



Simulated solar-light induced photoelectrocatalytic degradation of bisphenol-A using Fe³⁺-doped TiO₂ nanotube arrays as a photoanode with simultaneous aeration



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ABSTRACT

The aeration assisted photoelectrocatalytic (“PEC + Aeration”) degradation of bisphenol A (BPA), a representative endocrine-disrupting chemical, was studied on Fe³⁺-doped TiO₂ nanotube arrays (Fe/TNAs) under simulative solar-light irradiation. Fe/TNAs were prepared by anodization and subsequent dip-coating and characterized by field emission scanning electron microscopy, energy dispersive spectroscopy, X-ray diffraction and UV–Vis reflectance spectroscopy. Results showed that higher efficiencies of BPA degradation and mineralization could be achieved from “PEC + Aeration” process than those from conventional PEC process. Effects of current density, initial pH, initial BPA concentration and airflow rate were investigated. Moreover, active species were identified to reveal the PEC degradation mechanism of BPA. H₂O₂, ·OH and O₂^{·-} are the main reactive species responsible for BPA degradation and aeration performs in BPA elimination. Results reveal that the proposed process is an efficient method for BPA degradation and mineralization.

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1. Introduction

Bisphenol A (2,2-bis(4-hydroxyphenyl)propane, BPA) is considered as a representative endocrine-disrupting chemical. Human exposure to even very low levels of BPA may result in infertility as well as breast, ovarian, and testicular cancer. However, BPA is widely used in the plastic industry to produce polycarbonate plastics and epoxy resin [1] and as a consequence, BPA is universally released into the aquatic environment, including rivers, lakes, and oceans [2]. Thus, seeking an efficient treatment method to degrade BPA is of great importance. Several technologies for BPA removal from contaminated aqueous environments have been reported, including the biological method [3], ozonization [4], electrochemical oxidation (EO) [5] and photocatalysis (PC) [6,7].

The photoelectrocatalytic (PEC) process has recently been considered as an efficient advanced oxidation process for eliminating environmental pollutants [8]. This process introduces a reverse bias potential to the photoanode to drive the photoinduced electrons to the cathode and reduce the combination rate of photo-generated electrons/holes, thereby enhancing photocatalytic performance [9]. TiO₂ is one of the most commonly used photocat-

alysts owing to its great properties of non-toxicity, corrosion-resistance, wide availability and low cost [10,11]. It has been demonstrated that modification of TiO₂ could enhance the photocatalytic performance. For instance, TiO₂ nanotube arrays (TNAs) are generally regarded as an effective modified photocatalyst for improving PEC performance. However, up to date, few reports have been documented on BPA degradation by PEC [9,12,13]. Brugnera and his co-workers [13] reported that PEC on TNAs anodes could eliminate and mineralize BPA efficiently. Nevertheless, the wide bandgap of TNAs limits their use to UV irradiation, which makes up only 4% of the solar spectrum energy available [14]. Visible irradiation, by comparison, is more abundant than UV irradiation, and makes up 48% of the solar spectrum [15]. If visible light could be fully taken advantage of in the PEC process, it should be a cheaper and more environmental friendly technique [16]. To extend the photoresponse of TNAs from the UV to the visible region, doping with transition metal ions, especially Fe³⁺, has been reported [14,17]. Cathode materials with great properties are also essential to ensure desire PEC performance. Several researches [12,18], have shown that the use of various functional materials as cathodes is an effective way to enhance the efficiency of the PEC process. Carbonous materials, such as carbon cloth, can produce H₂O₂ via the two-electron reduction reaction of O₂ (Eq. (2)); H₂O₂ is an excellent oxidant for capturing photogenerated electrons (Eq. (3)) [18,19]

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and improving PEC oxidation. In theory, O₂ could scavenge photo-generated electrons and produce reactive radicals to improve PEC performance. However, the mechanisms have not been discussed in detail, and should be further studied.



The objective of the present work are: (1) to investigate BPA degradation by simulated solar-light PEC on Fe³⁺-doped TiO₂ nanotube arrays (Fe/TNAs) using carbon-cloth as a cathode with simultaneous aeration; and (2) to reveal the mechanisms of enhancing PEC performance by aeration. To the best of our knowledge, this work is the first to investigate BPA degradation by the proposed PEC system.

2. Materials and methods

2.1. Materials and chemicals

Titanium foil (purity, >99.6%; thickness, 0.3 mm) was purchased from Baoji Yihao Metal Materials Company (Baoji, China). Carbon-cloth was obtained from Shanghai Hesun Electric Company (Shanghai, China). BPA (99.9% purity) and methanol (HPLC grade) were purchased from Sigma–Aldrich Company (USA). Isopropanol and benzoquinone (HPLC grade) were purchased from Tianjin Kemiou Chemical Reagent Company (Tianjin, China). All other chemicals used were analytical grade and applied as received without further purification. Ultrapure water was generated from a Purifier water purification system (18.25 MΩ cm, Purifier). A stock solution of 100 mg L⁻¹ BPA was prepared by dissolving 100 mg of solid BPA in 5 mL of methanol, transferring to a 1000 mL volumetric flask, and then diluting with ultrapure water.

2.2. Preparations and characterizations

Amorphous TNAs were prepared by electrochemical anodization. Titanium foil measured 4 × 6 cm was polished with metallographic abrasive paper and then ultrasonically washed in distilled water and ethanol prior to use. The titanium foil was subsequently electrochemically anodized in glycerol solution (0.5 wt% NH₄F + 10 wt% distilled water) at room temperature for 2 h under a constant voltage of 20 V in a two-electrode system with a graphite plate cathode and a DC power supply (RXN-302D, Zhaoxin Electronic equipment Company, Shenzhen, China). After anodization, the samples were washed with a large amount of distilled water and then dried in air.

Fe/TNAs were prepared by dip-coating as follows: Amorphous TNAs were dipped in Fe(NO₃)₃·9H₂O solutions of different concentrations (i.e. 0.1, 0.5 and 0.9 mol L⁻¹) for 5 min and then carefully washed with distilled water and dried in air. This procedure was repeated twice. The samples were annealed at 500 °C in ambient conditions for 2 h with a heating rate of 2 °C min⁻¹ and then naturally cooled down to induce crystallization. The resultant TNAs were labeled Fe/TNA-1, Fe/TNA-5 and Fe/TNA-9. Undoped TNAs, labeled TNA, was prepared using the same procedures without dip-coating. The preparation method described above was modified from the report of Xu and Yu [14].

The crystallographic structures of TNA, Fe/TNA-1, Fe/TNA-5, and Fe/TNA-9 were characterized by X-ray diffraction (XRD, Rigaku D/MAX2500 18 Kw, Japan) using Cu Kα radiation at 80 mA and 40 kV at 2θ ranging from 20° to 70° and scan rate of 10° min⁻¹. The morphological features of the samples were characterized by

field emission scanning electron microscopy (FESEM, Hitachi SU8020, Japan). The compositions of the samples were determined by energy dispersive X-ray spectroscopy (EDS, Oxford X/MAX80, England), which was carried out in the FESEM system. UV–Vis diffuse reflectance spectroscopy (DRS) was also carried out using an UV–Vis spectrophotometer (Shimadzu UV-2501PC, Japan) at a scanning range of 250–700 nm.

2.3. Experimental setup and procedure

The experimental setup is shown in Fig. S1. The reactor was a quartz reactor (width, 5 cm; length, 10 cm; depth, 6 cm). The as-prepared electrodes were used as the photoanode to receive light irradiation. The photoanode and cathode were oriented vertically and their inter-electrode gap was 3 cm. A 150 W xenon lamp (AHD150, Shenzhen Anhongda Opto Technology Company, China) was used as the simulated solar-light source. The distance between the photosource and reactor was 10 cm, and the intensity of illumination at the photoanode was 250 lux. The current applied to the electrodes was regulated by a potentiostat–galvanostat power supply (DH1718E-4, Beijing Dahua Electronic Company, China). The quartz reactor was placed in a dark chamber to prevent the interferences from the daylight. The reaction solution was continuously stirred by a magnetic stirrer at 100 r min⁻¹ during reaction. All experiments were carried out at temperatures below 35 °C. For each test, a total volume of 200 mL was used.

In the experiment, reaction solution with 10 mg L⁻¹ BPA was prepared by diluting the stock solution with ultrapure water; 0.1 mol L⁻¹ Na₂SO₄ was added to the test solution as a supporting electrolyte. Solution pH was adjusted to 3 by 0.05 mol L⁻¹ H₂SO₄ and NaOH solutions. Prior to aeration assisted-photoelectrocatalysis (“PEC + Aeration”), solution was aerated at an airflow rate of 0.5 L min⁻¹ for 10 min to ensure a certain concentration of dissolved oxygen existing in reaction solution. When the experiment was begun, solution was continuously aerated at the same flow rate. At given time intervals, 2 mL samples were obtained from the system for analysis.

2.4. Analytical methods

BPA concentration in solution was monitored by an Agilent high-performance liquid chromatograph (HPLC, Agilent 1100 series, USA) with an Agilent Eclipse XDB-C18 column (5 μm, 4.6 mm × 150 mm) and column temperature of 25 °C. The mobile phase was composed of a mixture of acetonitrile and water (v: v = 35:65). Constant flow rate of 1.0 mL min⁻¹ and detection wavelength of 220 nm were set while running the HPLC.

Hydrogen peroxide (H₂O₂) concentrations were determined by spectrophotometric analysis using the potassium titanium (IV) oxalate method [20]. Total organic carbon (TOC) was determined by a TOC-V_{CPHD} analyser (Shimadzu).

To determine the concentration of Fe³⁺ dissolving into reaction solution from Fe/TNAs during PEC process, the concentration of total iron ions was measured by atom absorption spectrometry (Shimadzu AA-7000, Japan).

3. Results and discussion

3.1. Characterization of the photoanodes

Fig. 1 shows FESEM images of the TNA and Fe/TNAs. TNA had an inner diameter of about 40–60 nm and a wall thickness of about 10–15 nm (Fig. 1a). Fig. 1b–d reveals that the surface morphologies of Fe/TNA-1, Fe/TNA-5 and Fe/TNA-9 are similar to that of TNA, which suggests that Fe³⁺ doping did not damage the structure of

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