Supplementary materials

Efficient electrochemical oxidation of chloramphenicol by novel reduced TiO₂ nanotube array anodes: kinetics, reaction parameters, degradation pathway and biotoxicity forecast

Pengqi Wang [a], Guangyi Chu [b], Guangfei Gao [a], Fengchun Li [a], Yi Ren [a], Yue Ding [a],

Yawei Gu [a], Wenqiang Jiang [a], Xuan Zhang [a, 1]

[a] School of Environmental Science and Engineering, Qilu University of Technology

(Shandong Academy of Sciences), Jinan 250353, China;

[b] Jinan Water & Wastewater Monitoring Center, Jinan 250353, China.

* Corresponding author.

Prof. Xuan Zhang: zx@qlu.edu.cn

[1] *Corresponding author. Tel: +86-152-691--33848. E-mail: zx@qlu.edu.cn (First)
Note.

List of texts

Text S1 CAP conditions were determined by HPLC.

Text S2 Conditions for detection by HPLC-MS.

Text S3 Electrochemical test.

Text S4 Details of various characterization techniques.

Text S5 Calculation formula for electron transfer rate.

List of Figures

Fig. S1. Formation Mechanism of Anodic TiO_2 Nanotubes.

Fig. S2. EDS of TNTs.

Fig. S3. O 1s XPS spectra of (a) TNTs and (b) R-TNTs.

Fig. S4. The kinetic fit curve of CAP degradation using R-TNTs, (a) current density, (b) initial pH and (c) initial concentration on degradation of CAP.

Fig. S5. Absolute degradation of different initial pollutant concentrations.

Fig. S6. The results of liquid mass spectrometry for degradation intermediates of CAP.

Supplementary method:

Text S1: CAP conditions were determined by HPLC

The concentration of CAP in the samples was determined using high performance liquid chromatography (HPLC, LC-20ATvp, Shimadzu, Japan), with the wavelength set at 278 nm. The mobile phase was composed of aqueous solution: methanol = 70:30 (v:v), where the aqueous solution was prepared from 0.005 mol L^{-1} sodium heptanesulfonate, 0.05 mol L^{-1} KH_2PO_4, and 0.5vt% triethylamine. A pH meter (FE20, Mettler Toledo Instrument Co., Ltd.) was employed to determine pH.

Text S2: Conditions for detection by HPLC-MS

HPLC-MS (qtof 6550, Agilent, America) was applied to identify the intermediates resulting from CAP degradation. The injection volume (2 μL), sheath gas flow (12 L min^{-1}), sheath gas temperature (350 ℃), column (waters BEH C18) and flow rate (0.3 mL min^{-1}) were set, respectively. Formic acid (0.1%) and acetonitrile served as the mobile phases, and the gradient elution settings were 0–2 min, A:B = 5:95, 2–32 min, A:B = 95: 5, and 32–40 min, A:B = 5:95.

Text S3: Electrochemical test

A computer-controlled constant potential meter (CHI 760D) was connected to the electrode module. A single-chamber cell with three electrodes was used, consisted of an SCE reference electrode, a working electrode (TNTs or R-TNTs, 1×1 cm) and a Ti plate (1×1 cm) counter electrode. The anode and cathode were separated by a distance of 1 cm and 0.1 M Na_2SO_4 was chosen as the supporting electrolyte. With a scan rate of 100 mV s^{-1}, cyclic voltammetry (CV) was used over a potential range of -1.0 to +2.7 V (*vs.* SCE). Mott-Schottky experiments were performed at an alternate current (AC) level of 10 mV, a potential range of -0.5 to +0.7 V (*vs.* SCE), and a frequency of 1000 Hz.

Text S4: Details of various characterization techniques.

The sample was directly characterized by SEM without gold spraying, and the acceleration voltage was set to 15kv. The X-ray diffraction (XRD) conditions were set as Cu Kɑ radiation and operated at 40kV/40mA. The scanning interval was 10° ~ 85° and the scanning speed was set as 20° min^{-1}.The prepared materials were tested using UV-Visible diffuse reflection spectrometer (UH4100, Hitachi, Japan). Integrating sphere component was used, $BaSO_4$ was used as reference, and the test band was 200-800nm. Raman measurements were performed at room temperature using a Renish modular Raman system with a He-Ne laser 632.8 nm line as the excitation laser, in the range of 100-700 nm.

Text S5: Calculation formula for electron transfer rate.

$$\frac{1}{C_{sc}^2} = \left[\frac{2}{e\varepsilon_0 \varepsilon N_D}\right]\left[(E_S - E_{fb}) - \frac{KT}{e}\right] \qquad (1)$$

where Csc is the space charge capacitance (F/cm^2); e is elementary charge (1.602 × 10^{-19} C); ε is the relative dielectric constant of electrode material (48 for anatase TNTs; assumed to be identical for R-TNTs), ε_0 is the permittivity of vacuum (8.85 × 10^{-12} N^{-1} C^2 /m^2); E$_S$ is the applied potential (V); E$_{fb}$ is the flat band potential (V); k is the Boltzmann's constant (1.38 × 10^{-23} J/K), and T is the absolute temperature (K).

Supplementary Figures
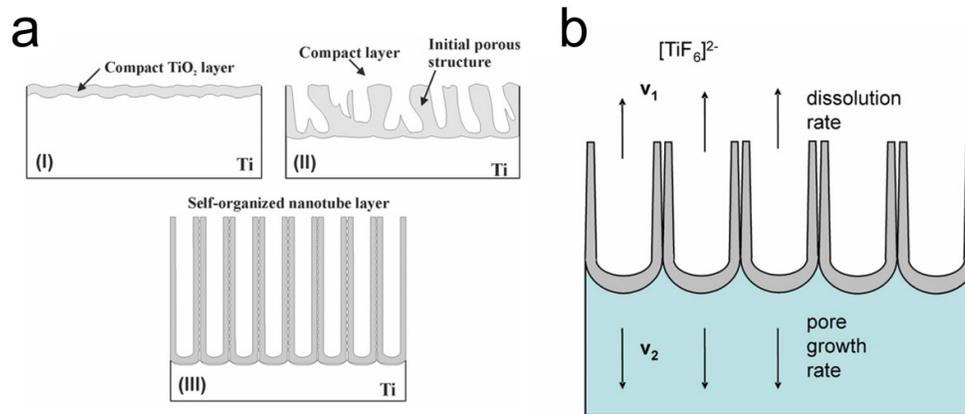
Figure S1. (a) The forming process of TiO$_2$ nanotube arrays. The formation of TiO$_2$ nanotube arrays can be divided into three different morphological stages (I–III). (I) A barrier oxide is formed. (II) The surface is locally activated and pores start to grow randomly. (III) Self-organized nanotube layer is formed reproduced. (b) steady state growth situation characterized by equal rates of TiO$_2$ dissolution (v1) and formation (v2)[1].

That is in the process of electrochemical anodization, TiO$_2$ nanotube arrays are formed by self-organization of titania because of three relatively independent procedures: electrochemical oxidation of Ti into TiO$_2$, the electrical field-induced dissolution of TiO$_2$, and the fluorine ion-induced chemical dissolution of TiO$_2$, reaching a delicate balance[1]. Indeed, if the pore initiation phase is followed in a concrete case by SEM images, exactly the sequence described in Fig S1b can be observed[2].

The fact that the layer thickness and the current density reach a limiting value after a certain polarization time can be explained by a steady state situation depicted in Fig S1b[1].
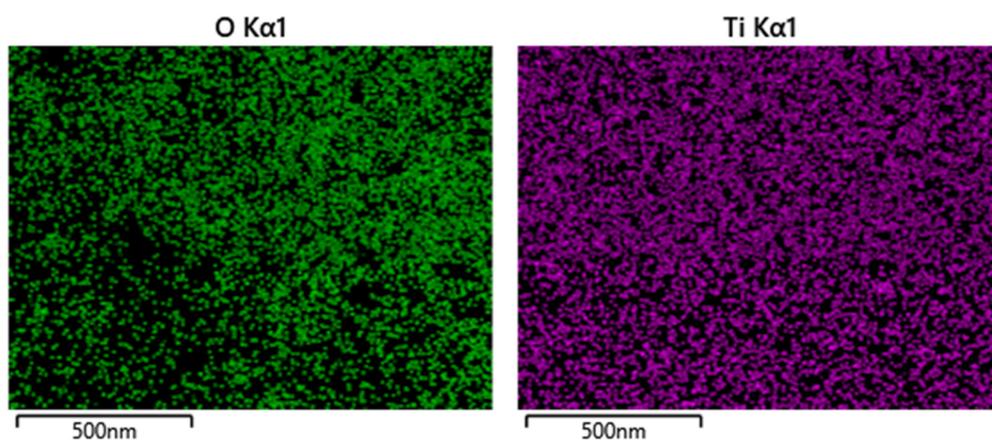
Figure S2. EDS of TNTs.
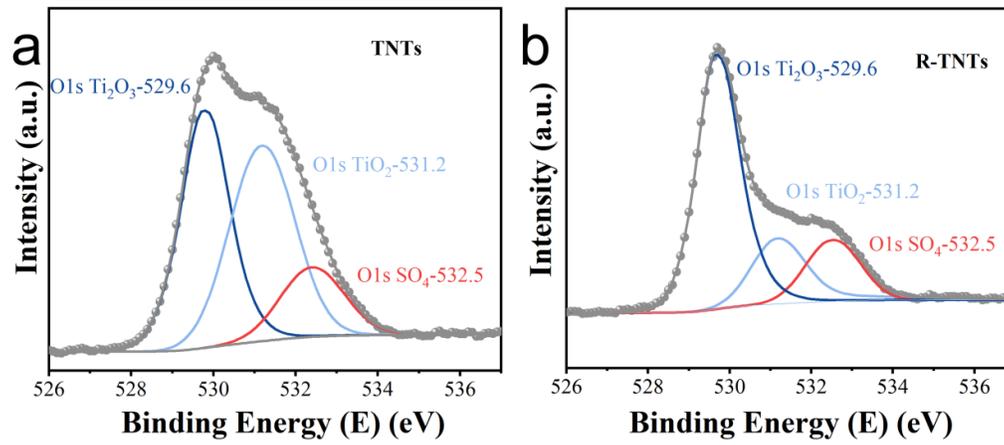
**Figure S3**. O 1s XPS spectra of (a) TNTs and (b) R-TNTs.
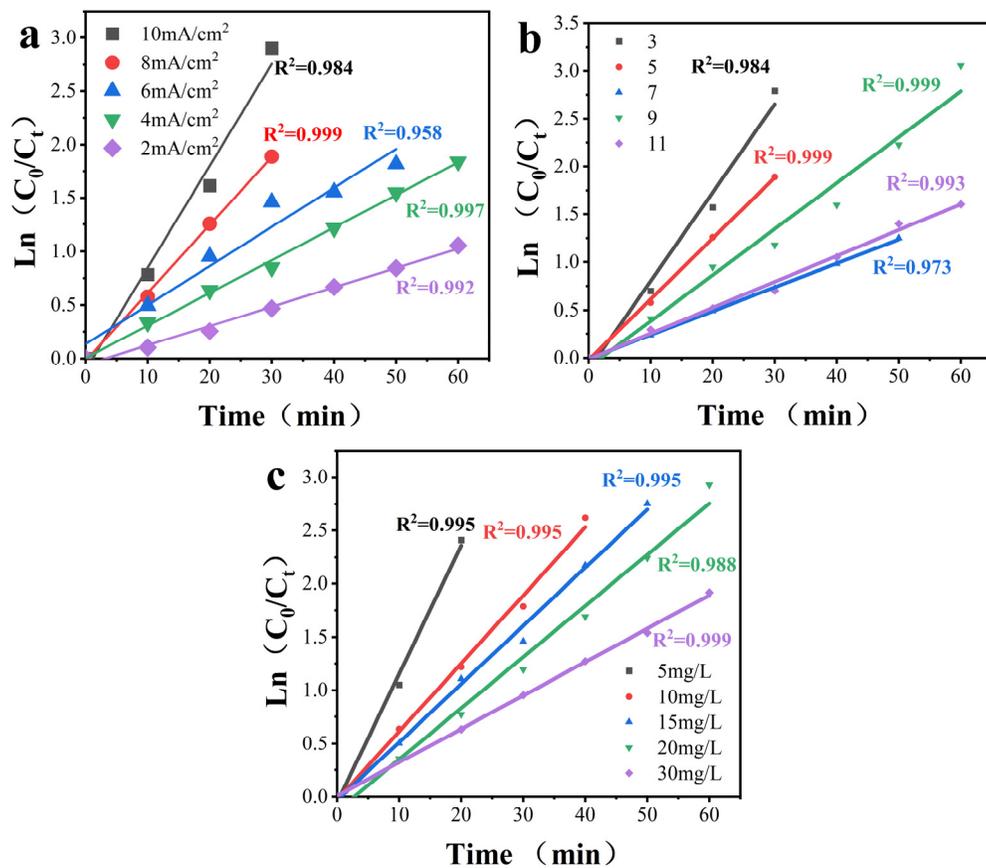
Figure S4. The kinetic fit curve of CAP degradation, (a) current density, (b) initial pH and (c) initial concentration on degradation of CAP.
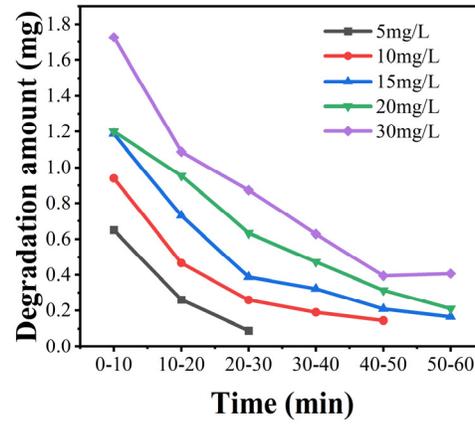
Figure S5. Absolute degradation of different initial pollutant concentrations.
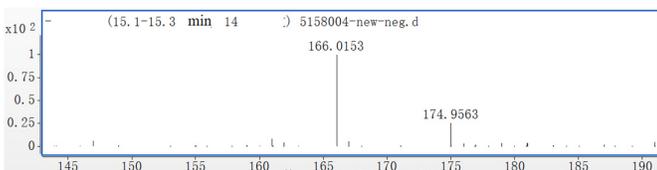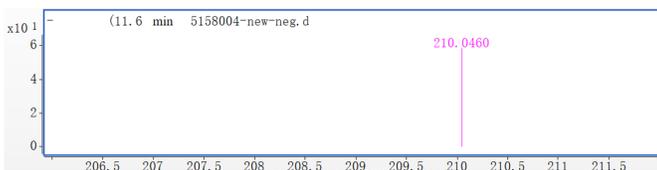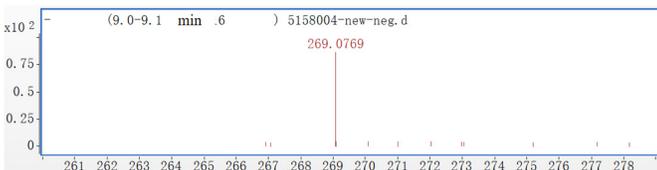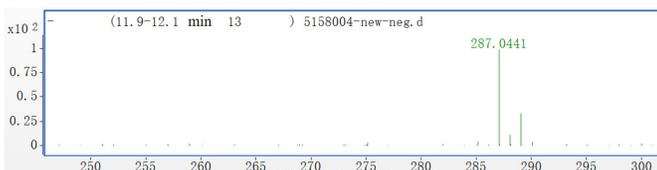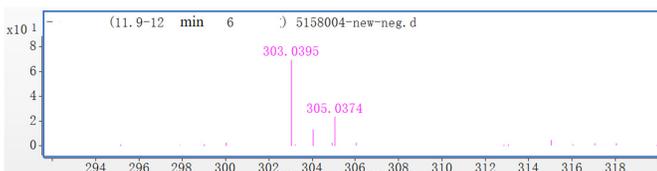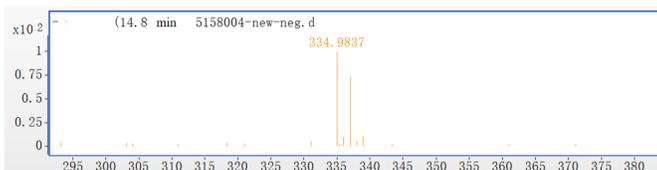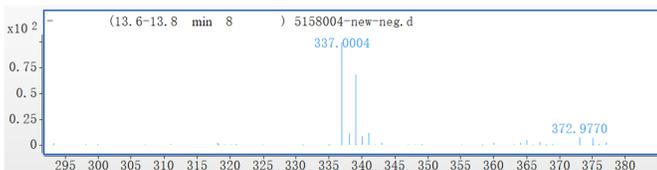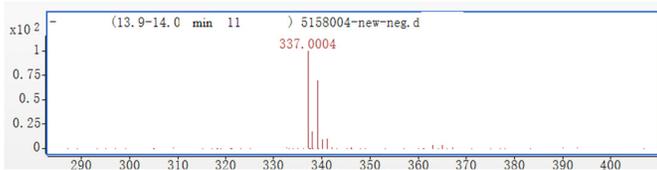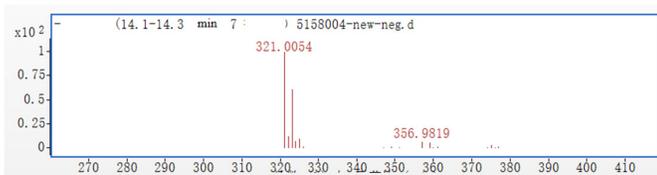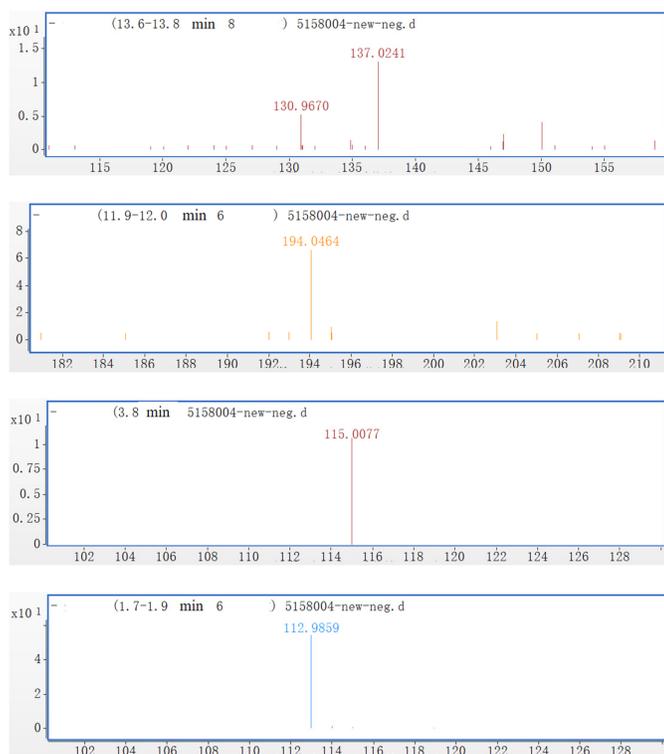
Figure S6. The results of liquid mass spectrometry for degradation intermediates of CAP.

1. Macak, J.M.; Tsuchiya, H.; Ghicov, A.; Yasuda, K.; Hahn, R.; Bauer, S.; Schmuki, P. TiO$_2$ Nanotubes: Self-organized Electrochemical Formation, Properties And Applications. *Curr. Opin. Solid State Mater. Sci.* **2007**, *11*, 3-18, doi:10.1016/j.cossms.2007.08.004.

2. Taveira, L.V.; Macák, J.M.; Tsuchiya, H.; Dick, L.F.P.; Schmuki, P. Initiation and Growth of Self-organized TiO$_2$ Nanotubes Anodically Formed in NH$_4$F / (NH4) $_2$SO$_4$ Electrolytes. *J. Electrochem. Soc.* **2005**, *152*, B405, doi:10.1149/1.2008980.