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Influence of Al_2O_3 nanoparticles structure immobilized upon glassy-carbon electrode on the electrocatalytic oxidation of phenolic compounds

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ABSTRACT

Electrocatalytic oxidation of catechol (CT), dopamine (DP) and tert-butylhydroquinone (TBHQ) is demonstrated on glassy-carbon electrode (GCE) surfaces modified with alumina nanoparticles of different structures and morphologies. Higher electrochemical activity for the oxidation of CT, DP and TBHQ (peak-to-peak separation reduced from 500 to 50 mV in average) was verified on a GCE polished with α-Al_2O_3 suspension in comparison with the surfaces modified with θ and γ-Al_2O_3. This result seems to be correlated with the alumina structure instead of the surface area, as the α-Al_2O_3 presented 10-fold lower surface area than θ and γ-Al_2O_3, or particle size. Gold and platinum surfaces were similarly modified with α-Al_2O_3 suspension and the distinguished electrochemistry of the phenolic compounds was not observed on the platinum-modified surfaces, which may indicate effect of the substrate on the immobilization of alumina. High stability of the GCE surface modified with α-Al_2O_3 was attested by continuous amperometric detection of the phenolic compounds under hydrodynamic conditions, and superior analytical sensitivity of the α-Al_2O_3-modified electrode was observed with comparable results to those obtained on GCE modified with multi-walled carbon nanotubes. These results demonstrate that α-Al_2O_3 particles commercially available for electrode polishing can be used to develop highly sensitive, reproducible and stable electrochemical sensors, but also indicate that electrode polishing may generate improved electrochemical responses attributed to "cleaned surfaces".

1. Introduction

The modification of electrodes has been intensively investigated in the development of improved electrochemical sensors. Increase in selectivity, sensitivity and anti-fouling properties are the advantages claimed by different research groups [1–4]. Carbon nanostructures, such as carbon nanotubes (CNTs) and graphene oxide, have been preferred in the modification of electrodes due to the claimed electrocatalytic properties attributed to defects located at their structures [5,6]. Nevertheless, the presence of metallic impurities on CNTs [7] as well as the alteration of mass transport regime to thin-layer diffusion (modified electrode behaves as conduction porous film) need to be considered on the investigation of the electrocatalytic properties of CNTs or other carbon-based nanostructures [8,9].

The modification of glassy-carbon electrodes (GCE) with alumina after simple abrasive polishing was reported [10–14]. It was demonstrated that the apparent catalysis of the oxidation of catechol to *o*-benzoquinone in acid media was caused by alumina particles immobilized on a GCE surface [9,10]. The adsorption of catechol on alumina particles immobilized on the electrode may facilitate the two-electron oxidation of the adsorbed species, in which alumina acts as a catalyst of this electrochemical process [10,11]. The anticipated oxidation potential towards the oxidation of dopamine was also reported [14] as well as the anticipated electrochemical reduction of nitrobenzene on alumina-polished electrodes [15]. Therefore, these works indicate that a possible contamination of GCE with alumina due to the common practice of electrode cleaning using alumina polishing may change the electrochemistry of different molecules. However, no investigation correlating the morphology and structure of Al_2O_3 particles on the

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electrocatalytic oxidation or reduction of different compounds was previously presented.

Within this context, we investigated the effect of morphology and structure of alumina nanoparticles used as a suspension for electrode modification by polishing on the electrochemistry of phenolic compounds, including catechol, dopamine and the antioxidant *tert*-buylhydroquinone (TBHQ). Additionally, this work demonstrates that the abrasive immobilization of alumina particles not only on a GCE but also on a gold electrode provides similar catalytic activity towards the oxidation of phenolic compounds. Finally, stability and analytical sensitivity of the alumina-modified GCE was demonstrated by the continuous amperometric detection of these compounds using batch-injection analysis (BIA).

2. Experimental section

2.1. Chemicals

Alumina powder 0.3 μm Micropolish II (α-Al_2O_3), mostly used in this work, was obtained from Buehler (Lake Bluff, Illinois, USA). Alumina powder 5.0 μm (α-Al_2O_3) from Buehler (Lake Bluff, Illinois, USA) and alumina powder 0.0058 μm Brockmann I (γ-Al_2O_3) from Aldrich (Milwaukee, USA) were also used for comparison. Catechol (<99%), dopamine (<99%) and *tert*-butyl-hydroquinone (<98%) were obtained from Acros (New Jersey, USA), Sigma Aldrich (St. Louis, USA) and Fluka Analytical (Steinheim, Germany), respectively. Perchloric acid (70% v/v) from Reagen (Rio de Janeiro, Brazil) was used to prepare the supporting electrolyte. Multi-walled carbon nanotubes (MWCNTs, D × L: 6–9 nm × 5 mm, >95%) purchased from Aldrich (Milwaukee, USA) was used to modify electrodes for comparison. $Al(NO_3)_3$ (98%), urea (99.0–100%) and citric acid (99%) were purchased from Aldrich (Milwaukee, USA).

Deionized water with a resistivity of less than 18.2 MΩ cm obtained from a Milli Q water purification system (Millipore, Bedford, MA, USA) was used for preparing all aqueous solutions. The stock solutions of the analytes were freshly prepared just before the experiments by dilution in 0.1 mol L^{-1} $HClO_4$.

2.2. Electrochemical instrumentation and measurements

The electrochemical measurements were all performed using a PGSTAT128N (EcoChemie–Metrohm, Utrecht, Netherlands) controlled by NOVA 1.11 software, responsible for data acquisition and treatment. The electrochemical cell with three electrodes was used in this system. A platinum wire was used as counter electrode and a miniaturized electrode Ag/AgCl/KCl (sat.) as reference electrode [16]. As working electrodes, glassy carbon, gold and platinum disc electrodes (all electrodes had diameter of 1.6 mm and were acquired from BAS Inc. – West Lafayette, USA).

All measurements were performed at room temperature and in the presence of dissolved oxygen. Cyclic voltammetric experiments were carried out using a 10 mL glass electrochemical cell containing the three-electrode system. Amperometric measurements were performed under using a lab-made batch-injection analysis (BIA) cell of 180 mL [17]. Briefly, the BIA system requires a micropipette or a syringe for the injection of a plug of sample or standard solution over the working electrode (wall jet configuration), which is immersed in a large volume of electrolyte (180 mL). Reference and counter electrodes are positioned through the top of cell while the working electrode is firmly introduced through the bottom of the cell. In this work an electronic micropipette (Eppendorf Multipette® stream) was used to control the dispensing rate (153 μL s^{-1}) and volume (100 μL), which is also inserted through the top of the cell in such a way that the micropipette tip is placed at around 2 mm from the working electrode surface.

2.3. Synthesis and characterization of Al_2O_3

2.3.1. Synthesis of θ and γ-Al_2O_3

The precursors were obtained from the addition of 0.1 mmol of $Al(NO_3)_3$ in 70 mL of distilled water under constant stirring. After complete dissolution of the salts 1.0 mmol of urea was added. The final solution was transferred into an autoclave, and then sealed and placed in the microwave-hydrothermal equipment. The solutions were heated at 140 °C for 2 min. The precipitate powder was washed several times with deionized water and ethanol and dried in air atmosphere. The as-prepared γ-AlOOH precursors were annealed at 600 °C and 1000 °C for 15 min in a microwave oven to obtain γ-Al_2O_3 and θ-Al_2O_3 nanostructures, respectively.

2.3.2. Synthesis of α-Al_2O_3

1.3 mmol of citric acid and 0.3 mmol of $Al(NO_3)_3$ were added into water with constant stirring and heating at 70 °C until formation of aluminum citrate. The resin was treated at 350 °C for 30 min. The obtained powder was calcined at 1100 °C for 2 h to generate α-Al_2O_3 nanostructures.

2.3.3. Characterization of Al_2O_3

The Al_2O_3 samples were characterized by X-ray diffraction (Shimadzu XRD 6000) using Cu Kα as the radiation source. The images were acquired using a field emission scanning electron microscope (FE-SEM, Zeiss Supra35) operating at 5 kV. The N_2 adsorption-desorption isotherms were performed at −196 °C using a NOVAtouch surface area and Quantachrome TouchWin software (version 1.1.). Brunauer, Emmett and Teller method (BET) was used to calculate the specific surface area [18]. All powders were degassed in vacuum at 90 °C during 3 h for obtaining of surface area values.

2.4. Surface preparation and modification

Glassy-carbon, gold and platinum electrodes free of alumina particles were obtained after sonication for 10 min in 1:1 (v/v) ethanol/water solution, followed by polishing on a felt-polishing pad using deionized water (without the presence of aluminum oxides), with posterior sonication for 10 min in 1:1 (v/v) ethanol/water solution. After this step, the electrode was placed in the electrochemical cell for measurements.

Surface modification with alumina particles was obtained after abrasive polishing of each working electrode on a felt-polishing pad (Ø = 2 cm diameter) containing alumina suspension (20 mg mL^{-1}) for 10 s. The electrode surface was polished in a circle motion, keeping the electrode facing parallel to the polishing pad. The modified electrode was cleaned with deionized water after 30 s and dried at room temperature. After that, the modified electrode was used for electrochemical measurements. The time of polishing (5–30 s) and drying (2–600 s) of the modified electrode was investigated. Moreover, reproducibility (n = 5) of the glassy-carbon electrode modification with alumina was evaluated.

Electrode activation was performed by cycling in background electrolyte until reproducible scans were obtained (typically five voltammetric cycles).

2.5. Atomic force microscopy (AFM)

The thickness of the alumina films was estimated in a Shimadzu AFM equipment (Kyoto, Japan) at dynamic mode (non-contact) and using a silicon tip (BudgetSensors) with curvature radio <10 nm, $k = 40\ N\ m^{-1}$, and frequency of 300 kHz.