The Quantitative Contribution of Interfacial Coexisting Mn, O Vacancies to MnO$_2$ Photocatalytic Degradation of Phenol

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The mechanism of V_{Mn} formation

During the formation of δ-MnO_2, because of the presence of excess interlayer K^+, in order to maintain charge balance, the reaction system is caused to form a mixed state with random distribution of $Mn^{4+}O_6$ and $Mn^{3+}O_6$. (**CrystEngComm., 2019, 1793-1805.**) Under high-temperature reaction conditions, $Mn^{3+}O_6$ is susceptible to deformation, and the severely deformed portion will be readily reconstructed with the increase of lattice strain, during which the Mn-O bond will be broken, thus detaching the Mn^{3+} and resulting in the formation of a V_{Mn} (**Journal of Energy Chemistry., 2021, 245-258**) Therefore, MnO_2 was prepared using a hydrothermal reaction of 1 g of $KMnO_4$ with 0.8 g and 1.8 g of ammonium oxalate, respectively, with ammonium oxalate acting as the reducing agent. Relative to 1.8 g ammonium oxalate, the 0.8 g ammonium oxalate system has a relatively higher content of K^+ and tends to produce more V_{Mn}. (**Applied Catalysis B: Environmental., 2017, 147-155**)
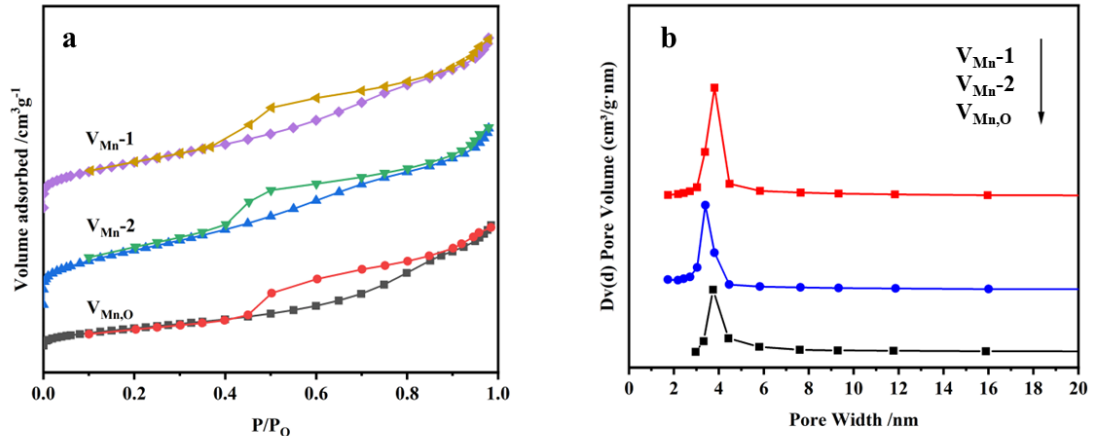
Fig S1. (a) Analysis of N_2 adsorption and desorption of MnO_2 samples; (b) Pore size distributions for V_{Mn}-1，V_{Mn}-2，$V_{Mn,O}$.
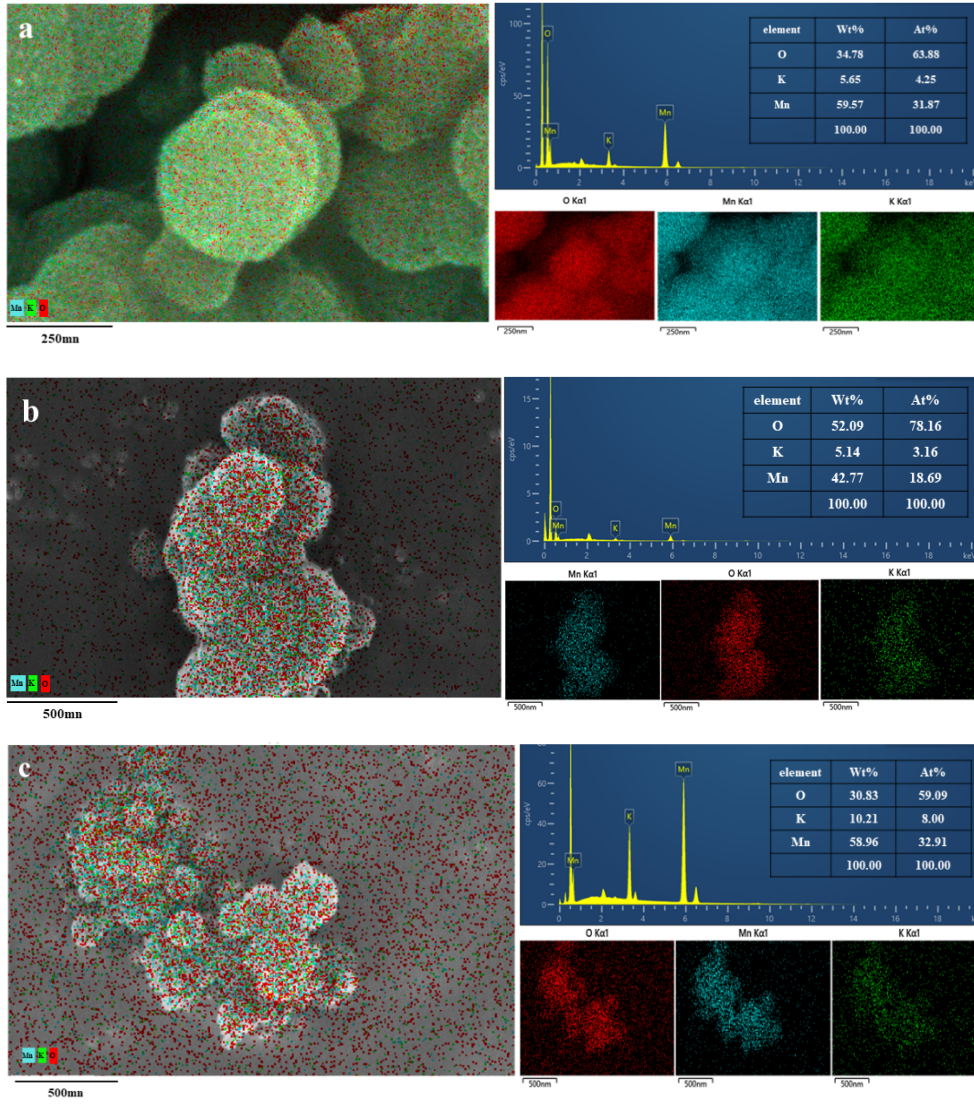
Fig S2. Energy dispersive spectra（EDS）of V_{Mn}-1，V_{Mn}-2，$V_{Mn,O}$.

Calculation process

From the chemical formulae of the three samples, the molar mass (M) of 50 mg of sample and the amount of substance (n) of V_{Mn} and V_O were calculated for VMn-1 ($K_{0.09}Mn_{0.98}$ $V_{Mn\ 0.02}O_2$), V_{Mn}-2 ($K_{0.11}Mn_{0.96}$ $V_{Mn\ 0.04}O_2$), $V_{Mn,\ O}$ ($K_{0.11}Mn_{0.96}$ $V_{Mn\ 0.04}$ $O_{1.97}$ $V_{O\ 0.03}$). The V_{Mn} content of V_{Mn}-1 and V_{Mn}-2 was calculated to be 1.12×10^{-5} mol and 2.24×10^{-5} mol by using the equation： $n = m/M$.

The contribution (487321.43 (mg/L) phenol/mol) of each mole of V_{Mn} to the degradation of phenol was obtained by dividing the difference between the degradation rates of the two by the V_{Mn} content. The contribution (125917.16 (mg/L) $_{phenol}$/mol $_{V_O}$) of single molar V_O to the degradation of phenol was calculated by the same method.

Models and computational methods

We have employed the Vienna Ab initio Simulation Package (VASP) to perform all density functional theory (DFT) calculations. The elemental core and valence electrons were represented by the projector augmented wave (PAW) method and plane-wave basis functions with a cutoff energy of 490 eV. Generalized gradient approximation with the Perdew-Burke-Ernzerh of (GGA-PBE) exchange-correlation functional was employed in all the calculations. Geometry optimizations were performed with the force convergency smaller than 0.05 eV/Å. Spin-polarization effect was also considered. The DFT+U approach was introduced to treat the highly localized Mn 3d states, using parameters of U–J = 2.5eV. Monkhorst-Pack k-points of 3×3×1 was applied for all the calculations.
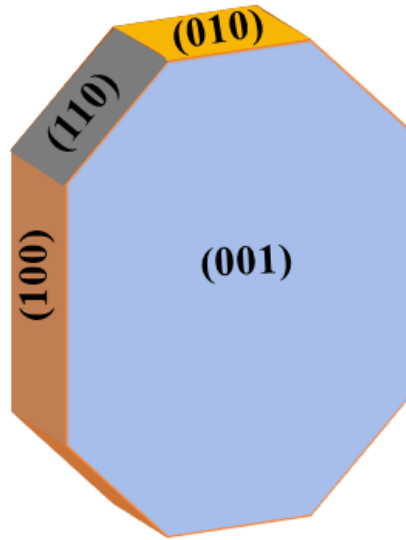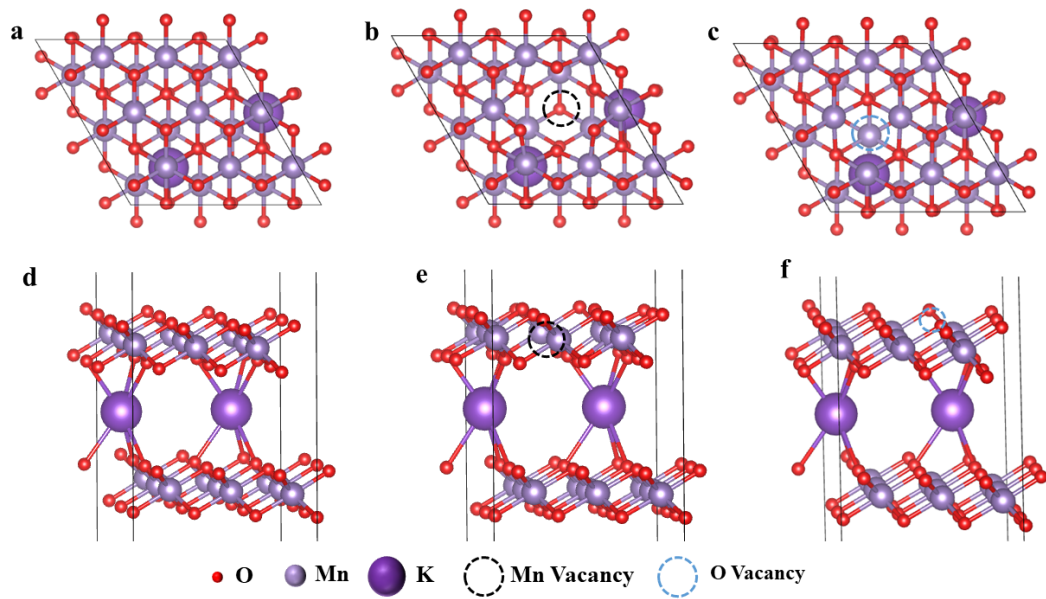
Fig.S3. Wulff construction of δ-MnO$_2$.

Fig S4. (a,d) perfect (001) MnO_2,(b,e) Mn vacancy (001) MnO_2,(c,f) (001) O vacancy (001) MnO_2.
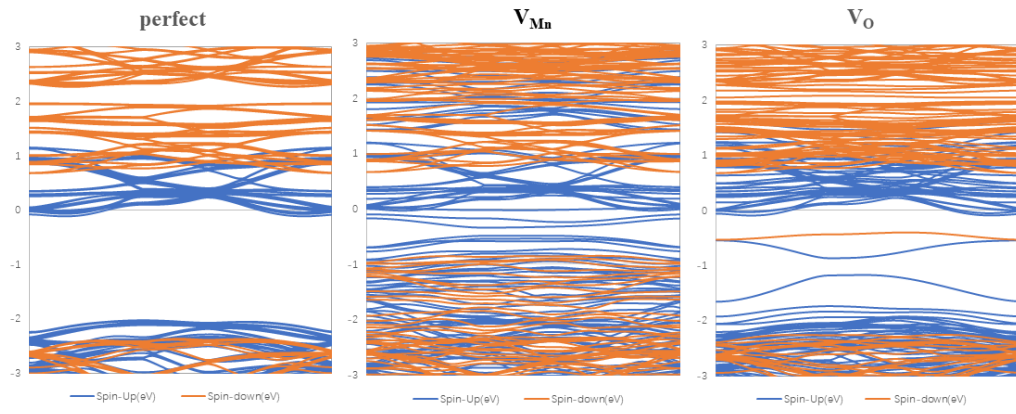
Fig S5. Band gap diagrams of perfect (001) MnO_2, Mn vacancy (001) MnO_2, (001) O vacancy (001) MnO_2
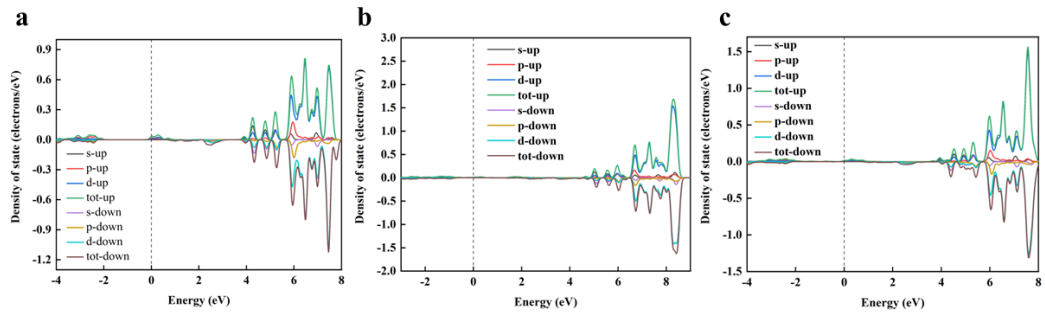
Fig S6. Density states of each orbital of element K in the three samples (a) perfect (001) MnO_2, (b) Mn vacancy (001) MnO_2, (c) (001) O vacancy (001) MnO_2.

Table S1. A comparison table with similar studies.

Sample	Dosage	Lighting conditions	phenol concentration	Time	Volume of solution	degradation rate	Temperature	
δ-MnO$_2$	100 mg	Visible light	1000 ppm	180 min	20 mL	100 %	70 ℃	[1]
MnO$_2$	50 mg	300 W ($\lambda >$ 420 nm)	100 mg/L	30 min	50 mL	10 %	25±2 ℃	[2]
MnO$_2$/g-C$_3$N$_4$	50 mg	Visible light	5 mg L^{-1}	100 min	100 mL	100 %	/	[3]
Sn doped MnO$_2$	25 mg	Uv 365 nm	/	100 min	/	98.5 %	/	[4]
Ag doped MnO$_2$	50 mg	Visible light	5 mg L^{-1}	100 min	100mL	90 %	/	[5]
g-C$_3$N$_4$/α-MnO$_2$	40 mg	300W xenon lamp ($\lambda >$ 400 nm)	10 mg L^{-1}	140 min	80mL	98 %	/	[6]
MnO$_2$@CQD	20 mg	Visible light	10 ppm	50 min	50 mL	90 %	/	[7]

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Table S2. The toxicity of the intermediates of phenol degradation

Compound	Acute Toxicity (mg/L)			Chronic Toxicity (mg/L)		
	Fish (LC50)	Daphnid (LC50)	Green Algae (EC50)	Fish	Daphnid	Green Algae
Phenol	27.7	9.64	2.4	2.61	0.969	4.53
HQ	2.22	256	4.9	14.2	101	0.568
CA	2.22	256	4.9	14.2	101	0.568
RO	2.22	256	4.9	14.2	101	0.568
BQ	0.095	0.738	0.047	0.0091	4.87	0.011