Supporting Information for

A TiO₂-nanotube-array-based photocatalytic fuel cell using refractory organic compounds as substrate for electricity generation

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1. Experimental

1.1. Materials

Titanium sheets (0.25 mm thick, 99.9% purity) were supplied by Sumitomo Chemical (Japan). Unless otherwise indicated, reagents were obtained from Sinopharm Chemical Reagent Company and were used as received. Tetracycline, oxytetracycline, and chlortetracycline were purchased from Wuhan Yuancheng Technology Development Co., Ltd. All solutions were prepared using high-purity DI water.

1.2. Preparation and Characterization of TiO₂ nanotube array

Details of the preparation of short, robust and highly-ordered TiO_2 nanotube array (STNA) have been published in previous work.¹ The anodized samples were then rinsed with DI water and dried in air. Subsequently, the as-prepared STNA samples were crystallized by annealing in air atmosphere for 3 h at 450 °C with heating and cooling rates of 1°/min.

The surface morphology of the as-prepared titanium oxide film was characterized with a field emission scanning electron microscope (PHILIPS, Netherlands, Sirion200). An X-ray diffractometer (BRUKER AXS-8 ADVANCE) was used to determine the crystalline structure of the samples.

Cadmium sulfide (CdS) was deposited on STNA film by sonoelectrochemical route in an electrolyte consisted of 0.05 mol L^{-1} CdCl₂ and 0.1 mol L^{-1} sulfur in dimethyl sulfoxide solution, according to the previous work.² Cuprous oxide (Cu₂O) modified STNA was synthesized by sonoelectrochemical deposition method in a solution contained 0.1 mol L^{-1} sodium acetate and 0.02 mol L^{-1} cupric acetate at -0.25 V for 5 min at room temperature.³ The traditional TiO₂ nanoparticulate film was fabricated according to the research work of our co-author.⁴

2.3. Apparatus and Methods

The current-voltage (J-V) characteristics of the PFC system were studied using a CHI electrochemical analyzer (CHI 660C, CH Instruments, Inc., USA) in a rectangular shaped quartz reactor (20 x 20 x 50 mm) using a two electrode system, with a TiO₂ photoanode and a Pt-black/Pt cathode. A 350 W Xe lamp (Shanghai Lansheng Electronic Co., Ltd) was used as the simulated solar light. For the visible light irradiation, the incident light was passed through an optical filter (Nanotong Zhenhua co.,Ltd), which cut off wavelength below 400 nm. Two 4 W UV lamps (GE, Japan G4T5) with central wavelength 254 nm was chosen as a UV light source. The degradation of tetracycline experiment was performed under the following conditions: UV irradiation (3.6 mW cm⁻² light intensity), pH 4.5, 0.1 mol L⁻¹ Na₂SO₄ as electrolyte, illumination area of the photoanode is $2 \times 3 \text{ cm}^2$ and with oxygen aeration. The initial concentration of tetracycline solution was $0.22 \text{ mmol } L^{-1}$ and the reaction solution was 10 ml during the experiment. The reaction solution was analyzed with a spectrophotometer (UV2102 PCS, UNICO, Shanghai) at different time intervals at wavelength of 355 nm. All runs were repeated at least three times, to check their reproducibility.

To identify the degradation products and the intermediate steps involved in the photocatalytic process, tetracycline (0.22 mmol L^{-1}) was selected as a model

compound. The compounds of tetracycline and degradation products were analyzed by Liquid chromatography–mass spectrometry (LC-MS, Q-Tof Premier) with a 10 μ L solution injected to column.⁵ Mobile phase is a mixture of 60% acetonitrile and 40 water (by volume) with a flow rate of 0.2 ml min⁻¹.

2. Characterization

Fig. S1 shows the X-ray diffraction (XRD) pattern of typical STNA electrode before and after annealing at 450 °C for 3 h. Curve a (without calcinations) exhibits an amorphous structure, only the titanium peaks showed up. The titanium peaks from substrate and anatase characteristic peaks are observed when annealed at 450 °C for 3 h. However, the characteristic peak of TiO₂ was weak, which can be ascribed to the short tube length (~280 nm) of the nanotube layer on the Ti foil.¹ The inset exhibits the typical morphologies of the as-prepared TiO₂ nanotubes with an average pore diameter of ~65 nm. As a comparison, we have fabricated traditional TiO₂ nanoparticulate film on the conducting glass using screen printing technique with a paste consisting of ~23 nm nanoparticles (Fig. S2).⁴



Fig. S1. XRD patterns of STNA electrode (a) before and (b) after annealing at 450 °C for 3 h; inset is the SEM image of STNA electrode.



Fig. S2. SEM (a) and TEM (b) of traditional TiO₂ nanoparticulate film prepared by screen printing method.



Fig. S3. SEM images of CdS/STNA (a) and Cu₂O/STNA (b) composite electrode materials.

Fig. S3a shows the scanning electron microscope (SEM) image of STNA after the the sonoelectrochemical deposition process of CdS for 10 min. As can be seen, the

nanotubular surface becomes extensively coated with a relatively uniform layer of CdS nanoparticles with an average diameter of ~50 nm. Fig. S3b presents the SEM image of STNA after the deposition of Cu_2O for 5 min. It is evident that the nanotube surface becomes extensively coated with a relatively uniform layer of octahedral Cu_2O deposits having side length of ~400 nm and some particles are inserted into the tubular structures.

3. PFC Performance

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Category	Reactant	J_{sc} (mA cm ⁻²)	V _{oc} (V)	JV_{max} (mW cm ⁻²)		
Aromatic Compounds	Pyridine $(0.05 \text{ mol } \text{L}^{-1})$	0.48	1.38	0.20		
	Cyanuric acid $(0.05 \text{ mol } \text{L}^{-1})$	0.72	1.28	0.38		
	4-Hydroxybenzoic acid (0.05 mol L ⁻¹)	1.10	1.11	0.33		
	Salicylic acid $(0.05 \text{ mol } \text{L}^{-1})$	1.09	1.12	0.32		
Organic Acids	Citric acid $(0.05 \text{ mol } \text{L}^{-1})$	1.11	1.45	0.42		
	Succinic acid $(0.05 \text{ mol } \text{L}^{-1})$	1.04	1.46	0.48		
Azo Dyes	Congo red (0.27 mmol L^{-1})	0.27	1.34	0.16		
	Crystal violet $(0.27 \text{ mmol L}^{-1})$	0.55	1.38	0.19		
Pharmaceutical and	Oxytetracycline (0.22 mmol L^{-1})	0.83	1.35	0.43		
Personal Care Products (PPCPs)	Chlortetracycline (0.22 mmol L^{-1})	0.72	1.30	0.45		
Endocrine Disrupting	4-Dichlorophenoxyacetic acid	0.02 1.29		0.20		
Chemicals (EDCs)	herbicide $(0.09 \text{ mol } \text{L}^{-1})$	0.95	1.28	0.29		
Surfactant	Sodium lauryl sulfate	0.56 1.64		0.43		
	$(0.05 \text{ mol } \text{L}^{-1})$	0.50	1.04	0.45		

 Table S1. System current-voltage characteristics of the PFC system using various refractory organic compounds as substrate.

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Reactant	Photoanode	J_{sc}	V_{oc}	JV_{max}
	Materials	$(mA cm^{-2})$	(V)	$(\mathrm{mW} \mathrm{cm}^{-2})$
Tetracycline	TiO ₂ nanofilm	0.20	1.42	0.22
	STNA	0.64	1.38	0.29
$(0.22 \text{ mmol } L^{-1})$	Cu ₂ O/STNA	0.71	1.38	0.29
	CdS/STNA	1.06	1.51	0.70
Congo red $(0.27 \text{ mmol } \text{L}^{-1})$	TiO ₂ nanofilm	0.15	1.38	0.12
	STNA	0.81	1.34	0.39
	Cu ₂ O/STNA	1.11	1.26	0.52
	CdS/STNA	1.36	1.37	0.54

Table S2. System current-voltage characteristics of the PFC system under solar light illumination (AM1.5) as affected by different photoanode materials.

Compared with traditional fuel cell system and microbial fuel cell (MFC), the proposed photocatalytic fuel cell (PFC) has its particular advantages in the conversion percentage of organic compounds. Different from traditional fuel cell and MFC, the generation of electrons in the PFC system comes from photoexcitation, which is a much fast and direct process. Moreover, In contrast to traditional TiO₂ nanoparticle photocatalytic systems where slow electron diffusion typically limits device performance, the precisely oriented nature of the crystalline (after annealing) TiO₂ nanotube arrays makes them excellent electron percolation pathways for vectorial charge transfer between interfaces. The nanotube-array architecture also offers the ability to influence the absorption and propagation of light through the architecture by precisely designing and controlling the architectural parameters including nanotube pore size, wall thickness, and length.

Fig. S4 shows the *J-V* characteristics of a STNA-based PFC system by using 0.05 mol L⁻¹ phenol and 0.1 mol L⁻¹ Na₂SO₄ as substrate. The PFC system produces, under the present non-optimized cell conditions, short-circuit current density (J_{sc}) 0.62 mA cm⁻², open-circuit voltage (V_{oc}) 1.29 V, and maximum power density output

 (JV_{max}) 0.26 mW cm⁻². The JV_{max} is the maximum value of the power density output (mW cm⁻²) as obtained from the JV vs. V plot. However, if substituting the STNA photoanode in the PFC system with traditional TiO₂ nanoparticulate film electrode, the system produces very poor cell performance under the same conditions with J_{sc} 0.28 mA cm⁻², V_{oc} 1.19 V, and JV_{max} 0.09 mW cm⁻² (Fig. S5). That means the STNA electrode is much more performing than the traditional TiO₂ nanoparticulate film electrode. The J_{sc} and JV_{max} value given by the former electrode was found ~2.21 and ~2.89 times, respectively, as high as that for the latter electrode under similar working conditions. The excellent transportation properties of photogenerated electrons and desirable mechanical stability of the STNA electrode make it a desirable photoanode material for PFC applications.

Since phenol is a typical refractory organic compound, the major photodecomposition mechanism of phenol was represented by Eq. 1-3.

At the photoanode,

$$TiO_2 + h\nu \to h^+ + e^- \tag{1}$$

$$C_6H_5OH + 11H_2O + 28h^+ \to 6CO_2 + 28H^+$$
 (2)

At the cathode,

$$28H^+ + 7O_2 + 28e^- \to 14H_2O \tag{3}$$



Fig. S4. System current-voltage characteristic and *JV* product of the STNA-based PFC system in the presence of 0.05 mol L^{-1} phenol + 0.1 mol L^{-1} Na₂SO₄ solution under UV illumination. Inset is the molecular structure of phenol.



Fig. S5. System current-voltage characteristic and *JV* product of the PFC system composed of a traditional TiO₂ nanoparticulate film photoanode and a Pt-black/Pt cathode in the presence of 0.05 mol L^{-1} phenol + 0.1 mol L^{-1} Na₂SO₄ solution under UV illumination.



Fig. S6. The comparison of tetracycline $(0.22 \text{ mmol } \text{L}^{-1})$ removal by direct photolysis and TiO₂ photocatalytic process. STNA electrode was used as photocatalyst.

In order to estimate the organic compounds removal performance, tetracycline was selected as a typical example. Fig. S6 compares the tetracycline removal by direct photolysis and photocatalytic process. It is evident that the direct photolysis with UV light alone only removes tetracycline for ~15% within 8 h. While the presence of short TiO_2 nanotubes results in the much effective photocatalytic decomposition and the tetracycline can be almost completely removed over 8 h reactions. This can be attributed to the photogenerated holes on TiO_2 surface to decompose adsorbed tetracycline molecular quickly.

The determination of the degradation products of tetracycline, a typical model compound, was conducted using the LC-MS technology and the obtained spectra are presented in Fig. S7. At retention time of 0.63 min, tetracycline molecular was eluted. After photocatalytic treatment for 2 h, a new flow peak can be seen at retention time of 0.55 min. Further increasing the reaction period to 4 h, 6 h and 8 h led to the increase in the abundance of the flow peak at 0.55 min and decrease in the flow peak at 0.63 min. For the flow peak at 0.55 min, two anions (M-H)⁻ with m/z of 380.8579 and 286.8783 can be found during the photocatalytic process. For the peak at 0.63 min, one anion with m/z of 443.1532 was observed. Based on the LC-MS results, the main degradation product of tetracycline are proposed in Scheme S1. Product 2 (m/z 380.8579) is stemmed from tetracycline degradation via loss of *N*-methyl, amino group and hydroxyl group due to the low bond energy of N-C and C-O. Further degradation of Product 2 (m/z 380.8579) leads to the generation of Product 3 (m/z 286.8783).



Fig. S7. LC-MS spectra of tetracycline degradation products by the photocatalytic process of STNA electrode (reaction time of 0, 2, 4, 6 and 8 h). The insets are the mass spectra eluted at 0.55 and 0.63 min.



Scheme S1. Proposed photocatalytic decomposition of tetracycline and the main degradation products.



Fig. S8. Current-time profile of the STNA photoanode in PFC system by applying 0.22 mmol L^{-1} tetracycline as substrate.



Fig. S9. Chemical structure of some azo dyes studied in this work.



Fig. S10. Four CdS/STNA-based PFC systems in series to light a LED indicative lamp under visible light (AM1.5) irradiation in 0.05 mol L^{-1} phenol + 0.1 mol L^{-1} Na₂SO₄ solution.



Fig. S11. The present CdS/STNA-based PFC systems can work outdoors under natural solar illumination and light a LED indicative lamp in 0.05 mol L^{-1} phenol + 0.1 mol L^{-1} Na₂SO₄ solution.

Notes and references

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