## **Electronic Supplementary Information for**

## Hierarchically shape-controlled mixed-valence calcium manganites for catalytic ozonation of aqueous phenolic

## compounds

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Figure S1. XRD patterns of manganese oxide prepared without addition of Ca source.



Figure S2. SEM image of manganese oxide prepared without addition of Ca source.





Figure S3. EDS for  $CaMn_3O_6$  (A) and EDS for  $CaMn_4O_8$  (B).



Figure S4.  $N_2$  sorption isotherm of commercial  $MnO_2$ .



**Figure S5.** 4-nitrophenol removal with commercial  $MnO_2$  and the corresponding TOC removal (inset). Reaction conditions: Catalyst loading = 0.1 g/L, Ozone flow rate: 100 mL/min, Ozone loading: 50 mg/L, Temperature: 25 °C.



**Figure S6.** 4-nitrophenol removal and corresponding TOC removal (inset) in catalytic ozonation by  $Mn^{2+}$  solution. Reaction conditions: [4-nitrophenol]<sub>0</sub>=50 ppm, Ozone flow rate: 100 mL/min, Ozone loading: 50 mg/L, Temperature: 25 °C.



**Figure S7.** Influence of  $Ca^{2+}$  on catalytic ozonation performance for decomposition of 4nitrophenol (A) and the corresponding TOC removal (inset). Reaction conditions: [4nitrophenol]<sub>0</sub>=50 ppm, Ozone flow rate: 100 mL/min, Ozone loading: 50 mg/L, Temperature: 25 °C.



**Figure S8.** Variations of ozone concentrations in liquid phase and off-gas in ultrapure water. Ozone flow rate: 100 mL/min, Ozone loading: 50 mg/L, Temperature: 25 °C, Solution pH=5.7.



**Figure S9.** Variations of ozone concentrations in liquid phase and off-gas during ozonation process using 4-nitrophenol solution. Reaction condition: [4-nitrophenol]<sub>0</sub>=50 ppm, Ozone flow rate: 100 mL/min, Ozone loading: 50 mg/L, Temperature: 25 °C, Solution pH=5.7.



**Figure S10.** Variations of ozone concentrations in off-gas and liquid phase during the catalytic ozonation. Reaction conditions:  $[4\text{-nitrophenol}]_0 = 50 \text{ mg/L}$ , Catalyst loading = 0.1 g/L, Ozone flow rate: 100 mL/min, Ozone loading: 50 mg/L, Temperature: 25 °C, Solution pH=5.7.



Figure S11. Kinetic study of ozonation and catalytic ozonation.



**Figure S12.** 4-nitrophenol removal with various 4-nitrophenol concentrations and the corresponding TOC removal (inset). Reaction conditions: Catalyst loading = 0.1 g/L, Ozone flow rate: 100 mL/min, Ozone loading: 50 mg/L, Temperature: 25 °C.



**Figure S13.** 4-nitrophenol removal with various catalyst loading (A) and the corresponding TOC removal (inset). Reaction conditions: [4-nitrophenol]<sub>0</sub>=50 ppm, Ozone flow rate: 100 mL/min, Ozone loading: 50 mg/L, Temperature: 25 °C.



**Figure S14.** 4-nitrophenol removal and corresponding TOC removal (inset) with various ozone concentrations. Reaction conditions:  $[4\text{-nitrophenol}]_0=50$  ppm, Ozone flow rate: 100 mL/min, catalyst loading = 0.1 g/L, Temperature: 25 °C.



**Figure S15.** EPR spectrum. EPR operating conditions: Centerfield: 3520 G; sweep width: 100 G; microwave frequency: 9.87 GHz; modulation frequency: 100 GHz; and power: 18.11 mW. Catalytic ozonation with DMPO was carried out in ultrapure water. Reaction conditions: [4-nitrophenol]<sub>0</sub> = 10 mg/L, catalyst loading= 0.2 g/L, Ozone flow rate: 100 mL/min, Ozone loading: 50 mg/L, Temperature: 25 °C.