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1. Introduction

Titanium dioxide (TiO₂) has been focused on its photocatalyst properties associated with its strong oxidizing power [1]. Boron doped diamond (BDD) also presents singular electrochemical properties such as low and stable background current and wide potential window, which allow it to reach a high anode potential to generate the hydroxyl radical (OH•) [2]. Thus, the deposition of TiO₂ associated with the BDD deposition has been used in investigation of improvements in electrodes applied for organic compounds degradation, due to their electrochemical properties [3]. In this context, carbon fiber (CF) also appears as an interesting substrate to grow BDD films to obtain a three-dimensional material by exhibiting high surface area as well as high active site density in a homogeneous porosity distribution. Thus, this work shows the production and characterization of ternary TiO₂/BDD/CF composites using CF substrates obtained at two different temperatures of 1000 and 2000 °C pointing out the CF structural organization effects on the composite photoelectrochemical responses.

2. Experimental

CF substrates were obtained from polyacrylonitrile (PAN) precursor heat treated at two different temperatures of 1000 and 2000 °C at nitrogen atmosphere and were cut 10 x 10 mm². BDD films were grown on CF1000 and CF2000 substrates by hot filament chemical vapor deposition the following growth parameters: 750 °C, 30 Torr, 8h and gas mixture of 2/198 % CH₄/H₂. Boron source was obtained by an additional hydrogen line passing through a bubbler containing B₂O₃ dissolved in methanol with B/C ratio of 15000 ppm in solution. TiO₂ depositions on BDD/CF1000 and BDD/CF2000 substrates was obtained by anodic hydrolysis of TiCl₃ under potentiostatic mode, at a fixed potential of 0.75 V for 60 min in a 5 mmol.L⁻¹ TiCl₃ + 0.1 mol.L⁻¹ KCl (pH = 2) aqueous solution. All the electrochemical experiments were performed in a conventional three-electrode glass cell, using a platinum wire as a counter electrode and Ag/AgCl/KCl_(sat) as the reference electrode. Both composite materials were characterized by field emission gun-scanning electron microscopy (FEG-SEM) images, Raman spectroscopy analyses, and photoelectrochemical responses, using a mercury/xenon lamp model 69920-450 W Tectraphysics in 0.1 mol L⁻¹ KCl at scan rate of 20 mV s⁻¹.

3. Results and Discussions

Fig. 1 shows FEG-SEM images for TiO₂/BDD/CF1000. Images demonstrate that CF1000 were completely covered by a diamond polycrystalline film and the rougher TiO₂ film texture is dominant and homogenous covering all diamond grains. The morphology of TiO₂ deposits in BDD/CF2000 were similar the TiO₂/BDD/CF1000 composite. The photoelectrochemical activities of all electrodes were measured by linear sweep voltammetry, under intermittent UV irradiation. As an example, the TiO₂/BDD/CF1000 electrochemical response considering the dark current (I_d) and the photocurrent (I_{ph}) densities are shown in the Fig 2 for TiO₂ deposition time of 60 min. No significant photoanodic current was verified for BDD/CF1000 sample in the same experimental conditions. Therefore, this photoanodic current density is certainly associated to the TiO₂ presence on the electrode surface. The results showed that anodic hydrolysis of TiCl₃ under potentiostatic mode was a suitable procedure to produce ternary composites on both BDD/CF samples. As expected, both ternary composites depicted similar photoelectrochemical responses. Slight differences in photocurrent values may be related to CF conductivity as well as to electrode surface area which are directly related to CF structural organization.

In summary, we have obtained preliminary results with success. The relationship among CF properties, BDD quality and morphology not to mention TiO_2 deposition on BDD surface are complex parameters and this work is exploring a systematic study also correlating the TiO_2 photocatalytic responses with all of them.



20 - TiO₂/BDD/CF1000 - Dark TiO,/BDD/CF1000 - Light 15 I / mAcm⁻² 10 -5 ∟ 0.4 0.6 1.0 1.8 2.0 0.8 1.2 1.4 1.6 Potential/ V vs. Ag/AgCI/KCI (sat)

Fig. 1. FEG-SEM images of TiO₂/BDD/CF1000 composite.



4. References

[1] Y. Zhang, X. Xiong, Y. Han, X. Zhang, F. Shen, S. Deng, H. Xiao, X. Yang, G. Yang, H. Peng, Chemosphere, 88, 145-154, (2012).

[2] C. Zhang, L. Gu, Y. Lin, Y. Wang, D. Fu, Z. Gu, J. Photochem. Photobiol., A, 207, 66-72, (2009).

[3] J. Qu, X. Zhao, Environ. Sci. Technol., 42, 4934-4939, (2008).

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