Role of defect sites and oxygen functionalities on preanodized screen printed carbon electrode for adsorption and oxidation of polyaromatic hydrocarbons

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ABSTRACT

We report here the application of "preanodized" screen printed carbon electrode without the need of adding catalysts for the adsorption and subsequent oxidation of polyaromatic hydrocarbons (PAHs). By suitably defining the preanodization condition, controlled amount of surface defects and oxygen functionalities are created to fulfill this purpose. Characterization of the modified electrodes and oxidized products specifies that both oxygen functionalities and edge/defect sites play a critical role in the adsorption of PAHs and their oxidation at lower overpotential. The results can assist in designing systems for efficient detection and toxicity degradation of a wide range of PAHs.

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1. Introduction

Polyaromatic hydrocarbons (PAHs) pose severe environmental and health hazard; therefore, reducing their toxicity is very important and oxidation route offers one of the best ways to achieve this purpose [1–10]. To the best of our knowledge, there is no report available for direct oxidation of PAHs without adding any external catalysts. Previously, Compton's group demonstrated the role of edge planes on the adsorption of substituted anthraquinone [11]. The carbonyl group and defect/edge plane electron density on activated carbon electrode were also reported to assist the efficient adsorption of aromatic compounds through π–π static and electrostatic interactions [12–17]. The electrochemical pretreatment process on screen printed carbon electrode (SPCE) not only creates both electron-rich active defect/edge sites and oxygen functional groups but also results in increased capacitive current depending on the conditions employed [18–21]. The formation of different functional groups depends on the condition employed during the preanodization process. We expect that the application of an appropriate preanodized SPCE (SPCE*) can assist in adsorption and subsequent oxidation towards PAHs. In this study, we quantitatively created different amount of defect/edge sites and surface oxygen functionalities by varying the preanodization process on SPCE. The surface functionality and defect sites, as investigated by Raman and XPS measurements, are applied to tune the best activity towards adsorption and oxidation of PAHs. The reaction mechanism was further elucidated through the identification of oxidation product by LC–MS.

2. Materials and methods

Anthracene (AN), naphthalene (NPh) and tetracene (TC) and all other chemicals were of analytical grade and used as received. The electrochemical experiments were carried out with a CHI 832 electrochemical workstation in a conventional three-electrode cell with SPCE or SPCE* as working electrode (0.196 cm^2), platinum wire as auxiliary electrode and Ag/AgCl as reference electrode. The LC–MS measurements were done with a Finnigan LCQ ion trap mass spectrometer. Raman spectra were recorded with Ocean optics QE65000 (532 nm) with an exposure time of 5 s, accumulation time of 1 s, laser power of 10 mW, spot size and focal distance of 2 μm and 17.38 mm, respectively. The XPS experiments were carried out by Omircron-DAR400, using an Al Kα source (1486.6 eV) with 0.1 eV resolution. The SPCE was pre-cleaned by cycling between −1.0 and 1.2 V, in 0.1 M, pH 7 PBS (SPCE). Preanodization of SPCE was achieved by applying 2.0 V for 300 s vs. Ag/AgCl in various electrolytes (SPCE*). The AN-modified electrode was prepared by drop casting 5 μL of AN from a solution containing 2 mg of AN dissolved in 500 μL acetonitrile.

3. Results and discussion

Both SPCE and SPCE* were subjected to electrochemical studies after drop-coated with AN. As shown in Fig. 1a, only at SPCE*, a redox peak at

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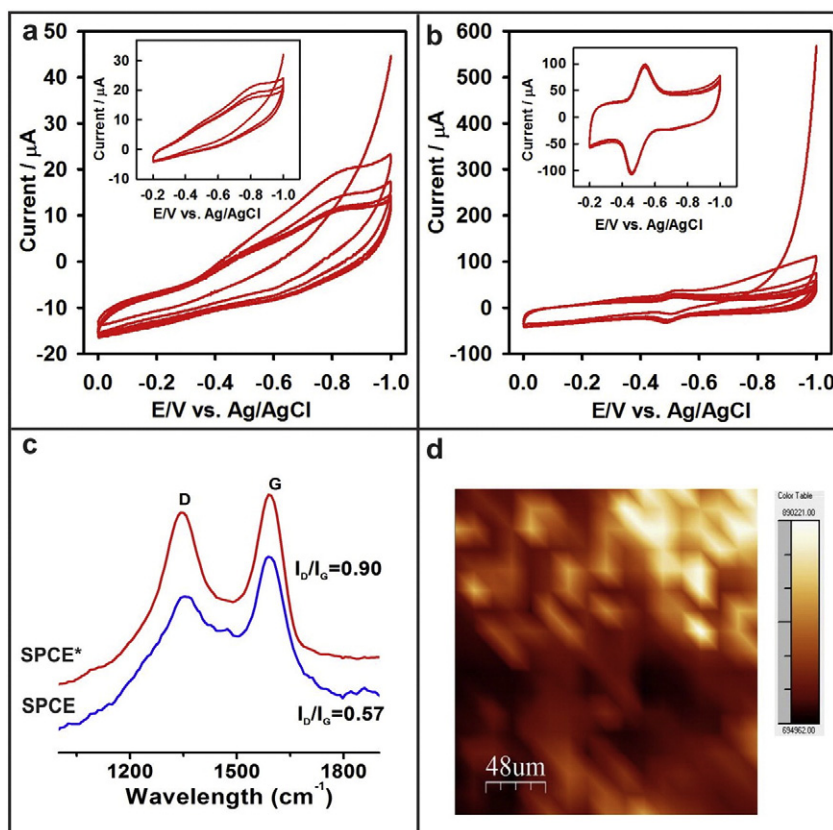
Fig. 1. Cyclic voltammograms of AN oxidation at SPCE (a) and PBS-SPCE* (b). Inset: Corresponding cyclic voltammograms after medium exchange in 0.1 M PBS (pH 7). (c) Raman spectra of SPCE and SPCE*. (d) Raman image of defect band intensity.

$\sim E° = -0.49$ V was observed. After medium exchange to a fresh pH 7 PBS, the presence of redox peak at the SPCE* verifies the adsorption of AN (Fig. 1b). More importantly, as reported by Compton's group, the absence of anodic shoulder peak between pH 3 and 11 confirms the dominant role of edge plane like sites [22]. The redox peak is coming from the quinone/hydroquinone conversion as shown below:
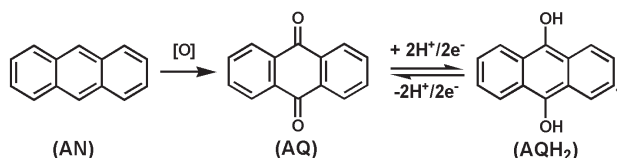
The defect sites with oxygen functionalities was then characterized by Raman spectroscopy. As shown in Fig. 1c, the increase of I_D/I_G ratio from 0.57 to 0.90 specifies more defect sites at the SPCE* [23,24]. Moreover, Raman image of D band intensity of SPCE* at different spots, with lighter and dark spots corresponding to higher and lower intensity of D band, also specifies numerous defect sites at the SPCE* (Fig. 1d).

A systematic study of SPCE* prepared at different 0.1 M-electrolyte of HCl, pH 7 PBS, H_2SO_4 and HNO_3 was further executed. Based on I_D/I_G ratio (Fig. 2a), the defect sites were found to decrease in the following order: $HNO_3 > H_2SO_4 >$ pH 7 PBS $>$ HCl. The surface coverage (Γ) were calculated as 3.90, 2.99, 1.49 and 0.17 nmol cm^{-2} with a RSD value ($n = 5$) of 2.16, 10.46, 7.09 and 13.97 for HNO_3-SPCE*, H_2SO_4-SPCE*, PBS-SPCE* and HCl-SPCE*, respectively. Note that this is parallel to the previous report of McCreery's group on glassy carbon electrode [25]. Most importantly, as shown in Fig. 2b, the same trend of defect sites and Γ values clearly confirms the status of defect sites to the process of AN adsorption/oxidation. The fact

that carbonyl functional group obtained from C1s core level XPS spectra was also consistent with those of Γ value (Fig. 2c) makes us believe that both oxygen functionalities and edge/defect sites are equally important to this process.

We then evaluated the effect of preanodization time on the adsorption/oxidation of AN at HNO_3-SPCE* (HNO_3-SPCE* was considered for further studies as it exhibited the highest Γ value). As shown in Fig. 3a, both the I_D/I_G ratio and Γ were found to increase with preanodization time and the amount of defect sites started to level off at ~180 s. However, the carbonyl content increased with increasing preanodization time, this validates the contribution of carbonyl functional group present at the defect sites in AN adsorption/oxidation. To further understand the oxidation mechanism, role of solvent, oxygen reduction intermediates and functional group of electrode surface were examined. First, the fact that no considerable change in Raman characterization after drop-coating 5 μL ACN at the SPCE* confirms no solvent effect on the electrode surface. Next, similar results obtained for AN oxidation under ambient, N_2-saturated, O_2-saturated conditions indicate no substantial involvement of dissolved oxygen during the oxidation process. Finally, to ascertain the role of surface oxygen functional groups in AN oxidation, the SPCE* was electrochemically reduced (designated as ER-SPCE*) and subjected to XPS and Raman studies. Based on the I_D/I_G ratio, the average crystallite size (L_a) was calculated using the equation: $L_a = (2.4 \times 10^{-10}) \lambda^4_{laser} (I_D/I_G)^{-1}$ [26,27]. The SPCE* and ER-SPCE* exhibited an average crystallite size values of 21.36 and 18.31 nm and I_D/I_G ratio of 0.90 and 1.05, respectively. The reduction of oxygen functionalities was confirmed from the increased I_D/I_G value due to regenerated SP^2 backbone with decreasing crystallite size. As expected, under the restricted potential window of -1.0 to 0.0 V, no redox peak was observed at the ER-SPCE* (Fig. 3b). Upon extending the potential to $+1.0$ V, the occurrence of redox peak indicates the AN