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Application of porous boron-doped diamond electrode towards electrochemical mineralization of triphenylmethane dye

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ABSTRACT

The aim of this study is to investigate the electrochemical degradation and decolorization of triphenylmethane dyexylenol orange (XO) on boron-doped diamond (BDD) electrodes. A series of parameters, including electrode materials, current density, initial dye concentration and electrolyte composition, are examined to discuss the effect of these factors in terms of chemical oxygen demand (COD) removal, current efficiency and decolorization rate. Complete decolorization and mineralization of XO could be realized on BDD electrodes while the oxidation is mass transfer controlled, and the degradation progress performs better performance in case of porous BDD electrode comparing with flat BDD electrode. The enhancement of effectiveness is highly correlated to the structure of electrode material, where porous BDD film provides more active sites for hydroxyl radicals. The presence of Cl^- in the solution promotes the COD and color removal due to the formation of active chlorine. Porous Ti/BDD electrode presents the excellent potential in electrochemical decolorization and mineralization of triphenylmethane dye.

1. Introduction

Triphenylmethane dyes (TPMs) are extensively used in the field of textile, leather and paper industries and coloring of various products. The features of genotoxicity, perdurability, mutagenicity and carcinogenicity have caused considerable environmental pollution and increased the potential harm to human after discharge to the aquatic environment or in presence in drinking water. Therefore, TPMs have emerged as novel contaminants and the removal of TPMs from industry wastewater is urgent and important [1]. To address this challenge, many technologies towards wastewater treatment have been developed to remove the TPM dyes, including adsorption [2], biological progress [3], photocatalytic degradation [4], UV/H_2O_2 [5], microwave induced catalytic [6], Fenton or Fenton-like processes [7], and electrochemical processes [8].

The previous studies have indicated that biological process may not be suitable to textile wastewater due to the toxicity of commercial dyes against the microorganism, though the progress is considered to be the most economical option to eliminate organics. The hydroxyl radical scavenger effect limits the application of physicochemical methods into the mineralization of pollutants, which are based on the production and usage of hydroxyl radicals. Electrochemical oxidation methods are considered as promising and effective alternatives, which have the potential to replace or precede already existing processes because of the features of versatility, environmental compatibility and potential cost effectiveness in handling different organic pollutants [9–11].

Electrochemical removal of TPMs has been conducted on different electrodes such as Pt, DSA and boron-doped diamond (BDD) electrode. It is well known that the efficiency of electrochemical oxidation is closely related to the nature characteristic of electrode material [12–15]. Complete decolorization and mineralization [16] could be realized on BDD electrode and the both progresses become slower when employing Pt or DSA electrodes as anodes. Especially, the superior features of high oxygen evolution potential and high stability endow the BDD electrode with potential widely electrochemical application in wastewater treatment.BDD electrode is regarded as the best known material for

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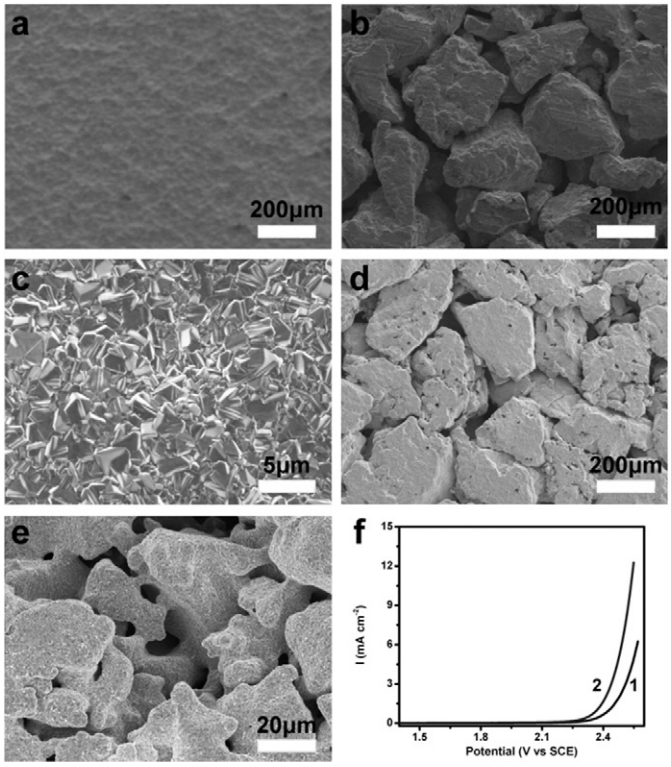

Fig. 1. SEM images of flat (a, c) and porous (b, d, e) Ti substrate before and after the deposition of BDD films; (f) Steady-state polarization curves in 0.5 M H_2SO_4 on (1) flat and (2) porous Ti/BDD electrodes.

electrochemical oxidation [17–19], and the degradation of different pollutants has been conducted on BDD electrode including phenols, surfactants, antibiotics and medical intermediate, pesticides, pigment and dyes, and so on.

Commonly, the oxidation is mediated by the hydroxyl radicals (•OH) [20,21] produced at the electrode surface. Hence, the amount of •OH could reflect the electrochemical activity of electrode material. BDD films are generally deposited on flat substrates, resulting in smaller specific surface area and space utilization. It is believed that electrochemical performance would be improved when porous electrode [22–25] is adopted as electrode material as the increase of specific surface area, and porous electrode with larger specific surface area would provide more active sites to accelerate •OH generation and contaminant incineration then. For example, Chai et al. [26] have prepared three-dimensional highly ordered macro-porous PbO_2 electrode and the electrochemical mineralization of refractory metalaxyl with 3DOM-PbO_2 anode demonstrated that apparent rate constant is about 2.4 times that with flat-PbO_2.

Earlier work [27] has proposed electrochemical oxidation of xylenol orange (XO), one typical TPMs, on RuO_2/Ti electrode, however, the electrochemical oxidation of XO on BDD electrode has not been reported. In the present study, the decontamination of XO by electrochemical oxidation is studied on flat and porous BDD electrode to evaluate the structure of BDD electrode on the effectiveness. To gain a better knowledge about the process, the influences of parameters as current density, initial concentration and electrolyte composition on the mineralization rate and current efficiency are also investigated.

2. Experimental

2.1. Materials and reagents

Xylenol orange and terephthalic acid were obtained from Aladdin Co., China. All the other reagents such as Na_2SO_4 and H_2SO_4 were purchased from Beijing Chemical Works, China with purity level > 98%. All of the chemicals were reagent grade and used without further purification. All solutions were prepared with deionized water with a resistivity of 18.25 MΩ cm.

2.2. Preparation of flat and porous BDD electrodes

The BDD film electrodes were prepared on flat and porous titanium substrates via HFCVD method. Before the deposition, the substrates were boiled for 15 min in the mixed solution of HCl and H_2O (the volume ratio is 1:2) to clean the surfaces firstly. Afterwards, they were pre-treated in a suspension of diamond powder for 30 min. At last, ultrasonically clean was conducted in acetone, ethanol, and deionized water in sequence for 5 min and the substrates were dried in nitrogen for use. During the deposition, the mixture of CH_4 and H_2 was used as the gas source, while $B(OCH_3)_3$ liquid taken out by bubbling H_2 gas was as the boron source. The total gas flux was kept at 300 sccm for all experiments with 1.0 vol% CH_4.

2.3. Electrochemical degradation experiments

Anodic oxidation of xylenol orange on flat and porous BDD electrodes (geometric surface area of 1.0 cm^2) was conducted in a single compartment cell without diaphragm. The cathode was a Ti/RuO_2-TiO_2-SnO_2 net with the electrode gap of 10 mm. The current density was controlled at 10, 30, 50 mA cm^{-2} using 8511C potentiostat/galvanostat. The electrolytes are chosen $NaClO_4$, Na_2SO_4 and NaCl and the concentration of Na^+ is kept constant as required.

2.4. Analytical methods

During the degradation experiments, the samples were drawn at various intervals and the degradation of xylenol orange was monitored by UV–Vis spectrophotometer (Shimadzu UV-2450, Japan). The value of chemical oxygen demand (COD) was measured with chemical oxygen demand analyzer. Terephthalic acid was used as a spin trap for the detection of •OH measured using a fluorescence spectroscopy (FluoroMax-4, Horiba, France).

The values of current efficiency (CE) on different electrodes are calculated by the following equation based on the variation of COD:

$$CE = \frac{COD_0 - COD_{\Delta t}}{I\Delta t} FV \times 100\%$$

where COD_0 is the initial COD value and $COD_{\Delta t}$ is the COD value (mg L^{-1}) at electrolysis time of Δt; I the charge current (A); Δt the electrolysis time (s); F the Faraday's constant, 96,500 (C mol^{-1}) and V is the volume of solution (L).

3. Results and discussion

3.1. Characterization of Ti/BDD electrodes

BDD films are fabricated on flat and porous Ti substrates via HFCVD technique. Fig. 1a and b present the SEM images of the flat and porous Ti substrates before the deposition of BDD film, respectively. The SEM images suggest that porous Ti substrate consists of holes and internal channel, which presents three-dimensional porous structure. After the deposition, the BDD films cover Ti substrate surface continuously without cracks, as shown in Fig. 1c, d. The images (Fig. 1c, e) reveal that the samples prepared show well-faceted crystal with the crystal size being in range of 1–2 μm. As a case of BDD film on porous Ti substrate, not only the outer surface of three-dimensional porous Ti substrate is deposited by BDD films, but also the deep surface while keeping well quality at the same time. It could be believed that BDD films deposited on porous Ti substrate exhibits porous structure under the condition. The