adsorption and desorption branches are calculated by following formulas derived from the Kelvin equation, where σ, V_m and μ refer to the surface tension, the molar ratio of water and the radius of cylindrical pores, respectively. [32]

$$\frac{P_{adsorption}}{P_s} = \exp\left(\frac{-\sigma V_m}{\mu RT}\right) \quad (1)$$

$$\frac{P_{desorption}}{P_s} = \left(\frac{P_{adsorption}}{P_s}\right)^2 \quad (2)$$

Above results demonstrate that the capillary condensation happens at higher RH in larger pores, and the moisture also desorbs more easily in larger pores, which implies the promoted humidity tolerance of enlarged porous structure.

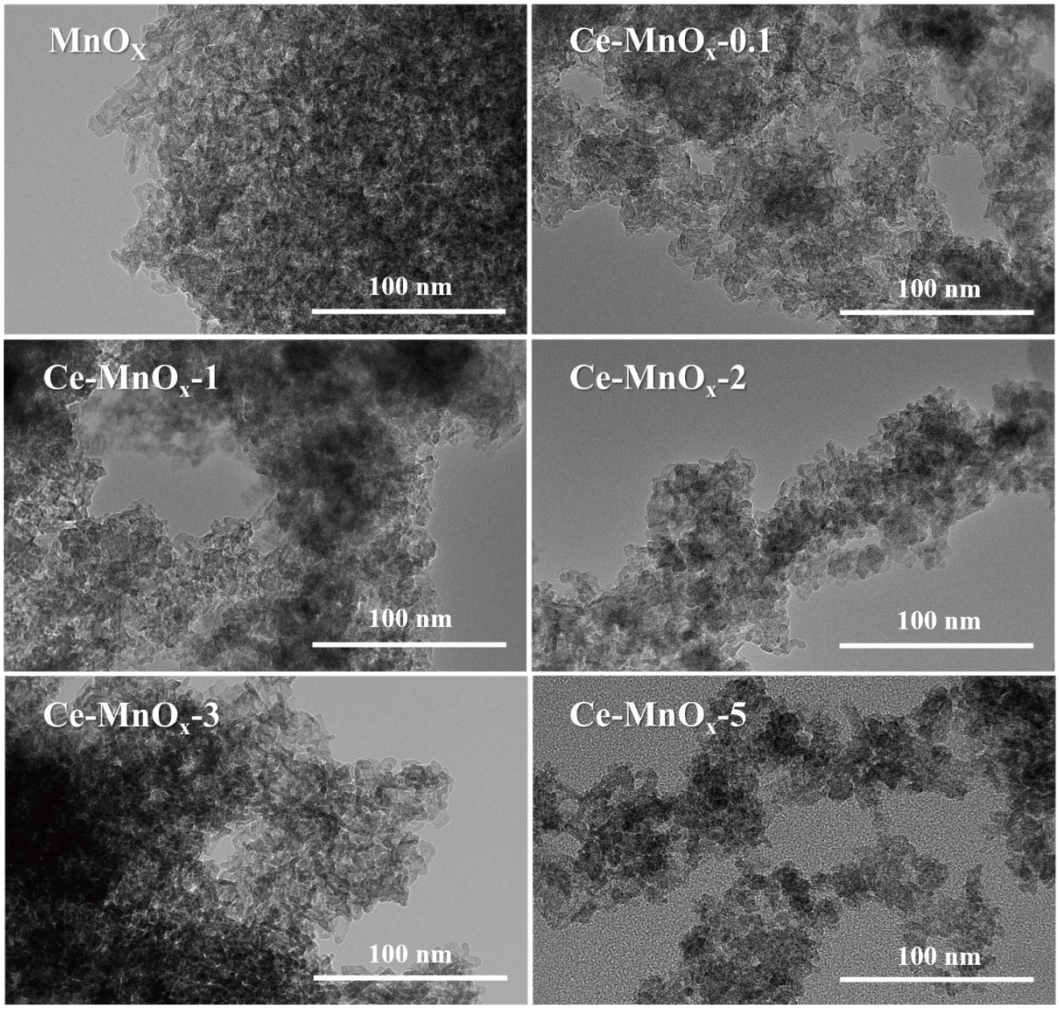

Fig. S5 TEM images of the undoped MnO_x and Ce-MnO_x.

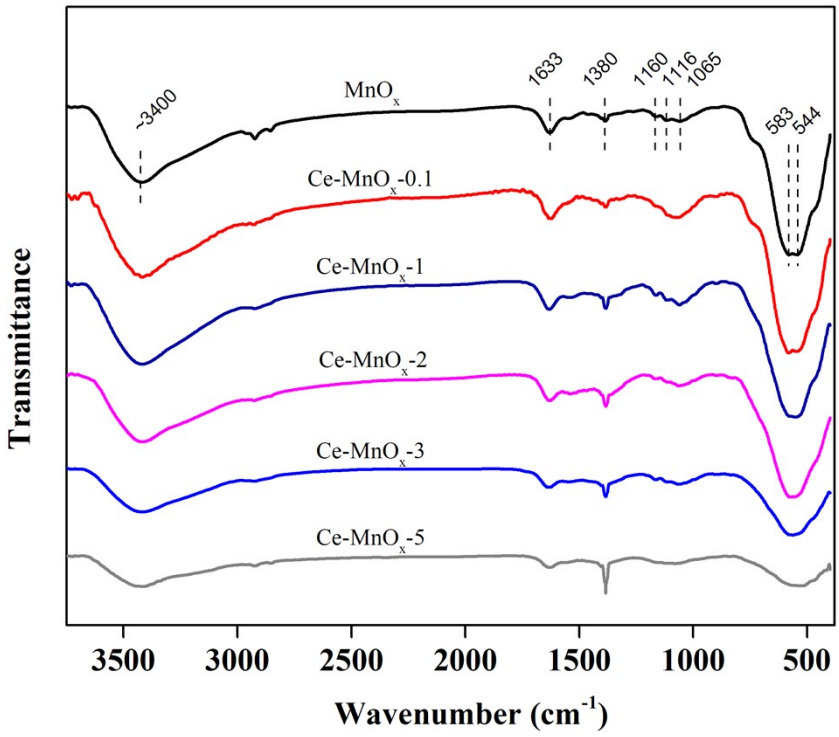

Fig. S6 FTIR profiles of the undoped MnO_x and Ce-MnO_x.

Synthesis of undoped MnO_x using different mass ratio of reactants

The synthesis is almost the same as the undoped MnO_x, except the dosage of $KMnO_4$. The weight ratios of $KMnO_4$ to dopamine hydrochloride adopted in samples, D-2, D-0.5 and D-0.33, were 5:2, 5:0.5 and 5:0.33, respectively. This ratio for the undoped MnO_x was 5:1. Therefore, the MnO_x is also denoted as D-1 here for convenience in analysis.

During the synthesis, obvious excess of $KMnO_4$ was observed of D-0.5 and D-0.33 from the color of solutions.

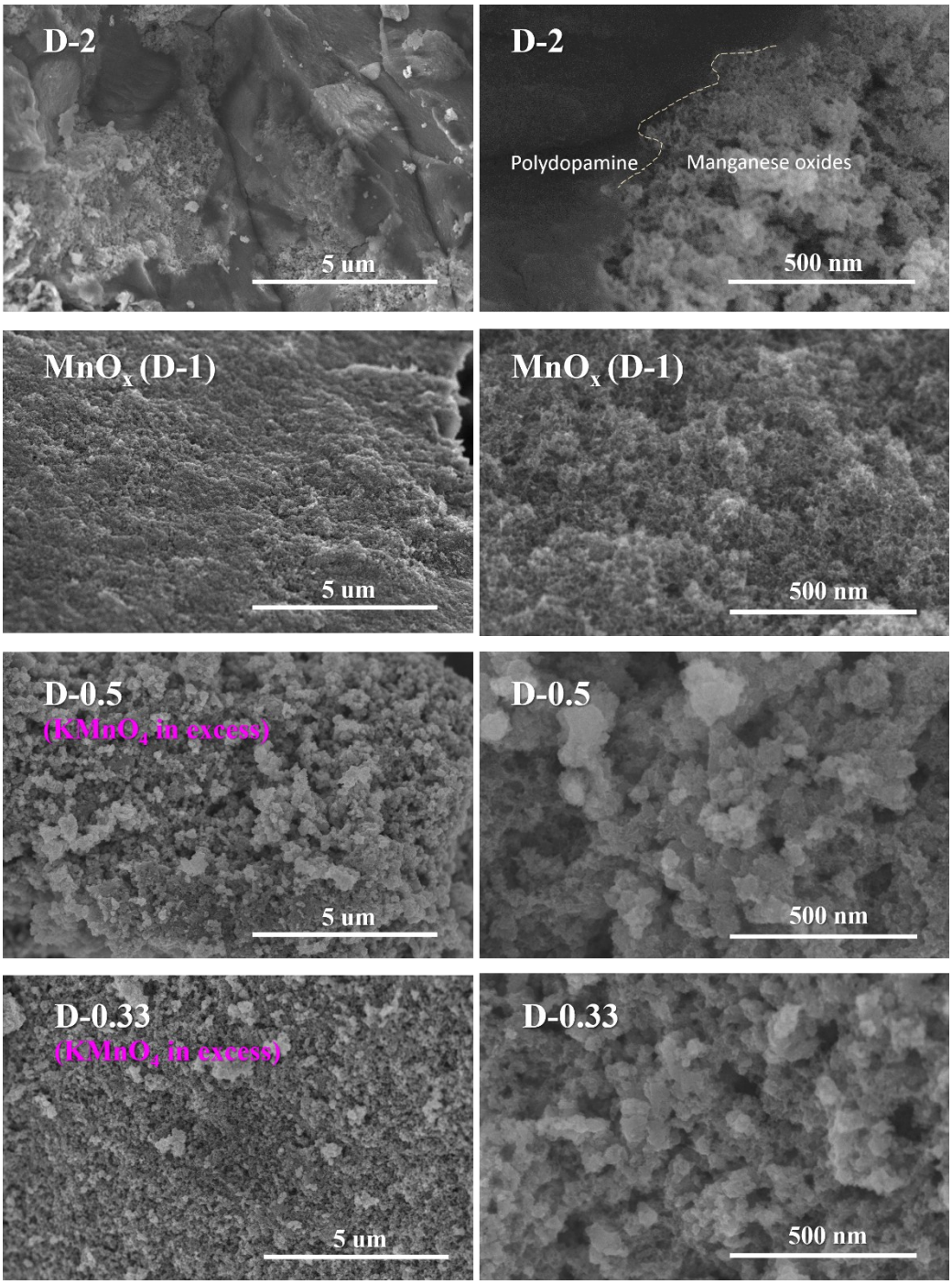

Fig. S7 SEM images of the undoped MnO_x samples synthesized with different mass ratios of $KMnO_4$ to dopamine.

Synthesis of H-MnO_x samples

The synthesis of H-MnO_x samples is similar to that of undoped MnO_x, except 1 or 2 g of HNO_3 was added into the $KMnO_4$ solution before the synthetic reaction. As obtained samples were denoted as H-MnO_x-1 and H-MnO_x-2.

Table S2 pH value of synthetic solutions after the reaction.

Samples	pH
	Solutions after the reaction
undoped MnO_x	7.83
H-MnO_x-1	6.43
H-MnO_x-2	4.30
Ce-MnO_x-1	6.89
Ce-MnO_x-2	5.76
Ce-MnO_x-3	4.58

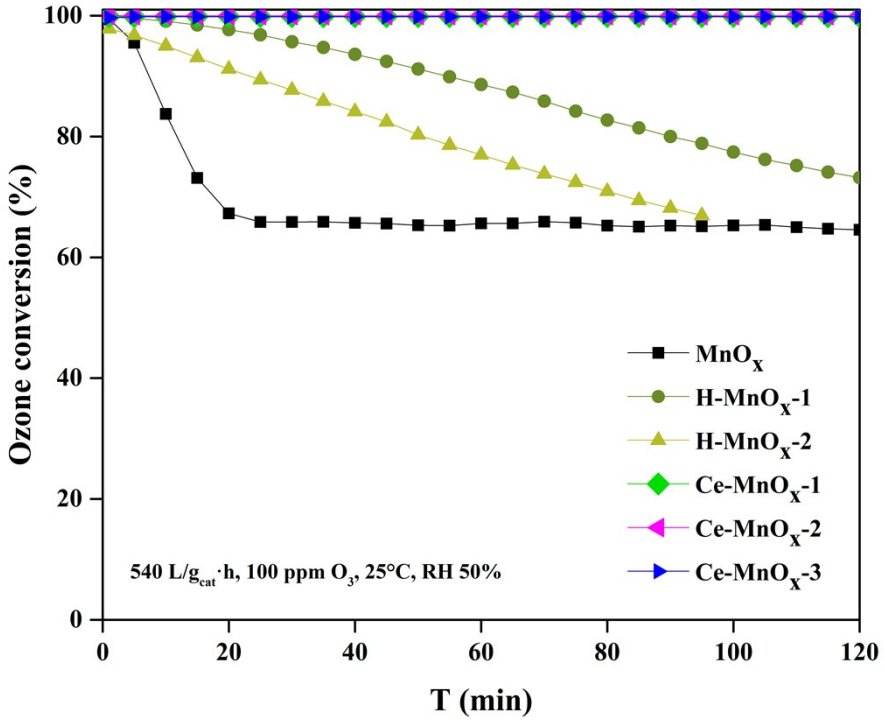

Fig. S8 Catalytic performance of the undoped MnO_x H-MnO_x and Ce-MnO_x. (25 °C, 540 L/g_{cat}·h, RH 50%, O_3: 100 ppm)

Synthesis of cerium doped manganese oxides with different dosage of dopamine

The synthesis of Ce-D-0.9/0.8/0.7/0.6 is almost the same as that of Ce-MnO_x-2, except the decreasing dosage of dopamine hydrochloride. The weight of dopamine hydrochloride used for Ce-MnO_x-2, Ce-D-0.9, Ce-D-0.8, Ce-D-0.7, Ce-D-0.6 were 1 g, 0.9 g, 0.8 g, 0.7 g and 0.6 g, respectively. For the convenience of analysis, Ce-MnO_x-2 is also denoted as Ce-D-1 here.

During the synthesis, obvious excess of $KMnO_4$ was observed in Ce-D-0.6 sample.

Table S3 The carbon content of cerium doped samples synthesized with different amount of dopamine.

Samples	Carbon content (wt.%)
Ce-MnO_x-2 (Ce-D-1)	1.5
Ce-D-0.9	1.37
Ce-D-0.8	0.91
Ce-D-0.7	0.45
Ce-D−0.6	0.44

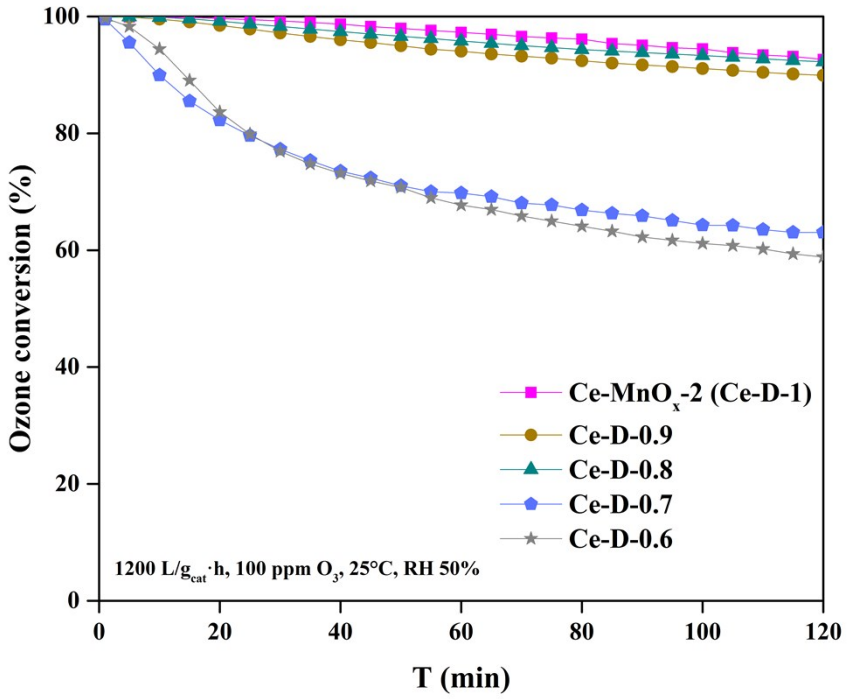

Fig. S9 Catalytic performance of cerium doped samples synthesized with different amount of dopamine. (25 °C, 1200 L/g_{cat}·h, O_3: 100 ppm)

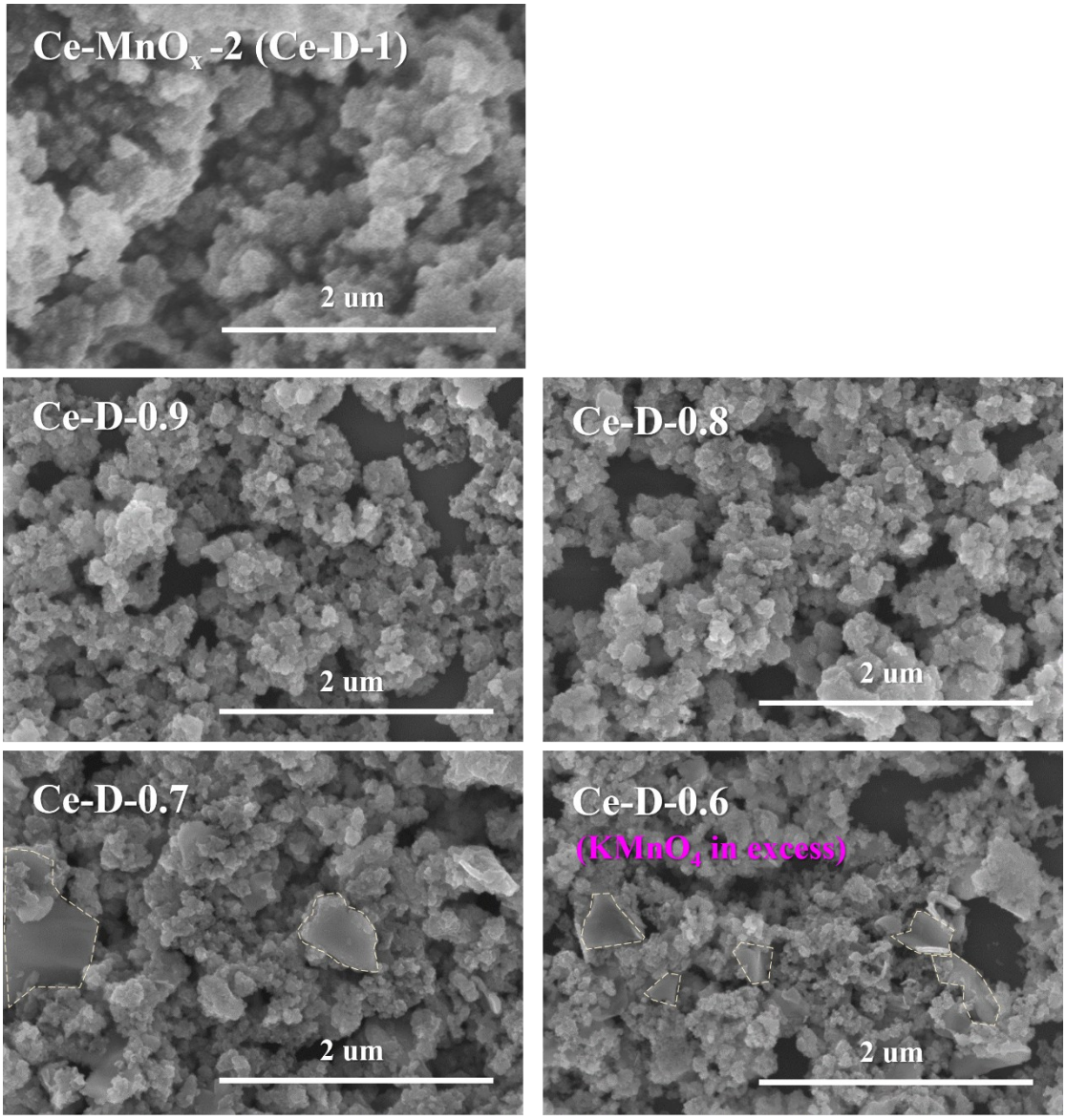

Fig. S10 SEM images of the cerium doped samples synthesized with different amount of dopamine.