

Support information for

**Water decontamination under high salinity via TiO₂
NTs/PbO₂-Cu electro-chemical oxidation system: kinetics
mechanism and DFT studies**

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Text S1 Preparation of TiO₂ NTS/PbO₂ electrode

The TiO₂ NTs substrate was made via anodization method, and the main steps are listed below¹⁻³: 1) Polished Ti sheet through abrasive papers was successively washed by twice-distilled water, ethanol, 0.1M hydrochloric acid, and twice-distilled water respectively in an ultrasonic cleaner (KH5200B, Kunshan Hechuang, China). 2) The anodization experiment was performed in a two electrodes system where earlier obtained Ti sheet served as anode which is parallel to Cu sheet cathode with a distance of 2.5cm. The electrolyte consisted of NaF (0.8 wt%), Na₂SO₄ (0.8 wt%), ethylene glycol (42 wt%), twice-distilled water (56.4 wt%), and the voltage was fixed at 25V using a DC power supply (PS-303D, Long Wei, Shenzhen, China). The anodization experiment was carried out at room temperature for 2 hours in a magnetic stirrer (DF-101S, Shanghai Yukang, China). After anodization, the obtained TiO₂ NTs sheet was ultrasonic cleaned with two-distilled water and then dried in an oven. 3) The as-formed TiO₂ NTs sheet was calcined at 500°C at ambient atmosphere for 2 hours in a muffle furnace (KSL-1200X, Hefei Kejing, China). The heating and cooling rate were set at 2°C/min and 1°C/min, respectively. The finally annealed TiO₂ NTs sheet was denoted as TiO₂ NTs substrate.

The PbO₂ layer was coated on TiO₂ NTs substrate through variable current electro-deposition method as introduced below^{4, 5}: The as-made TiO₂ NTs electrode was used as anode and graphite sheet was used as cathode in an electrolytic cell where the temperature set at 60°C. The deposition was performed in electrolyte containing 0.1M HNO₃, 0.5M Pb(NO₃)₂, 0.5g NaF, under two-stage currents where 25mA/cm² was applied first and 10mA/cm² was applied last. The obtained PbO₂ coated TiO₂ NTs electrode was then successively ultrasonic cleaned in ethanol, twice-distilled water and finally dried at 50°C for use.

Text S2 The calculation for service life of electrode:

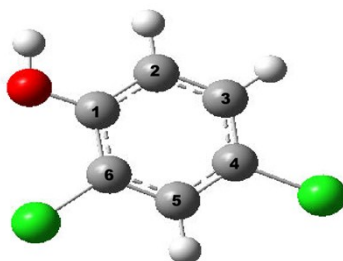
The empirical equation is according to the study of Hoffmann, as follows:⁶

$$T_1 \times i_1^n = T_2 \times i_2^n$$

Where T_1 is the lifetime obtained from current density i_1 , T_2 is the lifetime obtained from current density i_2 , n is the coefficient. In our study, $T_1 = 6.45\text{h}$ at current density $100\text{mA}/\text{cm}^2$ and $T_2 = 34.27\text{h}$ at $50\text{mA}/\text{cm}^2$ were used to calculate the lifetime of electrode at current density $10\text{mA}/\text{cm}^2$.

Table S1 Results of TOC removal, MCE (%), EEO in different salts solution. Condition: current density $10\text{mA}/\text{cm}^2$, pH 5.5.

Solutions with different salts	TOC removal (mg/L, the initial concentration was 3.8mg/L)	MCE (%)	EEO
0.1M Na_2SO_4	2.85	4.24	2.32×10^{-3}
0.1M NaCl	1.69	2.52	8.48×10^{-5}
0.1M Na_2SO_4 + 0.1M NaCl + 0.1M NaNO_3	1.79	2.67	0.82×10^{-4}



Optimized structure of 2,4-DCP, and the number 1 to 6 represent carbon atoms C1 to C6.

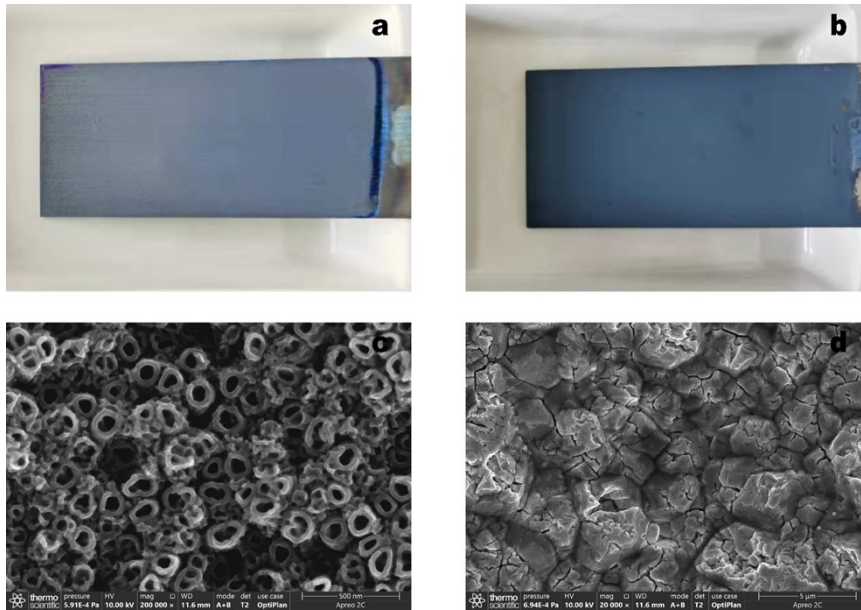


Figure. S1 Digital picture of TiO₂ NTs electrode (a); Digital picture of PbO₂ coated TiO₂ NTs electrode (b); SEM images of TiO₂ NTs electrode (c); SEM images of PbO₂ coated TiO₂ NTs electrode (d).

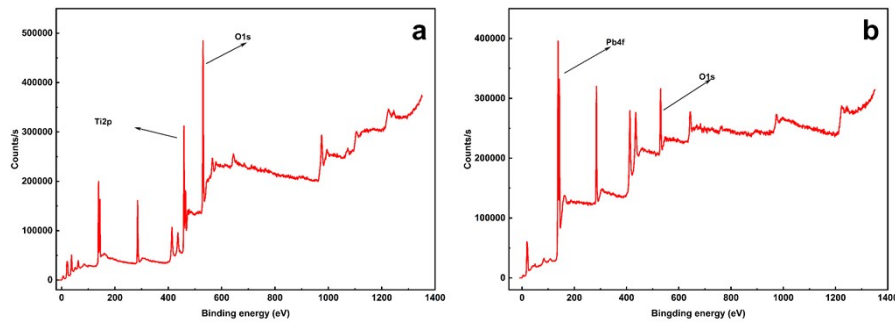


Figure. S2 XPS spectra of TiO₂ nanotube substrate(a); PbO₂ coated layer (b).

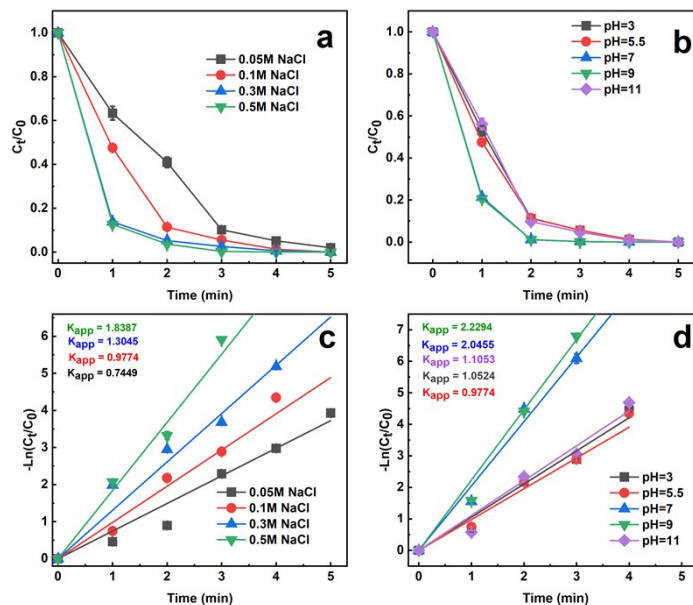


Figure. S3 Degradation of 2,4-DCP and kinetics performance NaCl solution (0.05mM 2,4-DCP):

the effect of NaCl concentration, current density 10mA/cm², pH 5.5 (a, c); the effect of pH,
current density 10mA/cm², NaCl concentration 0.1M(b, d).

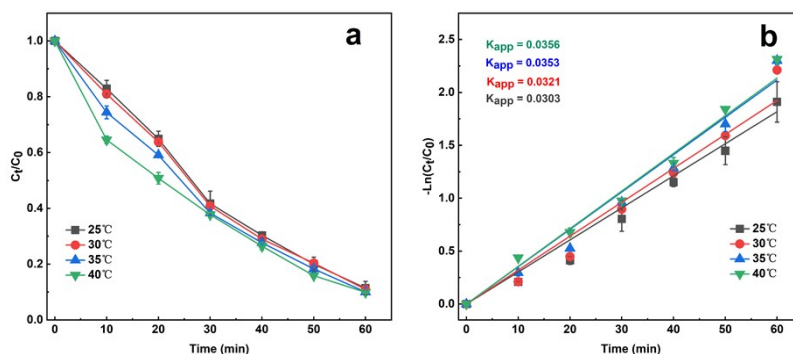


Figure. S4 degradation time course under different temperatures (a); degradation kinetics under different temperatures (b).

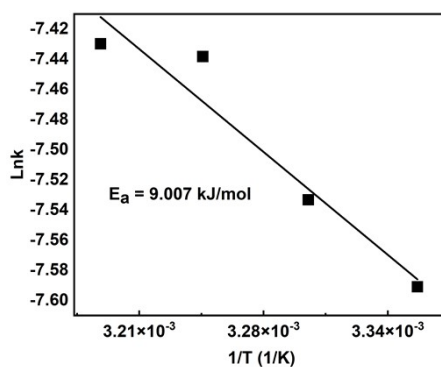


Figure. S5 $\ln k$ - $1/T$ plot for apparent activation energy calculation. Conditions: 2,4-DCP 0.05mM, current density 10mA/cm², pH 5.5, Na₂SO₄ concentration 0.5M.

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