Electronic Supplementary Material (ESI) for Nanoscale.

Manganese-based layered double hydroxide nanoparticles as highly efficient ozone decomposition catalyst with tunable valence state

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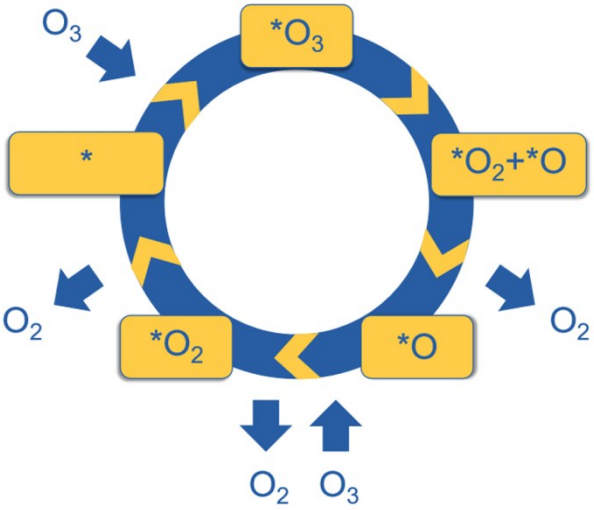
Supplementary Figures

Scheme S1 Schematic illustration of the elementary steps in ozone decomposition reaction.



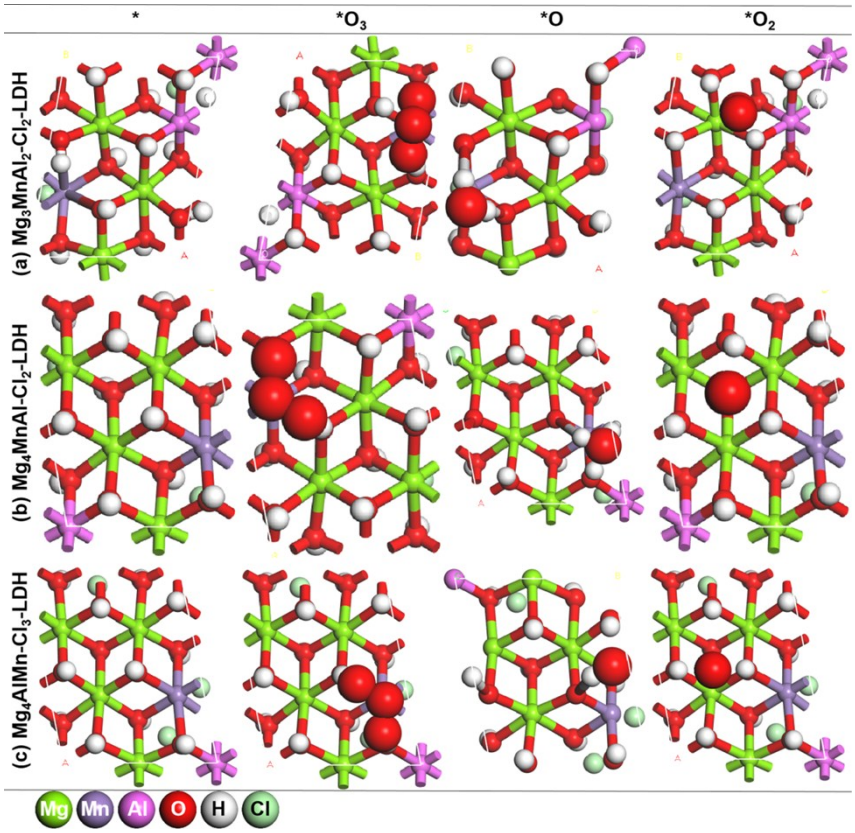


Fig. S1 Optimized geometries of ozone decomposition reaction intermediates for $Mg_3Mn(II)Al$-LDH, $Mg_4Mn(III)Al$-LDH and $Mg_4Mn(IV)Al$-LDH. The color of each element is labeled.

Table S1 Reaction formulae and calculation equations of the elementary steps in ozone decomposition reaction

label	reaction formula	calculation equation
1	$* + O_3 \rightarrow *O_3$	$\Delta G = G_{*O_3} - G_{O_3} - G_*$
2	$*O_3 \rightarrow *O + *O_2$	$\Delta G = G_{*O} + G_{*O_2} - G_{*O_3} - G_*$
3	$*O + *O_2 \rightarrow *O + O_2$	$\Delta G = G_* + G_{O_2} - G_{*O_2}$
4	$*O + O_3 \rightarrow *O_2 + O_2$	$\Delta G = G_{*O_2} + G_{O_2} - G_{O_3} - G_{*O}$
5	$*O_2 \rightarrow * + O_2$	$\Delta G = G_* + G_{O_2} - G_{*O_2}$

Table S2 The Gibbs free energy changes of the elementary steps for ozone decomposition reaction on $Mg_3Mn(II)Al_2$-LDH, $Mg_4Mn(III)Al$-LDH and $Mg_4Mn(IV)Al$-LDH

reaction formula	ΔG / eV		
	$Mg_3Mn(II)Al_2$-LDH	$Mg_4Mn(III)Al$-LDH	$Mg_4Mn(IV)Al$-LDH
$* + O_3 \rightarrow *O_3$	-2.128	-2.304	-2.542
$*O_3 \rightarrow *O + *O_2$	0.626	-0.553	-0.435
$*O + *O_2 \rightarrow *O + O_2$	0.762	1.377	1.495
$*O + O_3 \rightarrow *O_2 + O_2$	-1.894	-1.77	-1.885
$*O_2 \rightarrow * + O_2$	0.762	1.377	1.495

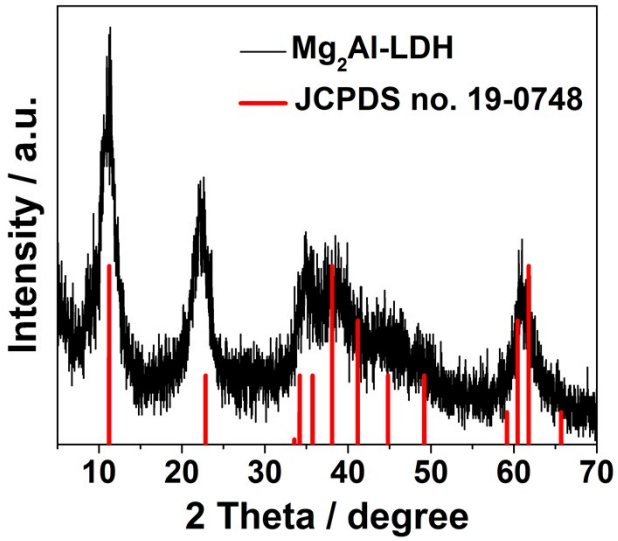


Fig. S2 XRD pattern of Mg_2Al-LDH and JCPDS no.190748.

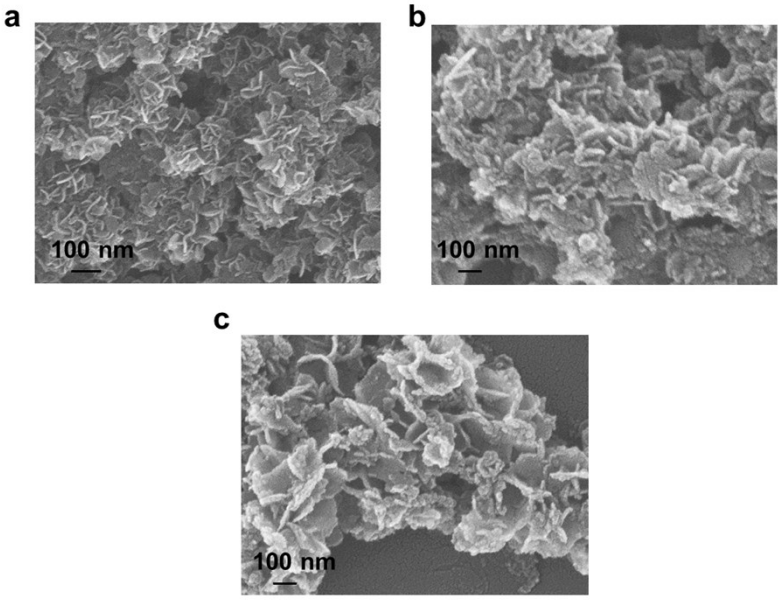


Fig. S3 SEM images of a) Mg_2Al-LDH, b) Mg_1Mn_1Al-LDH and c) $Mg_{0.6}Mn_{1.4}Al$-LDH.

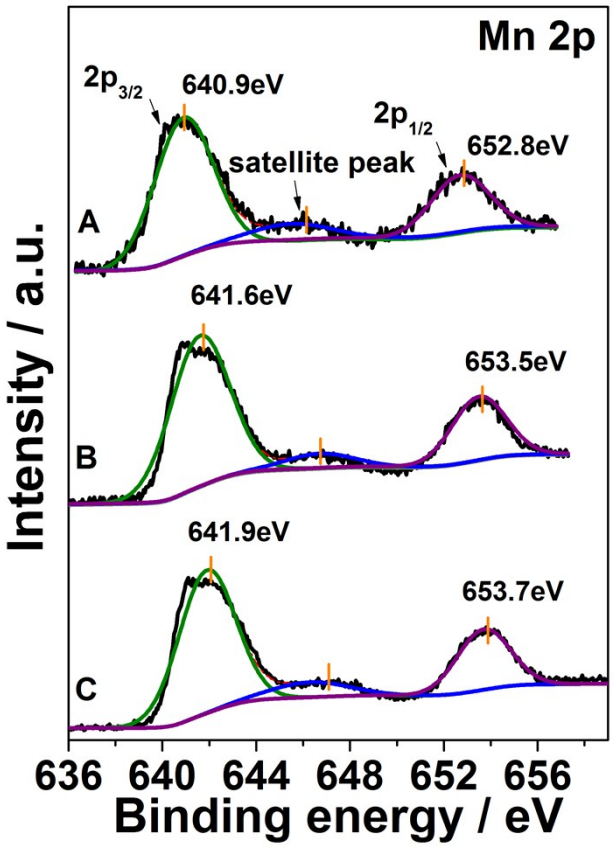


Fig. S4 Mn 2p XPS spectra of (A) $Mg_{1.4}Mn_{0.6}Al$-LDH, (B) Mg_1Mn_1Al-LDH, (C) $Mg_{0.6}Mn_{1.4}Al$-LDH.

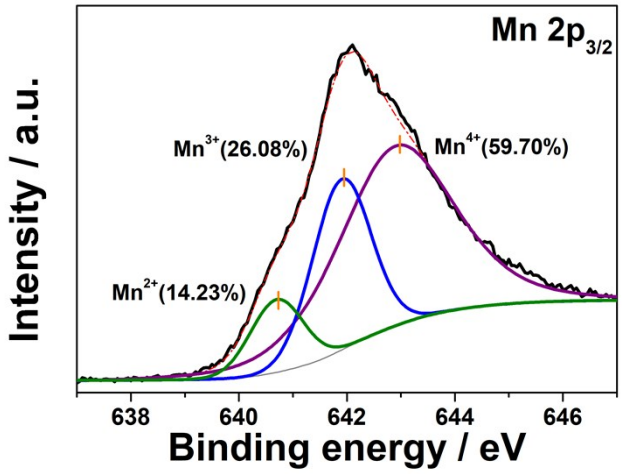


Fig. S5 Mn $2p_{3/2}$ XPS spectra of α-MnO_2.

Table S3 XPS results of surface Mn elements

Catalyst	Mn $2p_{3/2}$			AOS of
	M^{2+} (%)	M^{3+} (%)	M^{4+} (%)	Mn
$Mg_{1.4}Mn_{0.6}Al$-LDH	82.65	8.59	8.77	2.3
Mg_1Mn_1Al-LDH	46.39	34.66	18.95	2.7
$Mg_{0.6}Mn_{1.4}Al$-LDH	26.46	36.75	36.79	3.1
α-MnO_2	14.23	26.08	59.70	3.4

Table S4 Chemical compositions and manganese content

Sample	Chemical compositions	Mn% (w.t.%)
$Mg_{1.4}Mn_{0.6}Al$-LDH	$Mg_{0.43}Mn_{0.22}Al_{0.35}(OH)_2Cl_{0.41}$	15.01
Mg_1Mn_1Al-LDH	$Mg_{0.28}Mn_{0.38}Al_{0.34}(OH)_2Cl_{0.61}$	22.57
$Mg_{0.6}Mn_{1.4}Al$-LDH	$Mg_{0.15}Mn_{0.52}Al_{0.33}(OH)_2Cl_{0.90}$	26.69
Mg_2Al-LDH	$Mg_{0.66}Al_{0.34}(OH)_2Cl_{0.34}$	—
α-MnO_2	—	63.19

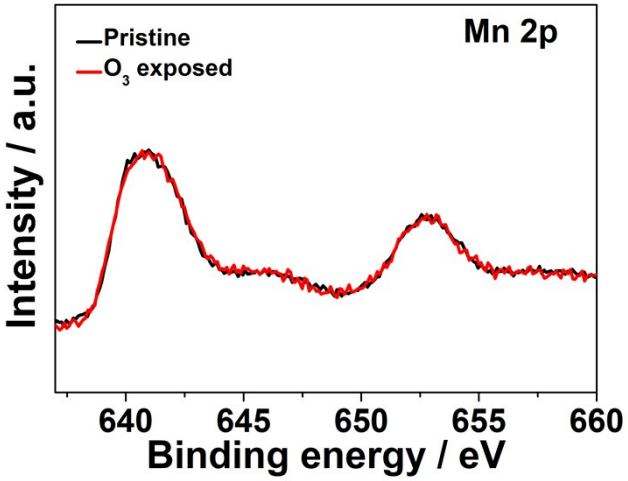


Fig. S6 Mn 2p XPS spectra of $Mg_{1.4}Mn_{0.6}Al$-LDH before and after exposed to ozone.