Silver-functionalized carbon nanofibers composite electrodes for Ibuprofen detection

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Abstract

Nanoscale carbonaceous materials, especially carbon nanotube (CNT) and carbon nanofibers (CNF) have attracted great research interests for electroanalysis field. The development of carbon nanofiber based composite electrodes combine the enhanced electrical properties and easy of processing exhibiting attractive electrochemical and economical features [1]. However, the improvement of the electroanalytical signal requires catalyst incorporation into composite matrix, and several studies have been directed to silver-decorated CNT [2]. In this study, two types of silver-functionalized carbon nanofibers composite electrodes, silver-decorated CNF-Epoxy (AgCNF) and silver-modified natural zeolite-CNF-Epoxy (AgZCNF) composites electrodes were prepared, morphologically and electrically characterized and applied for ibuprofen (IBP) detection in aqueous solution.

Experimental

Carbon nanofibers (CNFs) with average diameter of 60–150 nm and average length of 30–100 μm were purchased from Applied Sciences Inc., Cedarville, Ohio (Pyrograf III -PR24 AGLD). Silver-modified zeolite was prepared by ion-exchange using natural zeolite (NZ) from Mirsid, Romania, with 68% wt., as we previous described [3]. The two-component epoxy resin used in the study was Araldite®LY5052/ Aradur®5052, purchased from Huntsman Advanced Materials, Switzerland. The decoration of silver nanoparticles into CNF composite was carried out by reducing silver ions in the presence of DMF. 1.1 g of CNF were added into 550 ml of DMF and the mixture was subjected to ultrasonication (Cole-Parmer 8900, USA) for 1 h. 40 ml of $AgNO_3$ solution (0.02 M) was added into the mixture of 60-62 °C durin the stirring. After 1h heating the solution was kept without stirring at room temperature for 48 h for Ag deposition, and after filtration and sequentially washed with water, ethanol and acetone resulted silver-decorated CNF. The composite electrodes were prepared by dispersion of CNFs in DMF, 99.9% (DMF, Sigma Aldrich) and epoxy resin (Araldite®LY5052) by ultrasonication, followed by the homogenization of the resulting paste with the zeolite particles and also with the hardener using a two-roll mill. The mixture was then poured into PVC tubes and cured at 60^oC for 24 h, obtaining discs electrodes with the surface area of 0.196 cm^2. The ratios were chosen to reach 20 % (wt.) CNFs for AgCNF electrode; 20 % (wt.) CNFs and 20 % (wt.) Ag-modified zeolite for AgZCNF electrode. Electrochemical measurements were carried out using an Autolab PGSTAT101 (Metrohm Autolab, The Netherlands) controlled with NOVA 1.6 software and a three-electrode cell, with a Ag/AgCl reference electrode, a platinum counter electrode and the composite working electrodes. Cyclic voltammetry (CV), differential-pulsed voltammetry (DPV), square-wave voltammetry (SWV) and chronoamperometry (CA) were used to assess the electroanalytical performance of the both composite electrodes for IBP detection in the aqueous solution. A preconcentration-detection scheme was proposed for AgCNF composite electrode, which exhibited a greater affinity for IBP sorption on the electrode surface to enhance the electroanalytical parameters.

Results

Figure 1 a, b shows the series of the cyclic voltammograms (CVs) recorded at silver-decorated CNF-Epoxy (AgCNF) and silver-modified natural zeolite-CNF-Epoxy (AgZCNF) composites electrodes in 0.1 M Na_2SO_4 supporting electrolyte and in the presence of various IBP concentrations. A better sensitivity and correlation coefficient was reached for AgCNF in comparison with AgZCNF electrode. Also, using CA as the simplest electrochemical technique with real practical potential, very good electroanalytical performance for IBP detection at 1.3 V vs. Ag/AgCl was reached, even better than CV. Moreover, the AgCNF composite electrode exhibited useful peculiarities for applying the preconcentration-voltammetric detection technique, and no electrode fouling occurred. Under these last conditions, a better sensitivity and a lower limit of detection were achieved, this electrode being useful to detect low concentrations of IBP in aqueous solutions.

Acknowledgments

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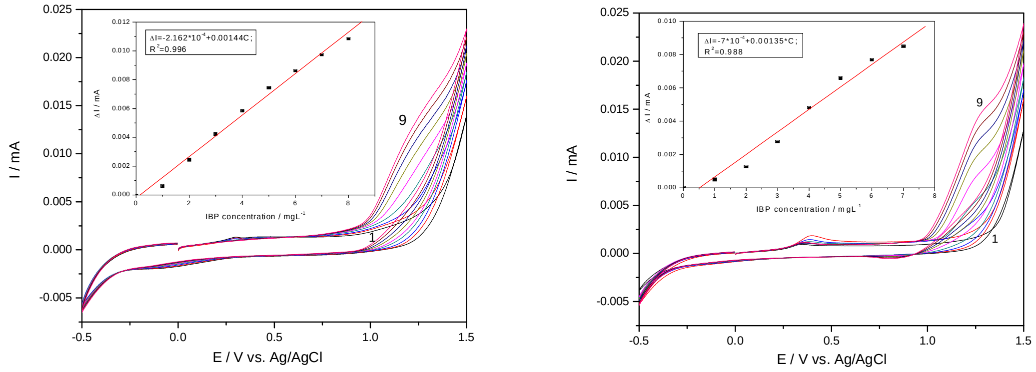
Figures



a)

b)

Fig. 1. CVs recorded at a) AgCNF, b) AgZCNF electrodes in 0.1M Na_2SO_4 supporting electrolyte (curve 1) and in the presence of various IBP concentrations: 1-8 mgL-1(curves 2-9); potential scan rate of 50 mV/s. Inset: Calibration plots of peak current vs. IBP concentration.

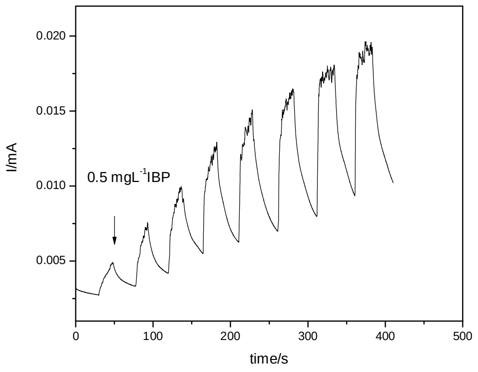


Fig. 2. CA of AgCNF electrode recorded at 1.3 V vs Ag/AgCl in 0.1 M Na2SO4 supporting electrolyte during continuous adding 0.5 mgL^{-1} IBP

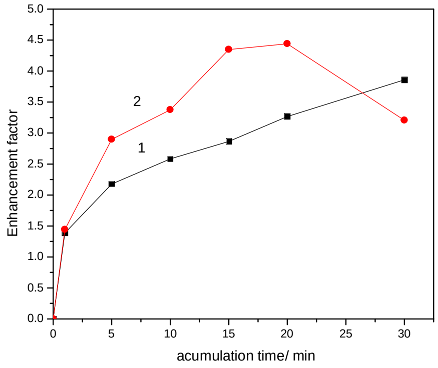


Fig. 3. Enhancement factor for the oxidation of 1 mgL^{-1} IBP as function of the accumulation time, with background current subtraction: 1-AgZCNF electrode and 2- AgCNF electrode. Detection was performed in 0.1 M Na_2SO_4 supporting electrolyte by DPVs recorded at 1 Vvs. Ag/AgCl, potential scan rate 0.05 Vs^{-1}.