Supplementary material

for

Microstructure modulation of α-MnO_2 via mild urea-induced phase transition for enhanced catalytic ozonation of emerging contaminants

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Text S1. Removal rate calculation method

The formula for calculating the sulfamethoxazole (SMZ) removal is defined as follows:

$$\text{Removal (\%)} = (C_0 - C_t) / C_0 \times 100\%$$

Where C_0 is the initial concentration of SMZ, and C_t is the concentration of SMZ at a specific reaction time t. All measurements were repeated in triplicate and reported as the average values.

Text S2. Preparation detail of simulated wastewater for water matrices assessment

To assess the effect of diverse anions (e.g., Cl^-, NO_3^-, SO_4^{2-}, HCO_3^{2-} and $H_2PO_4^{2-}$) and humic acid (HA) on SMZ removal, catalytic ozonation experiments were conducted with simulated wastewater. The simulated wastewater was prepared by adding specific salts to deionized water to achieve the desired background anion concentration. The concentration of each anion and HA was set as: Cl^- (100 mM), NO_3^- (100 mM), SO_4^{2-} (100 mM), HCO_3^{2-} (10 mM), $H_2PO_4^{2-}$ (10 mM) and HA (10 mg/L), respectively. A specific amount of sulfamethoxazole was then added to complete the preparation of each simulated wastewater.

Text S3. Semi-quantitative analysis of mass ratio of α-MnO_2 and Mn_3O_4

The reference intensity ratio (RIR) value of α-MnO_2 was first determined to be 0.527 using the internal standard method, where the samples were blended with a 1:1 mass ratio of corundum (α-Al_2O_3, JCPDS 46-1212) [1]. The RIR of Mn_3O_4 was 1.50 adopted directly from JCPDS 24-0734. The mass fractions of α-MnO_2 (W_A) and Mn_3O_4 (W_B) were then calculated using the equation:

$$W_A / W_B = (I_A / I_B) \times (K_B / K_A)$$

where I_A and I_B are the strongest peak intensity of α-MnO_2 and Mn_3O_4, respectively, which can be calculated based on the XRD patterns using Jade software. And K_A and K_B are their RIR values.

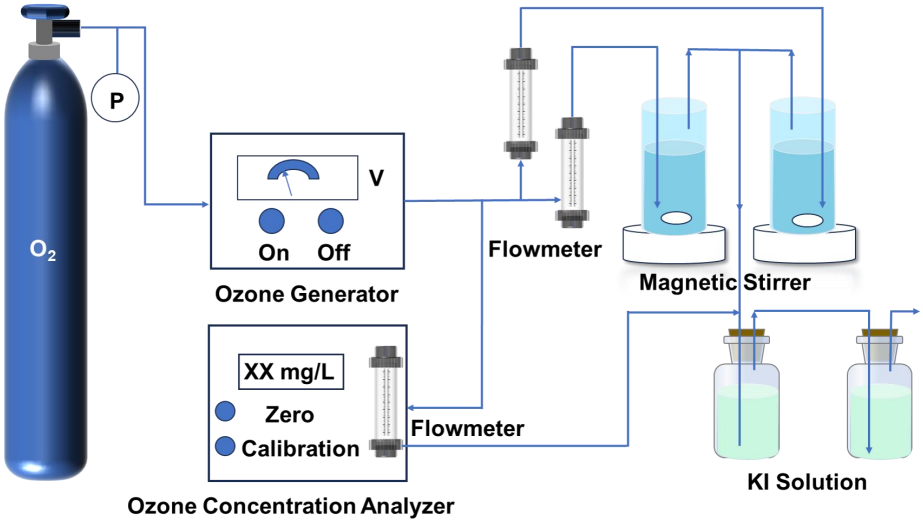

Fig. S1. Laboratory setup of catalytic ozonation system.

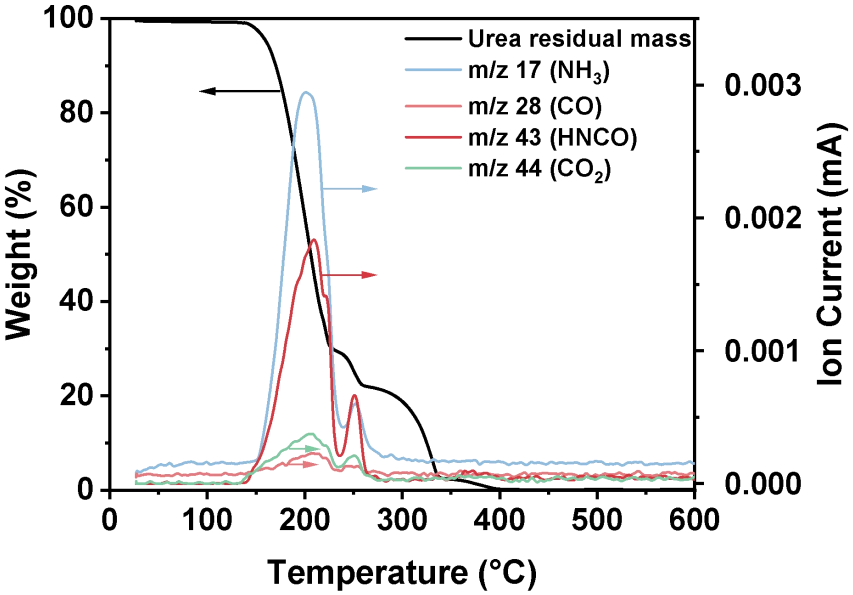

Fig. S2. TG-MS curves of urea pyrolysis process.

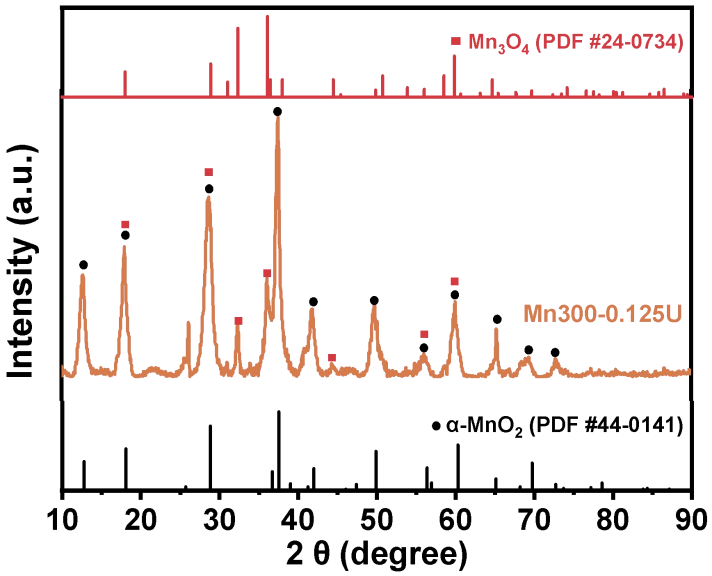

Fig. S3. XRD patterns of Mn300-0.125U.

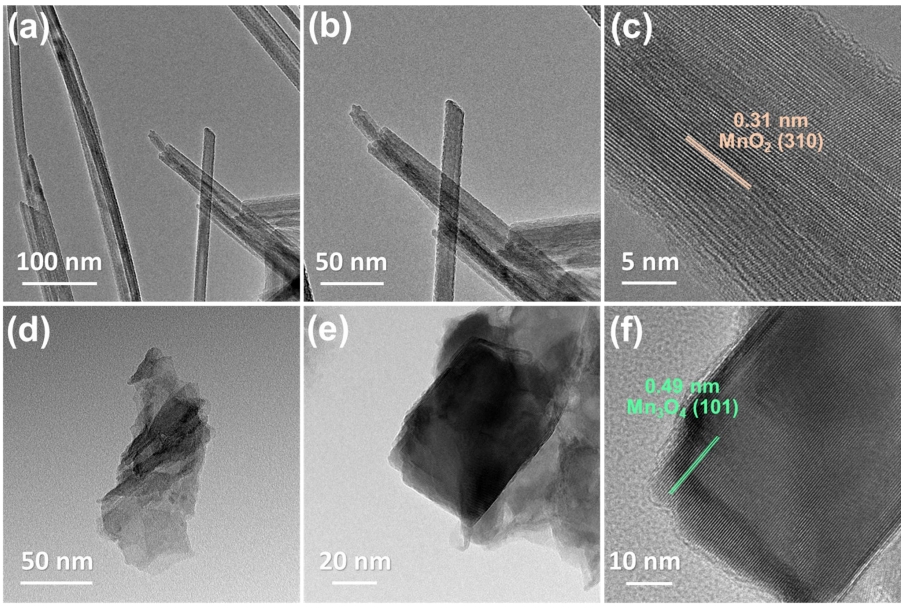

Fig. S4. (a−c) TEM and HRTEM images of Mn400-0U (α-MnO_2); (d−f) TEM and HRTEM images of Mn400-0.25U (Mn_3O_4).

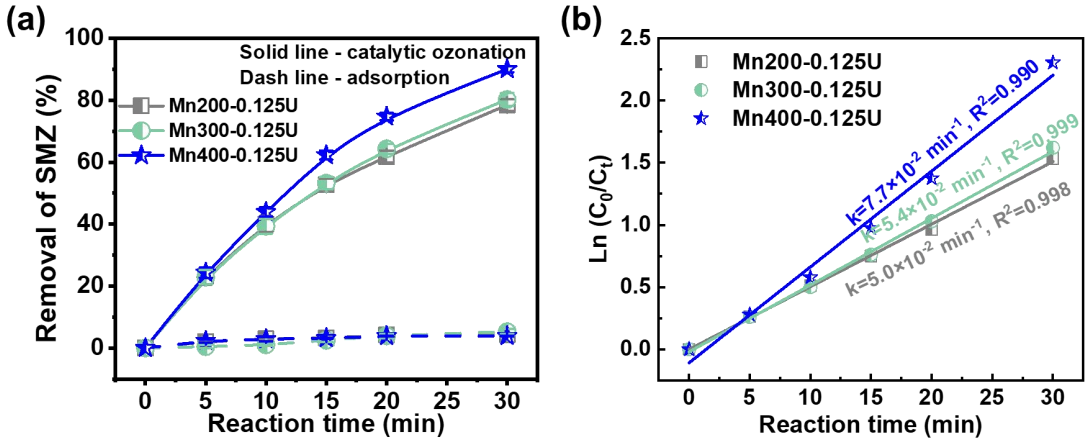

Fig. S5. (a) Removal of SMZ and (b) pseudo first-order kinetics fitting for SMZ removal in O_3/Mn200-0.125U, O_3/Mn300-0.125U and O_3/Mn400-0.125U systems.

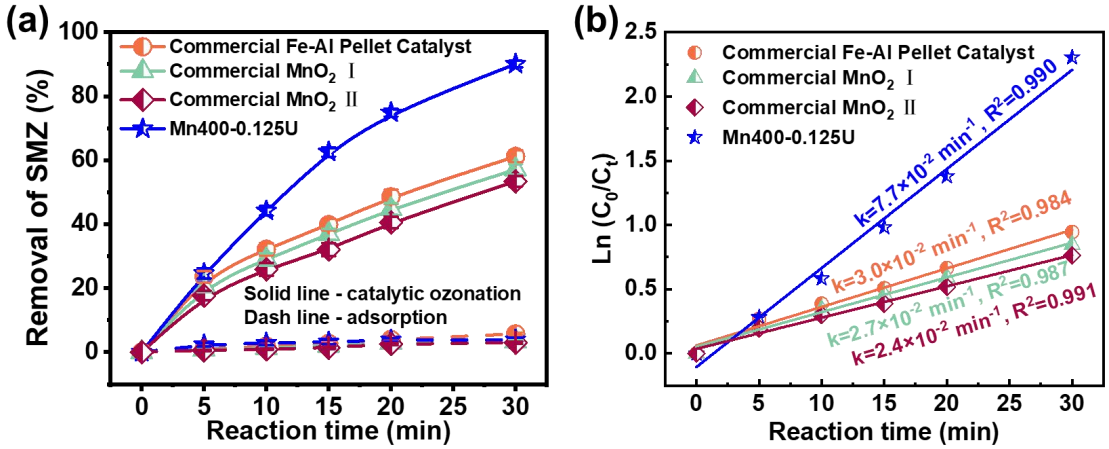

Fig. S6. Comparison of different commercial catalysts with Mn400-0.125U in the catalytic ozonation system: (a) removal of SMZ and (b) pseudo first-order kinetics fitting for SMZ removal. Commercial MnO_2 I was purchased from Tianjin Fuchen Chemical Reagent Factory, commercial MnO_2 II was purchased from Tianjin Damao Chemical Reagent Factory, and commercial Fe-Al pellet catalyst was purchased from Pingxiang Rongjian Environmental Protection Chemical Packing Co., Ltd.

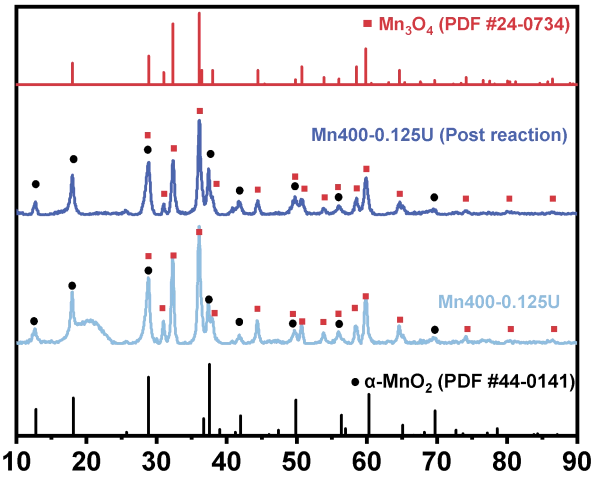

Fig. S7. XRD patterns of Mn400-0.125U before and after reaction.

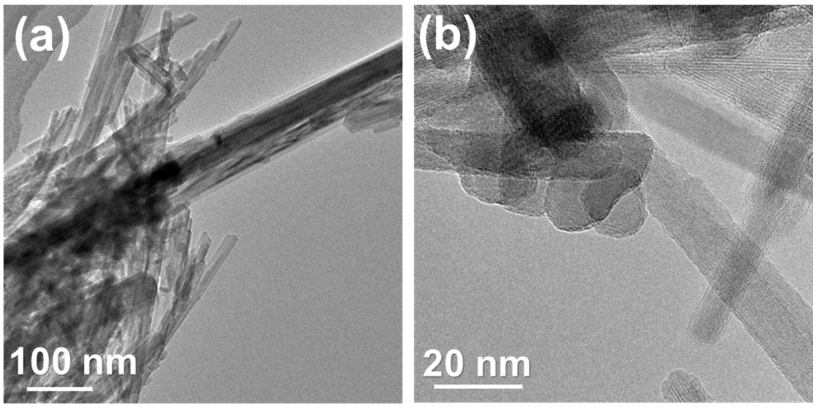

Fig. S8. TEM images of Mn400-0.125U (α-MnO_2/Mn_3O_4) after cycled reaction.

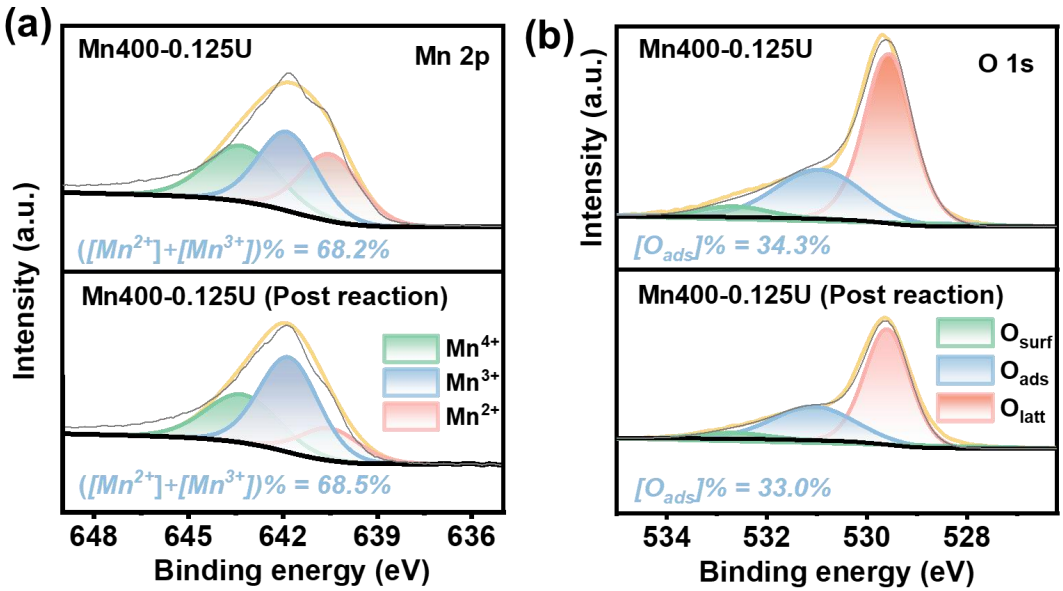

Fig. S9. XPS spectra of Mn 2p (a) and O 1s (b) Mn400-0.125U before and after reaction.

Table S1. BET surface aera of different catalysts.

Samples	BTE surface aera (m^2/g)
α-MnO_2	91.13
Mn400-0U	70.90
Mn400-0.125U	44.06
Mn400-0.250U	47.19

Reference

[1] W.Q. Li, Z.H. Wen, S.H. Tian, L.J. Shan, Y. Xiong, *Catal. Sci. Technol.*, **2018**, 8, 1051-1061.