Supporting Information

Performance and mechanism of sulfamethoxazole degradation on Magnéli-phase Ti_4O_7 reactive electrochemical membrane

Qiang Liu, [a] Yinuo Wang, [a, b] Boxuan Yang, [*b] Jinwei Li, [b] Chengchun Jiang [b] and Huan Wang [b]

[a] School of Municipal and Environmental Engineering, Shenyang Jianzhu University, Shenyang 110168, China

[b] School of Materials and Environmental Engineering, Shenzhen Polytechnic University, Shenzhen 518055, China

[*]Corresponding author: Boxuan Yang

E-mail address: yangboxuan@szpu.edu.cn

Tel.: +86 13316507255

List of Supplementary Data

Text S1 Chemicals.

Text S2 The fabrication method for Ti_4O_7 REM.

Text S3 Analytical methods.

Table S1 The functional relationship between the removal efficiency of SMX and current density.

Table S2 Removal of pollutants by similar electrochemical system.

Table S3 The functional relationship between the removal efficiency of SMX and supporting electrolyte.

Table S4 Degradation products of SMX in Ti_4O_7 REM system.

Fig. S1. The schematic diagram of the reaction apparatus.

Fig. S2. Nyquist spectra of Ti_4O_7 REM.

Fig. S3. Effect of circulation on SMX degradation (a) and TOC removal (b).

References.

Text S1. Chemicals

Sulfamethoxazole (SMX), sodium sulfate (Na_2SO_4), sodium chloride (NaCl), sodium nitrate ($NaNO_3$), hydrochloric acid (HCl), tert-butanol (TBA), methanol (MeOH), humic acid (HA), and 5,5-dimethyl-1-pyrroline N-oxide (DMPO) were sourced from Shanghai Macklin Biochemical Technology Co., Ltd. (Shanghai, China). Sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) were procured from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). During the experiment, 0.1 mol/L H_2SO_4 and 0.1 mol/L NaOH were utilized to regulate the pH of the solutions, with all aqueous solutions in the experiment employing purified water.

Text S2. The fabrication method for Ti_4O_7 REM

In an environment saturated with hydrogen, a porous Magnéli phase Ti_4O_7 electrode was fabricated through the high-temperature reduction of TiO_2. In simpler terms, rutile TiO_2 powder (Degussa) was blended with a solution of isopropanol in water at a 1:1 ratio and subsequently dried before the incorporation of a 5% polyethylene oxide binder. The resultant mixture was then compressed to 20 MPa to form a tubular shape, which underwent sintering in air at 1050 ℃ for 24 hours. Following this, the sample was transferred to a furnace and sintered at 1050 ℃ for an additional 4 hours in an atmosphere filled with hydrogen.

Text S3. Analytical methods

SMX concentration was determined using a Shimadzu LC-20A HPLC system (Japan) equipped with an Agilent SB-C18 column (4.6 × 250 mm, 5 μm). The mobile phase consisted of methanol and ultrapure water (60:40, v/v) delivered at a flow rate of 1.0 mL/min. Detection was performed at 254 nm with an injection volume of 10 μL. The column temperature was maintained at 25°C. The TOC content in the SMX degradation solution was measured using a ZQYC 6-TOC-A TOC analyzer. The removal rates of SMX and TOC can be calculated using Eq. (S1):

$$\eta = \frac{C_t}{C_0} \qquad \text{(S1)}$$

Where C_t represents the concentration of SMX or TOC at electrolysis time t (mg/L), and C_0 denotes the initial concentration before electrolysis (mg/L). The electrochemical oxidation kinetics of SMX were calculated using a pseudo-first-order kinetic model, as described in Eq. (S2):

$$-\frac{dC}{dt} = kC_0 \qquad \text{(S2)}$$

Where C_t represents the concentration of SMX at electrolysis time t (mg/L), C_0 denotes the initial concentration before electrolysis (mg/L), and k (min^{-1}) stands for the pseudo-first-order rate constant. Kinetic parameters were calculated through linear regression fitting of experimental data. The specific energy consumption per unit mass of TOC (Esp in kWh/kg TOC) was calculated using Eq. (S3) to determine the energy consumption of the Ti_4O_7 electrode during the electrocatalytic oxidation process:

$$E_{sp} = \frac{1000\, U \cdot I \cdot T}{\left(TOC_0 - TOC_t\right)V} \qquad \text{(S3)}$$

Where U represents the average electrolysis voltage (V), I denotes the applied current (A), T signifies the electrolysis time (h), and V stands for the wastewater volume (L). TOC_0 (mg/L) represents the TOC value at time 0, and TOC_t (mg/L) represents the TOC value at electrolysis time t.

Using the high-frequency resistance of electrochemical impedance spectroscopy to measure the ohmic resistance of the system. Electrochemical impedance spectroscopy (EIS) is a commonly used interface response information processing technology in electrochemical research. It obtains the frequency response of the impedance by applying a sine wave disturbance with very small amplitude to the system. The Nyquist spectrum is obtained by making complex diagrams of the capacitive reactance and impedance at different angular frequencies, and then further fitting and analyzing the impedance parameters of the electrode, electrolyte and interface (i.e., the ohmic internal resistance of the electrode, Faraday reaction resistance and diffusion impedance). In this project, the electrochemical workstation was used to test the AC impedance of the three electrode systems in the frequency range of 1 Hz to 10 kHz. The working electrode was Ti_4O_7 REM electrode, the counter electrode was SS, and the reference was saturated calomel electrode. The obtained data were analyzed and matched by equivalent circuit analysis to obtain the corresponding impedance information.

Using DMPO as a solvent, the EPR signals of hydroxyl radicals and superoxides were studied on a Bruker A300 spectrometer. The intermediate products generated during sulfamethoxazole (SMX) degradation were identified using high-performance liquid chromatography coupled with quadrupole time-of-flight tandem mass spectrometry (HPLC-Q-TOF-MS/MS). Chromatographic separation was performed on a Waters Symmetry C18 column (3.5 μm, 4.6 mm×150 mm) with a mobile phase consisting of 0.1% formic acid in water (solvent A) and methanol (solvent B) at a flow rate of 0.5 mL/min. The gradient elution program was set as follows: 0-15 min, 20% B; 15-23 min, linear increase to 90% B; 23-24 min, maintained at 90% B; 24-30 min, returned to initial 20% B. Mass spectrometric detection was carried out using a Bruker micrOTOF-Q II high-resolution mass spectrometer. The acute and chronic toxicity of SMX and its electrochemical oxidation degradation products were assessed using the ECOSAR (Ecological Structure-Activity Relationship) program.

Table S1. The functional relationship between the removal efficiency of SMX and current density.

Current density (mA/cm^2)	**SMX removal** (%)	**Reaction constant** (min^{-1})	**Voltage drift** (V)	**Energy consumption** (kWh/kg TOC)
0.008	83.78	0.00642	1.53~1.57	3.25
0.04	95.23	0.02343	1.64~1.68	7.06
0.08	99.48	0.06002	1.89~1.92	9.89
0.2	99.52	0.08642	2.18~2.23	24.00
0.4	99.56	0.08799	2.28~2.30	38.64
0.8	99.68	0.09843	2.43~2.45	57.63

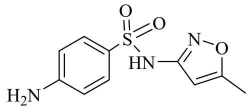
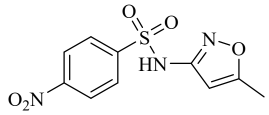
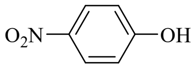
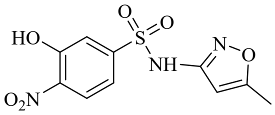
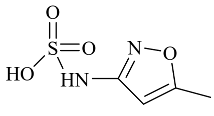
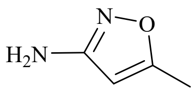
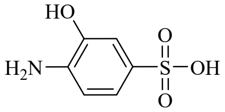
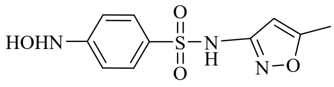
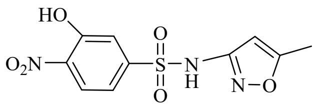
Table S2. Removal of pollutants by similar electrochemical system

System description	**Current density** (mA/cm^2)	**Target pollutant**	**Energy consumption**	**References**
Ti_4O_7 (anode)-SS (cathode)	0.08	Sulfamethoxazole	9.89 kWh/kg TOC	in this study
BDD (anode)-SS (cathode)	11.53	Phenol	17.20 kWh/kg COD	1
Ti/RuO_2-IrO2 (anode)-Pt (cathode)	2	Tetracycline	167 kWh/kg TOC	2
Ti_4O_7 (anode)- Ti (cathode)	15	Coking wastewater	110.5 kWh/kg COD	3
BDD (anode)-Si (cathode)	100	Real wastewaters discharged by textile industry	11.12 kWh/kg COD	4
EO	4.73	Slaughterhouse wastewater	14.12 kWh/kg COD	5
Ti/IrO_2–SnO_2–Sb_2O_5 (anode) and graphite (cathode)	100	Reactive Orange 84	113.70 kWh/kg COD	6
BDD (anode) and SS (cathode)	20	Synthetic urine	29.77 kWh/kg TOC	7

Table S3. The functional relationship between the removal efficiency of SMX and supporting electrolyte.

Supporting electrolyte	**SMX removal** (%)	**Reaction constant** (min^{-1})	**Voltage drift** (V)	**Energy consumption** (kWh/kg TOC)
Na_2SO_4	99.48	0.07466	1.89~1.92	9.89
NaCl	95.16	0.04711	2.12~2.23	26.01
$NaNO_3$	92.13	0.0.773	2.31~2.45	23.67

Table S4. Degradation products of SMX in Ti_4O_7 REM system.

Serial number	Mass to charge ratio (m/z)	Formula	Proposed structure
SMX	254	$C_{10}H_{11}N_3O_3S$	
TP1	284	$C_{10}H_9N_3O_5S$	
TP2	140	$C_6H_5NO_3$	
TP3	299	$C_{10}H_9N_3O_6S$	
TP4	179	$C_4H_6N_2O_4S$	
TP5	99	$C_4H_6N_2O$	
TP6	190	$C_6H_7NO_4S$	
TP7	270	$C_{10}H_{11}N_3O_4S$	
TP8	300	$C_{10}H_9N_3O_6S$	

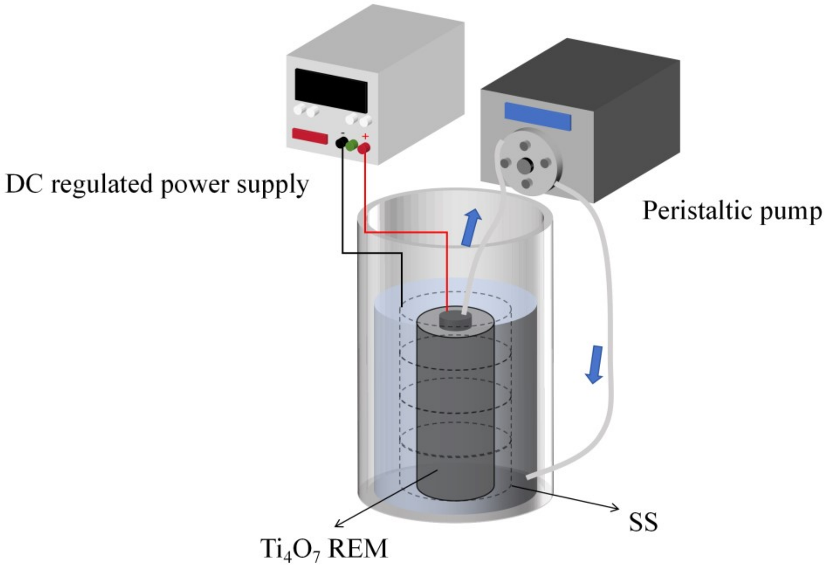


Fig. S1. The schematic diagram of the reaction apparatus.

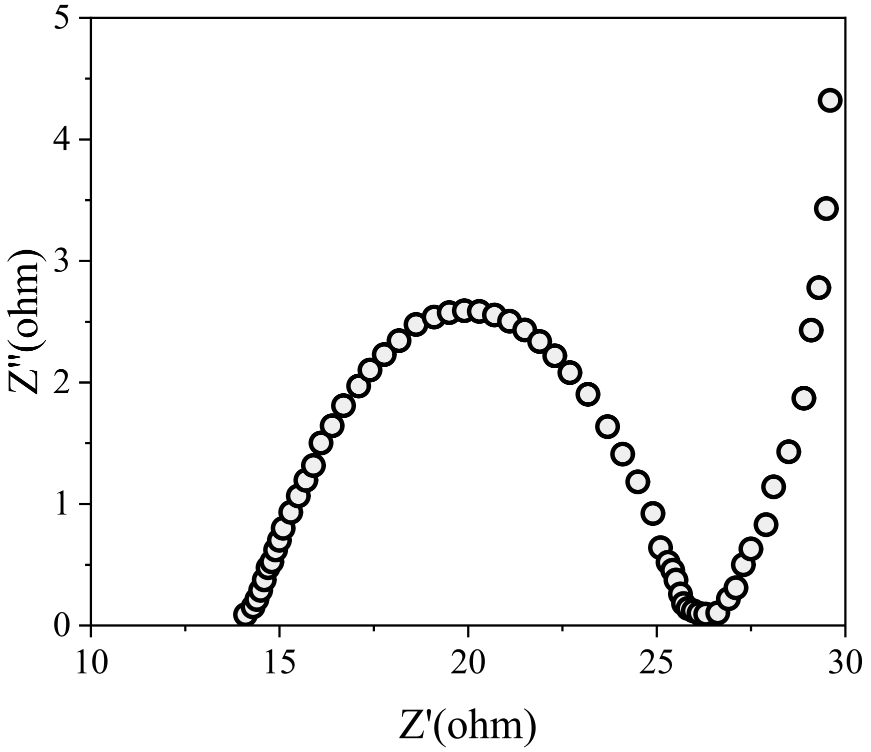


Fig. S2. Nyquist spectra of Ti_4O_7 REM.

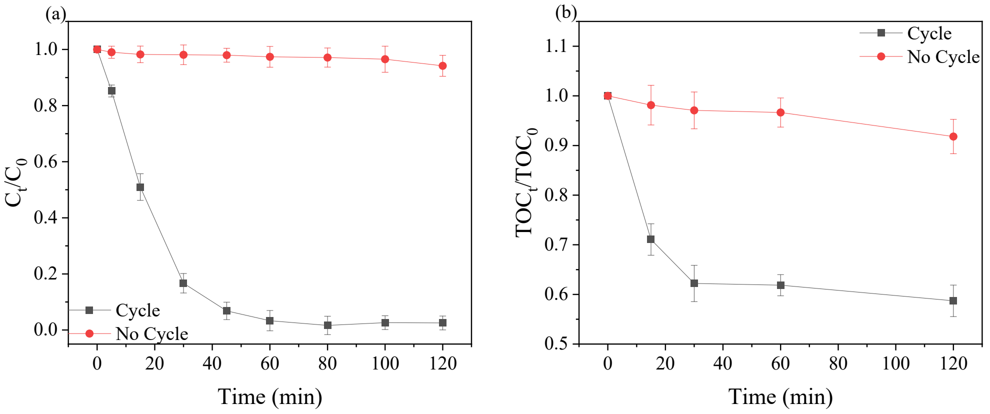


Fig. S3. Effect of circulation on SMX degradation (a) and TOC removal (b). (Conditions: initial concentration of SMX is 10mg/L, electrolyte Na_2SO_4 concentration is 0.1 mol/L, current density is 0.08 mA/cm^2, pH=7, HA is 0 mg/L.)

References

1. X. Xing, J. Ni, X. Zhu, Y. Jiang and J. Xia, *Chemosphere*, 2018, **205**, 361-368.
2. Y. Zhu, B. Li, Y. Wang and T. Wang, *Journal*, 2023, **28**.
3. J. Yu, H. Yu, C. Wang, J. Ma and J. Wang, *Journal*, 2023, **15**.
4. J. Zou, X. Peng, M. Li, Y. Xiong, B. Wang, F. Dong and B. Wang, *Chemosphere*, 2017, **171**, 332-338.
5. D. Ozturk and A. E. Yilmaz, *Journal of Water Process Engineering*, 2019, **31**, 100834.
6. M. Pacheco-Álvarez, R. Fuentes-Ramírez, E. Brillas and J. M. Peralta-Hernández, *Chemosphere*, 2023, **339**, 139666.
7. R. J. A. Felisardo, G. A. Cerrón-Calle, M. R. d. V. Lanza, E. B. Cavalcanti and S. Garcia-Segura, *Journal of Environmental Chemical Engineering*, 2025, **13**, 118211.