Supporting information

Formation of oxygenated polycyclic aromatic hydrocarbons by photoelectrocatalysis using TiO₂ nanotubes

Meng Qiao, Bochuan Liu, Xu Zhao*, Yan Gong, Yanbin Wang, Wei Cao

Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

* Corresponding author:

Xu Zhao; Tel.:+86 10 62849667; E-mail address: zhaoxu@rcees.ac.cn.

Text S1: Preparation of the TNTs electrode

TNTs electrode was synthesized using the anodization method following the previous paper ¹. The TNTs electrode was fabricated by anodic oxidation at room temperature. Before anodization, the Ti foil was cleaned with ethanol and acetone in an ultrasonic bath for 10 min respectively, and then dried at room temperature. After polishing with abrasive paper for metallograph, the Ti foil was cleaned with ultrapure water, and then immersed in a mixture solvent (HF/HNO₃/H₂O, 1:4:5) for 1 min. The electrolyte for anodization was the water solution including 0.5% NH₄F, 1.0% (NH₄)₂SO₄ and 90% glycerol. The prepared Ti foil served as the anode, and Pt foil served as the cathode. The two electrodes were subject to anodization at 20 V for 10 h. The obtained anode was rinsed with ultrapure water and dried with nitrogen. Finally, the anode was calcined up to 450°C for 2 h by programming temperature rise with a rate of 5°C/min.

Text S2: Characterization method for TNTs electrode

The surface morphology of TNTs anode was characterized by scanning electron microscopy (SEM, Hitachi SU8020, Hitachi Ltd., Japan). The crystalline structure of TiO₂ nanotubes anode was analyzed by X-ray diffraction (XRD, X'pert PRO MPD PC system, utilizing Cu K α radiation at a scan rate (2 θ) of 0.5° s⁻¹). Liner sweep voltammetry (LSV) was performed using the CHI 660E electrochemical workstation mentioned above.

Text S3: TiO₂ nanotubes characterization and photochemical performance

The SEM imaging showed that the TNTs array was exhibited highly ordered, vertically aligned with the tube diameter of 40-60 nm (Fig. S1a).

Fig. S1b presents the XRD patterns of TiO_2 and Ti, showing that TiO_2 was developed on Ti substrate, containing peaks at 25.3°, 37.9° and 47.9° of (101), (103) and (200). Therefore, the TiO_2 was deemed as the anatase phase, which exhibited the photocatalytic activity.

The TNTs was also tested for the solar performance. The LSV results of Ti/TiO_2 both in dark and under the simulated solar light were shown in Fig. S1c. The current ranged from 0 to 0.22 mA/cm² under solar, with the voltage between -0.2 V and 3.0 V. Compared with the TiO₂ film prepared by a sol-gel method, the TNTs prepared by an anodize method was more sensitive to the current ².



Fig. S1 (a) SEM image of TiO₂ nanotubes; (b) XRD patterns of TiO₂ nanotube; (c) Linear sweep voltammetry of Ti/TiO₂ in dark and under simulated solar light condition, sweep rate = 50 mV/s.



Fig. S2 The reported possible pathway of anthracene during the photolysis ³.

References:

- 1. X. Zhao, J. J. Zhang and J. H. Qu, *Electrochim. Acta*, 2015, **180**, 129-137.
- Z. Frontistis, V. M. Daskalaki, A. Katsaounis, I. Poulios and D. Mantzavinos, *Water Res.*, 2011, 45, 2996-3004.
- 3. S. Sanches, C. Leitao, A. Penetra, V. V. Cardoso, E. Ferreira, M. J. Benoliel, M. T. B. Crespo and V. J. Pereira, *J. Hazard. Mater.*, 2011, **192**, 1458-1465.