Copper-decorated carbon nanotubes based composite electrodes for non-enzymatic detection of glucose

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Nowadays, a large community of researchers is focusing on the development of different applications for carbon nanotubes (CNTs), and in the field of electrochemical sensing, CNTs receive considerable attention. The high sensitivity, chemical stability, excellent electrical conductivity, modifiable surface which provide the possibility to fabricate multifunctional electrochemical sensors are only a few important properties that which recommend them for sensing applications [1,2]. Using CNTs in composites gives also the possibility to fabricate sensors with high electroanalytical performances with easy renewable surface and also having a very good mechanical strength. Glucose determination in medical applications by electrocatalytic oxidation is of great interest to electrochemists. Fabrication of high performance sensors for glucose continues to be a provocative challenge. In this paper three types of multi-wall carbon nanotube (CNT)-based composite electrodes, *i.e.,* CNTs embedded in an epoxy matrix (CNT-Epoxy); CNTs – synthetic A-type zeolite (SZ) in an epoxy matrix (SZCNT-Epoxy), CNT – natural clinoptilolite zeolite (NZ) in an epoxy matrix (NZCNT-Epoxy), were prepared, and then modified with copper particles by electrodeposition and tested for direct electrochemical detection of glucose.

Experimental

Multi-wall carbon nanotubes (MWCNTs) with average diameter of 9.5 nm and average length of 1.5 μm were purchased from Nanocyl, Belgium. Synthetic A-type zeolite (SZ) was prepared using natural clinoptilolite as a silicon source and sodium aluminate as aluminum source, 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 composite electrodes were prepared by dispersion of MWCNTs in tetrahydrofuran, 99.9% (THF, Sigma Aldrich) and epoxy resin (Araldite®LY5052) by ultrasonication, followed by the homogenization of the resulting paste with the zeolite particles and the hardener using a two-roll mill. The mixture was then poured into PVC tubes and cured at 60^{o}C for 24 h, obtaining discs electrodes with the surface area of 0.196 cm^2. The ratios were chosen to reach 20 % (wt.) CNTs for CNT-Epoxy electrode; 20 % (wt.) CNTs and 20 % (wt.) SZ for SZCNT-Epoxy electrode; and 20 % (wt.) CNTs and 20 % (wt.) NZ for NZCNT-Epoxy electrode, respectively. The surface of prepared electrodes was then decorated with copper by electrodeposition at a potential of -0.5 V for 20s in the presence of 0.1 M $CuSO_4$ solution. 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 an Ag/AgCl reference electrode, a platinum counter electrode and the composite working electrodes.

Results

Figure 1 shows the SEM image of SZCNT-Epoxy composite material decorated with Cu particles. The EDX data for the electrode composite material revealed the presence of copper on the composite surface. The electrocatalytic activities of the copper-decorated CNT-Epoxy, SZCNT-Epoxy and NZCNT-Epoxy electrodes towards the oxidation of glucose in an alkaline solution were demonstrated. Some examples of the cyclic voltammograms (CVs) recorded in 0.1 M NaOH solution and in the presence of different glucose concentrations are presented in the Figure 2. The differences between the electroanalytical performances of the electrodes are related to composite structure and morphology, which influenced copper particle size and distribution on the surface of the composite material. Best electroanalytical performances obtained for the detection of glucose by cyclic voltammetry were recorded with the copper-decorated CNT-Epoxy electrode, *i.e.,* electrode sensitivity of 8.45 mA·mM^{-1} and a LOD of 0.2 μM glucose. All copper-decorated composite electrodes exhibited useful properties for the direct oxidation and simple non-enzymatic determination of glucose on tested electrodes surface.

Acknowledgments
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Figures

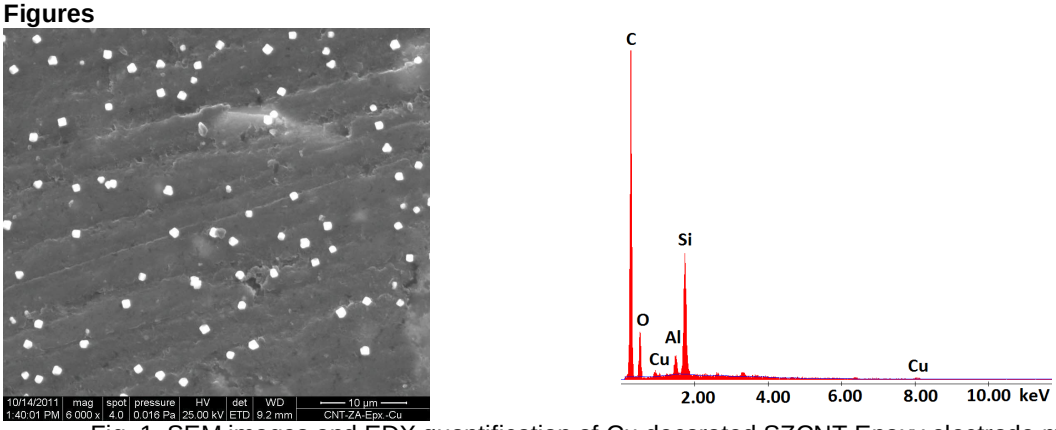
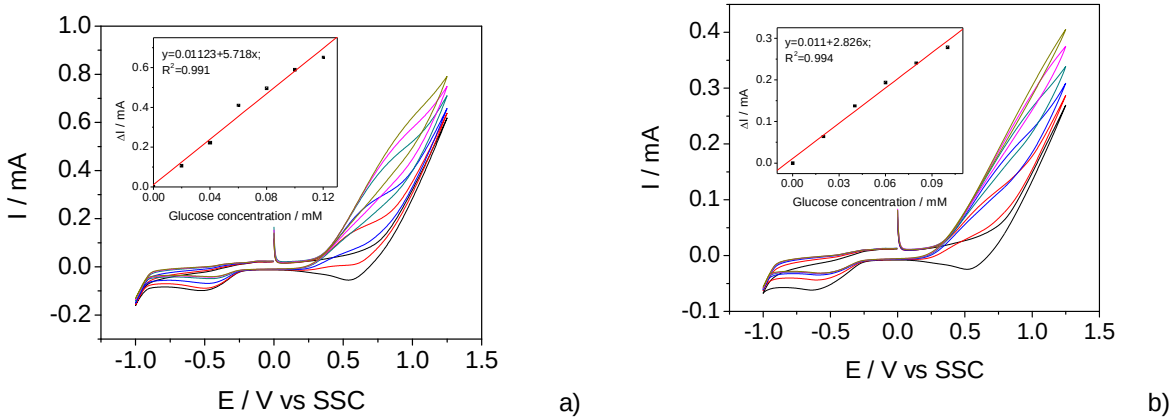


Fig. 1. SEM images and EDX quantification of Cu decorated SZCNT-Epoxy electrode material.



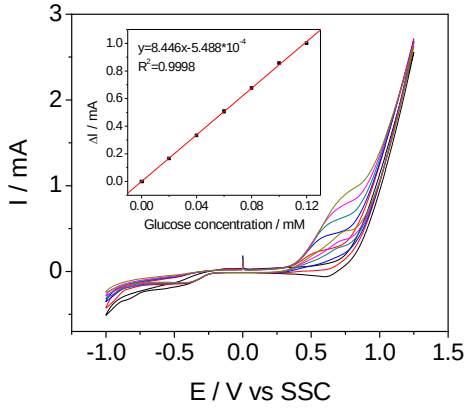


Fig. 2. CVs of a) Cu-SZCNT-Epoxy, b) Cu-NZCNT-Epoxy, c) Cu-CNT-Epoxy electrodes recorded supporting electrolyte and by 5 successive additions of 0.02 mM glucose in NaOH; potential scan rate 50 mV/s. Insets: calibration plots of peak currents vs. glucose concentrations.