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Anodic oxidation of anthraquinone dye Alizarin Red S at Ti/BDD electrodes

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ABSTRACT

The boron-doped diamond (BDD) thin-film electrode with high quality using industrially titanium plate (Ti/BDD) as substrate has been prepared and firstly used in the oxidation of anthraquinone dye Alizarin Red S (ARS) in wastewaters. The Ti/BDD electrodes are shown to have high concentration of sp^3-bonded carbon and wide electrochemical window. The results of the cyclic voltammetries show that BDD has unique properties such as high anodic stability and the production of active intermediates at the high potential. The oxidation regions of ARS and water are significantly separated at the Ti/BDD electrode, and the peak current increases linearly with increasing ARS concentration. The bulk electrolysis shows that removal of chemical oxygen demand (COD) and color can be completely reached and the electrooxidation of ARS behaves as a mass-transfer-controlled process at the Ti/BDD electrode. It is demonstrated that the performances of the Ti/BDD electrode for anodic oxidation ARS have been significantly improved with respect to the traditional electrodes.

1. Introduction

The development of the synthetic dye industry has resulted in an increase of colored wastewaters containing toxic and biorefractory organic compounds, which were discharged in the environment [1]. These highly colored components when discharged with wastewater into the water bodies stop the reoxygenation capacity of the receiving water and cut-off sunlight, thereby upsetting biological activity in aquatic life [2]. Alizarin Red S (ARS, $C_{14}H_7NaO_7S{\cdot}H_2O$, see Scheme 1) is a water-soluble and widely used anthraquinone dyes and belong to the group of most recalcitrant and durable pollutants [3]. Unfortunately, removing dyes from wastewaters is a difficult and expensive process. The classical dye degradation processes are based on chemical, physical and biological oxidation [3,4], but they are not enough efficient. In recent years, various advanced oxidation technologies have been proposed for the color removal including chemical oxidation with ozone [5] or Fenton's reagent [1,6], photocatalytic oxidation [7,8], electrochemical treatments [9–11] and other techniques [12]. Among electrochemical treatments, electrochemical coagulation and electrochemical oxidation are more effective than others in decolorizing textiles effluents. Electrocoagulation of wastewater containing textile dyes has been revealed good removal efficiencies of COD, color, turbidity and dissolved solids at varying operating conditions [11]. It provides a simple, reliable and effective method for the treatment of wastewater and reduces the amount of sludge. The electrochemical oxidation has been accepted as one of the most promising technologies that is easy applicability to automation, friendly to environment, and can oxidize the toxic organic compounds effectively [13].

Note that electrode material is a crucial factor for optimizing electrochemical oxidation conditions, more attention has been focused on the exploration of novel anode materials to improve the current efficiency. The materials as the anode in the electrochemical oxidation include IrO_2 [14], Pt [15], SnO_2 [16], PbO_2 [17] and boron-doped diamond (BDD) [18,19], etc. Among these electrodes, the BDD has numerous unique properties, such as extremely wide potential window, corrosion stability in very aggressive media, inert surface with low adsorption properties, strong tendency to resist deactivation and robust oxidation capacity [18], and it has been widely investigated and applied in waste water treatment. However, the reports on the BDD electrode as an anode to remove ARS from textile wastewaters are rare [20,21]. In these studies, the BDD electrodes were generally grown on Si. Since Si is fragile and its conductivity is strongly dependent on the experimental environments, it is impossible used in industrial production with large scale due to the high consumption. It is therefore desirable to find appropriate substrates for depositing BDD electrodes. The titanium plate as a substrate possesses many advantages for the BDD thin film electrode: good electrical conductivity, high mechanical strength and very cheap, therefore it is considered to be a good substrate

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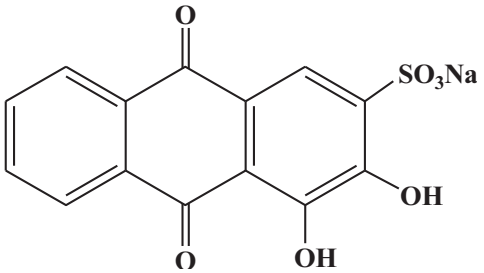

Scheme 1. Chemical structure of Alizarin Red S.

material. In recent years, Ti/BDD electrodes have became a focus of many researches in wastewater treatment because of its wide electrochemical window and their high efficiency in oxidizing various compounds such as acetic acid, maleic acid, phenol [22], bisphenol A [23], p-substituted phenols [24] and so on. Chen et al. [25] also found Ti/BDD electrodes were very active in dyes wastewater treatment and low current density, high temperature are favorable for dye degradation.

In this work, the boron-doped diamond (BDD) thin-film electrode deposited on industrial titanium plate has been fabricated and firstly used in the oxidation of anthraquinone dye Alizarin Red S in textile wastewaters. The removal of the dye from the solution was followed by chemical oxygen demand (COD) and UV visible spectrophotometry. Compared with the conventional F-doped PbO_2 anode, the BDD anode for the electrochemical oxidation of ARS showed more superior electrocatalytic properties. The reaction mechanism and kinetics of the ARS oxidation at the BDD anode are investigated.

2. Experimental

The BDD electrodes were synthesized by the microwave plasma-assisted chemical vapor deposition (MP-CVD) technique at industrially titanium plate with diameter of 14 mm. The substrates were abraded by diamond paste for 30 min and then cleaned ultrasonically in acetone solution for 15 min. The mixture of methane and hydrogen (1% CH_4 in H_2) was used as the gas source. Boron doping was carried out by adding diborane into the gases with a [B]/[C] ratio of 8000 ppm. The pressure of the experiment is 7 kPa, and the power is 380 W.

The quality of the BDD film was characterized by Raman spectroscopy (Renishaw inVia Raman microscope, using the 514 nm Ar^+ laser as the excitation source). Cyclic voltammetric and linear sweep voltammetric curves were measured in a conventional three-electrode cell by using a PARSTAT 2273 potensostat/galvanostat (USA). Working electrodes were Ti/BDD plates of 1.5 cm^2 geometric area. Counter electrode was a $Ti/RuO_2–TiO_2–SnO_2$ net, which is very stable in the electrolyte. The reference electrode was an $Hg/Hg_2Cl_2/KCl$ (sat) (SCE). In order to improve the reproducibility of measurements, all working electrodes were polarized at 20 mA cm^{-2} in 0.5 M H_2SO_4 solution for 5 min before every new experiment.

Bulk anodic oxidation of ARS was carried out using an electrolytic cell with a single compartment without diaphragm. The anodes were Ti/BDD with 1.5 cm^2 area and the cathode was a $Ti/RuO_2–TiO_2–SnO_2$ net with 9 cm^2 area with an interelectrode gap of 10 mm. The electrolysis at constant current was performed using an 8511 C potentiostat/galvanostat (Eternal Electrochemical Instrument Company, China). The electrolyte was 100 ml of 0.278 mM ARS solution (its initial value in COD is 124 mg L^{-1}) and it was stirred by a magnetic stirrer, Na_2SO_4 (0.5 mol L^{-1}) was used as the supporting electrolyte, and the pH value of the solution was adjusted to 2, the current density was controlled at 40 mA cm^{-2}.

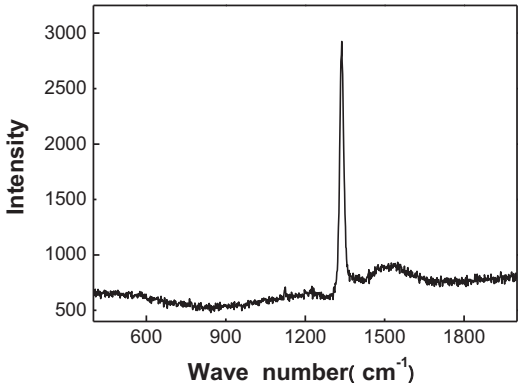

Fig. 1. Raman spectrum of the BDD film deposited on titanium substrate.

The temperature was performed at 15 °C. For comparison purpose, anodic oxidation of ARS at $Ti/F–PbO_2$, one of the most active oxide-coated electrodes, was also investigated. The $Ti/F–PbO_2$ electrode had a dimension of 1.5 cm^2, and was prepared using a standard electrodeposited method [26].

The value of COD was based on the standard method of potassium dichromate (GB-11914-89), measured with COD analyzer. The electrochemical treatment of ARS was detected by means of an Ocean Optics Miniature Fiber Optic Spectrometer over the 210–600 nm range.

3. Results and discussion

3.1. Raman analysis

Fig. 1 shows the Raman spectrum of the Ti/BDD. There is a sharp peak around 1337.9 cm^{-1}, the position is shifted toward higher values relative to that of 1332.5 cm^{-1} known for the characteristic signature of the diamond structure, revealing the presence of diamond. This shift, as well as the specific asymmetric peak shape is due to the Fano interaction [27]. A broad, less intense band centered near 1520 cm^{-1} is also observed, indicating the presence of graphitic or amorphous carbon impurities (sp^2 carbon) in the BDD film. The ratio of the graphite to the diamond is low, so the high concentration of sp^3-bonded carbon indicates that the prepared diamond thin film is of high quality.

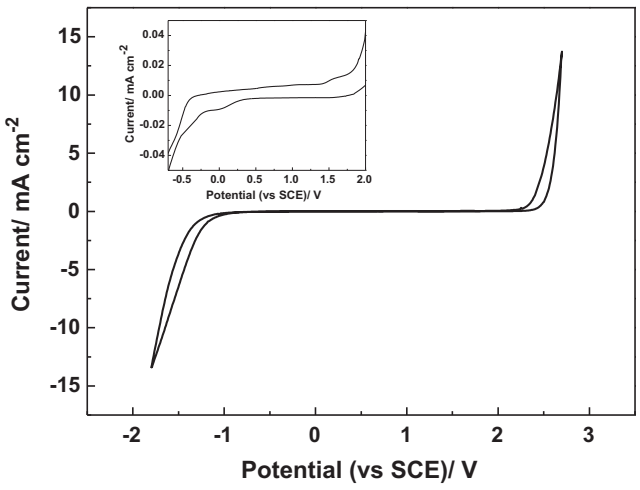

Fig. 2. Cyclic voltammogram of the boron-doped diamond film deposited on titanium substrate at a scan rate of 100 mV s^{-1} in 0.5 M H_2SO_4 solution. Inset is the potential region between −0.5 and 2.0 V.