Preparation and application of electrochemical sensor based on Ag-doped synthetic zeolite modified multiwall carbon nanotube electrode for arsenic detection

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Introduction

Carbon nanotubes (CNTs) have extensively been used for electroanalytical applications due to their unique structure, mechanical strength and electronic properties. Because of their enhanced electrochemical properties and large surface area, CNT are used to fabricate highly sensitive electrodes for detection of different kinds of pollutants. With regard to detection of heavy metals, several authors have reported the use of different forms of CNT composite electrode material for the detection of different heavy metals with enhanced sensitivity and/or selectivity [1-6].

Arsenic (As) is an environmentally and toxicologically important element known to cause a variety of adverse health effects, including dermal changes and respiratory, cardiovascular, gastrointestinal, genotoxic, mutagenic, and carcinogenic effects. Till now, the commonly employed techniques for the determination of arsenic in drinking water are based on spectrometry [7]. Since these techniques have expensive instrumentation, running costs and most of them cannot detect arsenic below 10 ppb, the use of simpler, faster, and cheaper, yet sensitive, electrochemical techniques can be interesting alternatives, especially those based on electroanalytical techniques.

In this work, we are developing a new approach to prepare Ag- doped synthetic zeolitemultiwall carbon nanotubes- epoxy composite electrode. The composite material was characterized by microscopic and electrochemical techniques. Furthermore, the electrode was tested for the detection of arsenic in aqueous solutions.

Experimental

The composite electrode used in this study was made of multiwall carbon nanotubes (CNT_NC7000 with 90% purity; length 1.5 μm; average diameter 9.5 nm and surface area around 250-300 m2/g ; produced by catalytic carbon vapor deposition method (CCVD)), supplied by Nanocyl, Belgium and from the epoxy resin Araldite®LY5052/ Aradur®5052 produced by Huntsman Corporation. Tetrahydrofuran (THF 99.9%), used as dispersing agent was obtained from Sigma- Aldrich. Synthetic zeolites (ZA) were synthesized from natural clinoptilolite as Si source and the details regarding the synthesis method were presented in our previous work [8].

A dilute suspension of nanotubes in THF was sonicated using a Cole-Parmer® 750-Watt Ultrasonic Processor for 10 min to spread out the nanotubes. First step in achieving high level of dispersion was to mix the suspension and the liquid epoxy resin (without hardener). The mixture was left overnight in a vacuum oven at 60°C in order to extract the solvent. In the processing step, the resulting mixture was then mixed with Ag-doped synthetic zeolite, and the batch was two-roll milled for several times on a laboratory scale two-row mill (Collin) at different shear intensities and then the hardener was added and mixed again to ensure a uniform homogeneity. Finally, the mixture was poured into PVC tubes and cured in an oven at 80°C for 24 h, which after it was left to cool down at room temperature for 24 hrs.

Electrochemical measurements were recorded using a computer controlled Autolab potentiostat/galvanostat PGSTAT 302 (ECO CHEMIE, The Netherlands) with a standard three electrode configuration. A MWCNTs-ZA-Ag electrode with a geometric area of 0.196 cm2 was used as working electrode, a platinum wire as counter electrode and a saturated calomel reference electrode (SCE).

Scanning electron microscopy (SEM) imaging of the electrode surfaces was carried out using a (SEM XL20, Philips) with an acceleration voltage of 15 kV. Raman spectra were recorded using a Renishaw In- Via spectrometer (Renishaw PLC, UK) equipped with a high power 785 nm line-focus NIR laser (100mWpower at sample).

Results and Discussion

SEM microscopy was used to gain the surface characteristics of the modified electrode. Fig. 1 shows the SEM image of the MWCNTs-ZA-Ag- epoxy composite electrode, and a good dispersion of CNTs and Ag-doped synthetic zeolite within the polymer matrix is revealed.

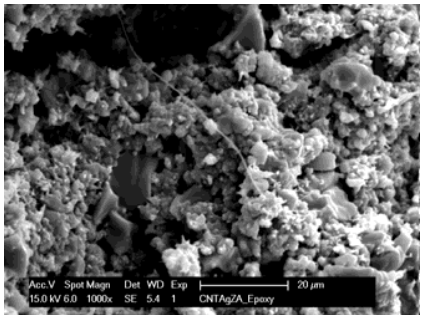

Fig 1. - SEM image of the MWCNTs-ZA-Ag- epoxy composite electrode surface

The electrochemical behaviour of the modified electrode was studied by cyclic voltammetry (CV) in 0.09 M Na2SO4 and 0.01 M H2SO4 supporting electrolyte solution, and in the presence of different arsenic concentrations: 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1 ppm (curves 2-11) in the potential range from 0-1.0 V (vs.SCE), scan rate of 50 mVs-1 (Fig. 2)

Based on Fig. 2, two main oxidation peaks are observed on the CVs, where peak at +0.30 V is attributed to the oxidation of As (0) to As (III) and the second peak at +0.5 V corresponds to the oxidation of As (III) to As (V). The reduction peak observed at 0.2 V is typically due to the reduction of Ag oxide layer formed on the surface of Ag nanoparticles during the anodic scan.

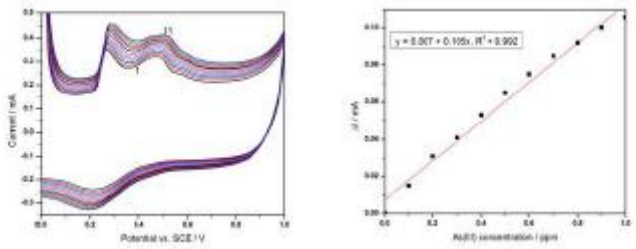

Figure 2. (a) (b)

Conclusions

MWCNTs-ZA-Ag-epoxy composite electrode was successfully prepared. The electroanalytical performance of this electrode for arsenic detection together with the very easy preparation and surface regeneration give the potential for practical applications.

Acknowledgements

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Figures

Fig.1- SEM image of the MWCNTs-ZA-Ag- epoxy composite electrode surface

Fig. 2- (a) CV curves of MWCNTs-ZA-Ag- epoxy composite electrode in 0.09 M Na2SO4 and 0.01 M H2SO4 supporting electrolyte (1) and in the presence of: 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1 ppm As (curves 2- 11); potential range from 0-1.0 V/SCE; scan rate 0.05 Vs-1 with pre-treatment at - 0.5V/SCE for 60 s. (b) Calibration plot of the currents recorded at E= +0.50 V/SCE vs. Arsenic concentrations.