Supplementary file

for

Oriented generation of singlet oxygen in H_2O_2 activation for water decontamination: Regulation of oxygen vacancy over α-MnO_2 nanocatalyst

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Text S1. Quantitative detection of $^1O_2$.

Since 1,3-diphenylisobenzofuran (DPBF) could react with $^1O_2$ in a molar ratio of 1:1, it was applied to quantitatively reflect the production amount of $^1O_2$ in the H_2O_2 activation system[1]. Typically, 30 mg of different K^+-modified α-MnO_2 catalysts was dispersed in 100 mL of solution with 0.05 mmol/L of DPBF for adsorption−desorption equilibrium. Then, 50 mM of H_2O_2 was added to initiate the reaction. The concentration of DPBF was measured by UV-2700 spectrophotometer (Shimadzu Corporation) at 411 nm. In the background experiments (**Fig. S8**), sole H_2O_2 system had no degradation ability to DPBF, and the K^+-modified α-MnO_2 catalysts showed negligible adsorption performances for DPBF.

Text S2. Density functional theory (DFT) calculation.

We have employed the first-principles[2] to perform all (DFT) calculations within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) formulation[3]. We have chosen the projected augmented wave (PAW) potentials[4] to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 400eV. Partial occupancies of the Kohn−Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller than 10^{-5} eV. A geometry optimization was considered convergent when the energy change was smaller than 0.03 eV $Å^{-1}$. In our structure, the U correction is used for Mn atoms. The vacuum spacing in a direction perpendicular to the plane of the structure is 18 Å for the MnO_2 surfaces. The Brillouin zone integration is performed using 3×3×1 Monkhorst-Pack k-point sampling for a structure. Finally, the adsorption energies (E_{ads}) were calculated as Eads= $E_{ad/sub} - E_{ad} - Es_{ub}$, where $E_{ad/sub}$, E_{ad}, and E_{sub} are the total energies of the optimized adsorbate/substrate system, the adsorbate in the structure, and the clean substrate, respectively. The free energy was calculated using the equation:

$$G=E_{ads} + ZPE - TS$$

where G, Eads, ZPE and TS are the free energy, total energy from DFT calculations, zero point energy and entropic contributions, respectively.

Table S1. Parameters of pharmaceutical wastewater.

Parameters	Pharmaceutical wastewater
pH	5.6
COD (mg/L)	66.4
TOC (mg/L)	18.7
UV_{254} (cm^{-1})	0.457
Turbidity	9.04
DO (mg/L)	7.38

Table S2. Detected emerging organic contaminants in the pharmaceutical wastewater.

Number	Emerging organic contaminants	Concentration (μg/L)
1	Oxytetracycline	0.81 ± 0.10
2	Lincomycin	1.73 ± 0.22
3	Tetracycline	1.95 ± 0.46
4	Bisphenol A	3.46 ± 0.12
5	Amoxicillin	4.19 ± 0.22
6	Naproxen	6.67 ± 1.29
7	Roxithromycin	11.09 ± 0.22
8	Erythromycin	18.88 ± 1.01
9	Ciprofloxacin	19.80 ± 0.10
10	Paracetamol	36.49 ± 3.75

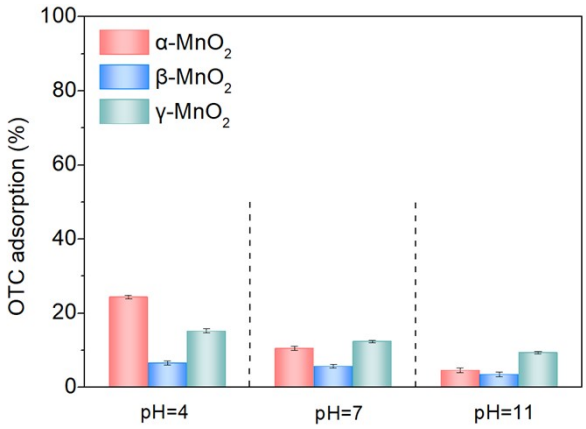


Fig. S1. Adsorption of OTC by different MnO_2 catalysts under various pH conditions. Conditions: [catalysts] = 300 mg/L, [OTC] = 5 mg/L, pH = 4.0−11.0.

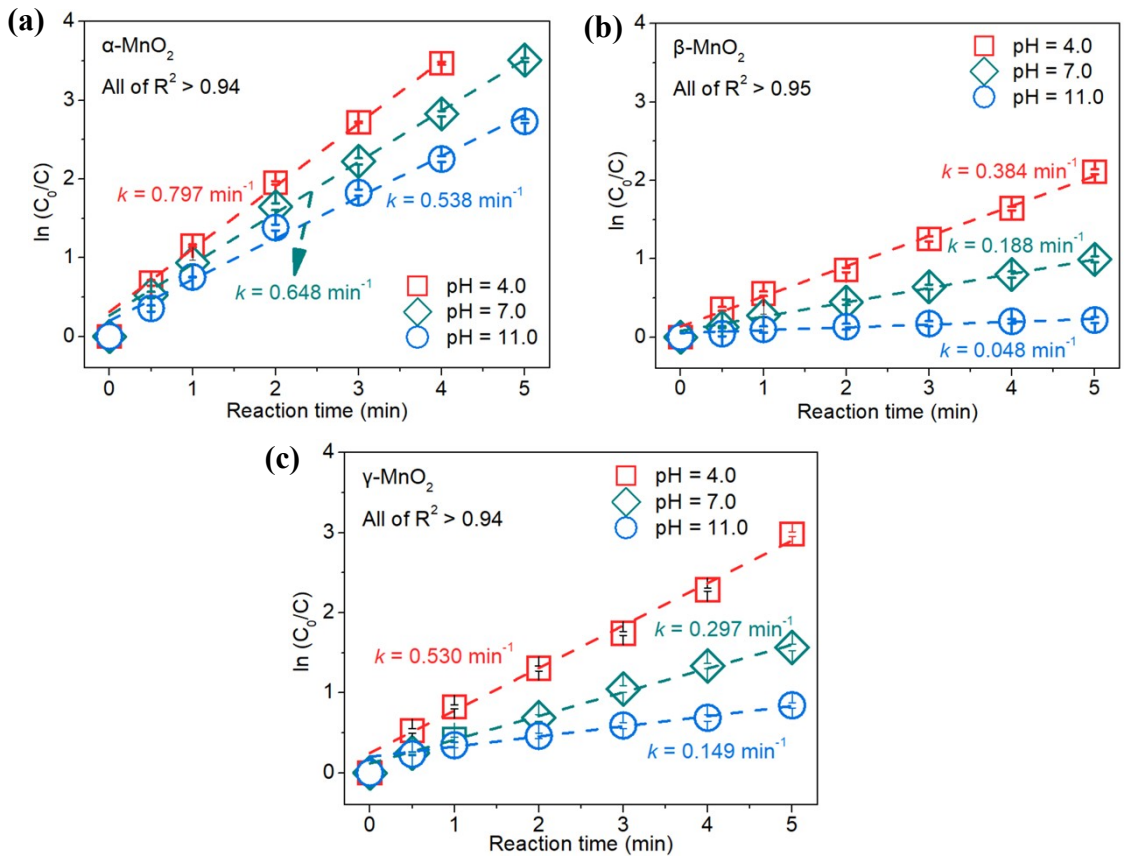


Fig. S2. Pseudo-first-order rate constant versus solution pH for the Fenton-like oxidation of OTC with (a) α-MnO_2, (b) β-MnO_2 and (c) γ-MnO_2. Conditions: [catalysts] = 300 mg/L, [H_2O_2] = 50 mM, [OTC] = 5 mg/L, pH = 4.0−11.0

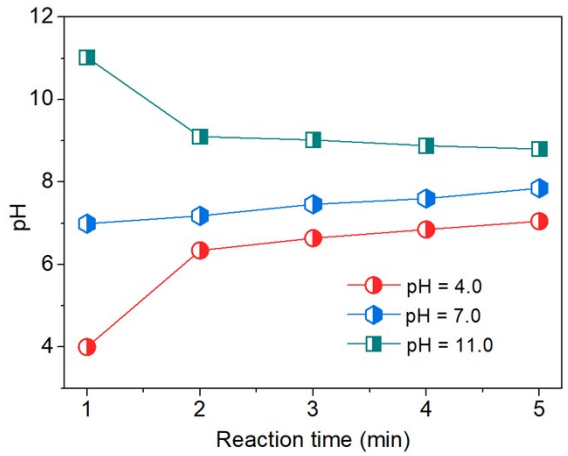


Fig. S3. The pH variations versus reaction time in OVs-rich α-MnO_2/H_2O_2 system at initial pH levels of 4.0 to 11.0.

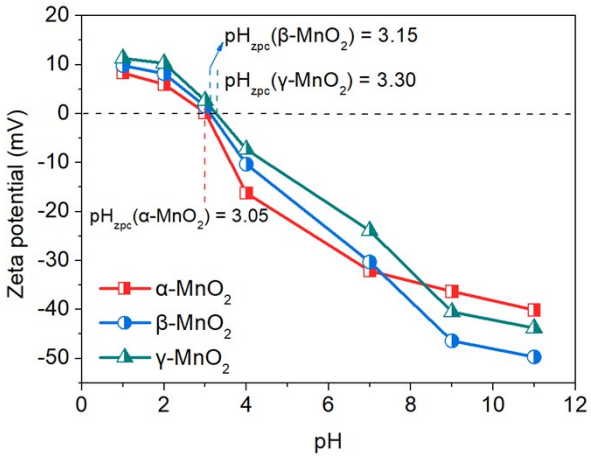


Fig. S4. Zeta potentials of MnO_2 catalysts as a function of solution pH.

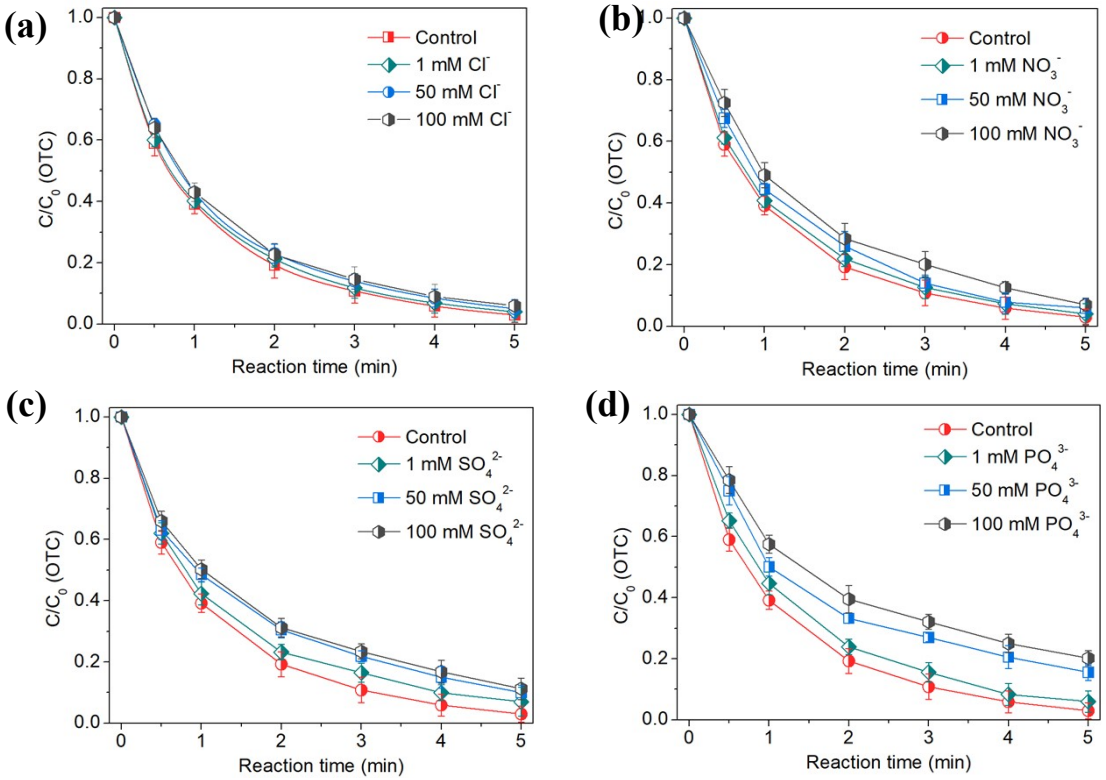
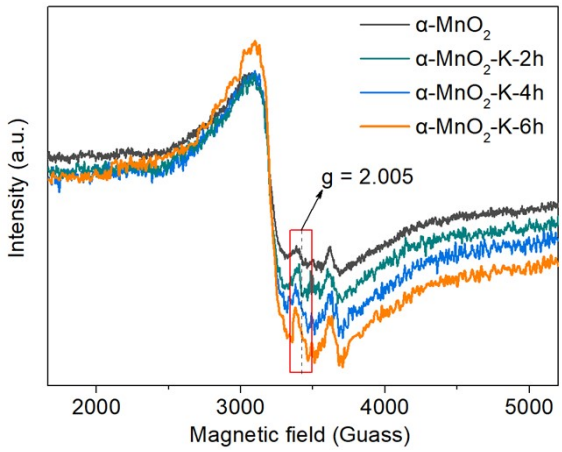


Fig. S5. The effect of various anions on OTC degradation in α-MnO_2/H_2O_2 system. Conditions: [H_2O_2] = 50 mM, [OTC] = 5 mg/L, [Cl^-] = [NO_3^-] = [SO_4^{2-}] = [PO_4^{3-}] = 1−100 Mm, pH = 7.0.



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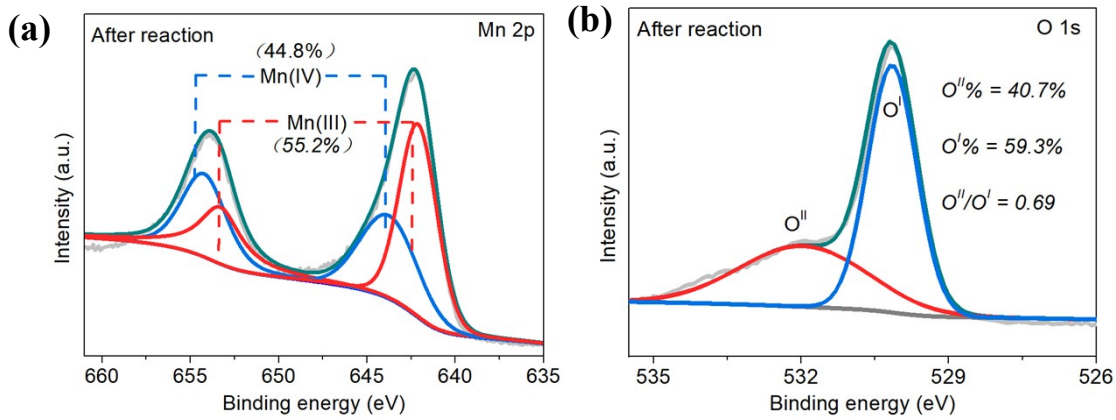
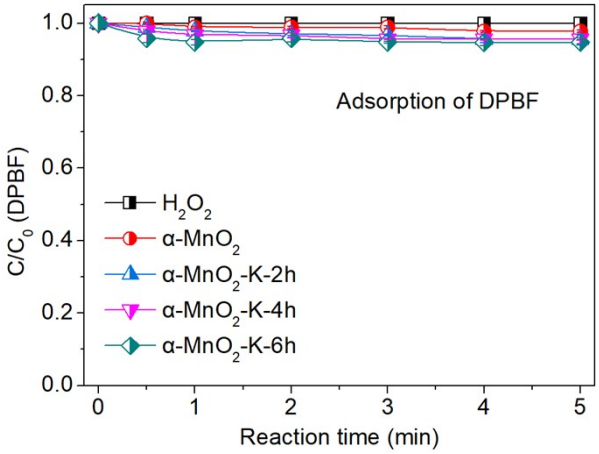


Fig. S7. XPS spectra of Mn 2p (a) and O 1s (b) of α-MnO_2 after the reaction.



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References

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