GOLD NANOPARTICLES-CYSTEINE-MULTIWALL CARBON NANOTUBE MODIFIED ELECTRODE FOR HEAVY METAL IONS DETECTION

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Abstract

The environmental contamination by heavy metals is one of the global problems that disturb the ecological balance. A platform for the simultaneous electrochemical detection of trace heavy metal ions has been developed based on the gold nanoparticles-cysteine-multiwall carbon nanotubes (AuNPs-Cys-MWCNTs) modified carbon paste electrode using square wave anodic stripping voltammetry. The voltammetric method was optimized with respect to accumulation time, accumulation potential and other parameters. The syntheses of AuNPs-Cys-MWCNTs composite with different AuNPs diameters were described and characterization using Dynamic light scattering and Scanning electron microscopy was performed. The AuNPs-Cys-MWCNTs composite significantly increases the electrode sensitivity towards Cd(II), Pb(II), Cu(II) and Zn(II). The AuNPs-Cys-MWCNTs composite has promising significance for future using, for example as a modification of the screen printed electrodes (SPEs), which would be used for low-cost and fast *in situ* measurement.

Keywords: Gold nanoparticles-cysteine-multiwall carbon nanotube composite, electrochemistry, paste electrode, screen printed electrode, ecological problems, heavy metals

1. INTRODUCTION

One of the global problems that disturb the ecological balance is the environmental contamination by heavy metals. Heavy metals, is a term for a group of toxic substances, which are dangerous for the environment. The group includes for example lead, mercury, cadmium, copper, zinc, chromium. The most common sources of these substances come from anthropogenic activities of different sectors (heavy industry, agriculture, and pharmaceutical industry) [1,2]. The accumulation of these substances in nature, watercourses and the soil, is a major problem. In fish and agricultural crops there is accumulation of these hazardous substances, through the food chain, heavy metals get into the human body [3,4]. Most of these heavy metals are carcinogens. For this reason it is necessary to check the concentrations of heavy metals in waste water [5,6].

Electrochemical methods are a suitable tool for detecting heavy metals in an aqueous environment. The multiwall carbon nanotubes (MWCNTs) and gold nanoparticles (AuNPs), both materials have recently received increased attention as materials suitable for use in electrochemical detection [7,8]. Their advantage is that they increase the conductivity of the electrode, facilitate the transfer of electrons, and have good chemical stability and MWCNTs increase the active surface area of the electrode. The aim of this study was to make use of nanotube, gold and cysteine connections to obtain excellent material for the formation of a paste electrode that would be sensitive to the determination of heavy metals [9]. The next step was to use the properties of this composite material and modify the surface of the SPEs and then use them for in situ analyzes.

2. MATERIALS AND METHODS

2.1. Chemicals

All chemicals were obtained from Sigma-Aldrich (St. Louis, MO, USA). High purity deionized water (Milli-Q Millipore 18.20 MΩ/cm, Bedford, MA, USA) was used throughout the study.

2.2. Preparation of gold nanoparticles-cysteine-multiwall carbon nanotubes composite (AuNPs-Cys-MWCNTs)

0.1 g MWCNTs were suspended in 30 mL 2.2 mM trisodium citrate. The solution was heated to boiling under vigorous stirring. Upon reaching the boiling point, 25 mM $H[AuCl_4]$ added. After 10 min of interaction, the temperature from 100 ºC was lowered to 90 ºC. After setting the temperature to 90 ºC, 200 µL 60 mM sodium citrate solution was added with stirring and 200 µL 25 mM $H[AuCl_4]$ was added after an additional 2 min. After 10 min of interaction, the process with adding 60 mM sodium citrate solution and 25 mM $H[AuCl_4]$ was repeated 12 times. Thereafter, heating and stirring were stopped and the resulting product was cooled to room temperature and then 9 times washed. 30 mL of the resulting solution was dried.

2.3. Characterization of AuNPs-Cys-MWCNTs

The size of the presented AuNPs was measured by the Zetasizer Nano ZS Instrument (Malvern Instruments Ltd., Worcestershire, UK). The Scanning Electron Microscopy (SEM) MAIA3 (Tescan, a.s., Brno, Czech Republic) was used for visualization of presented composite material (AuNPs-Cys-MWCNTs).

2.4. Preparation of carbon paste electrode modified by AuNPs-Cys-MWCNTs (CPE-AuNPs-Cys-MWCNTs)

To prepare the modified carbon paste, 300 mg of expanded graphite and 75 mg of composite material (AuNPs-Cys-MWCNTs) were used. These materials were homogenized in a mortar with a pestle for 30 min. Subsequently, 260 µL of mineral oil was added. Again homogenization was carried out for 30 min. This mixture was transferred with a spatula into electrode body with 2.5 mm diameter.

2.5. Electrochemical determination of for Cd^{2+}, Pb^{2+}, Cu^{2+} and Zn^{2+}

Determination of Cd(II), Pb(II), Cu(II) and Zn(II) by square wave anodic stripping voltammetry (SqWASV) were performed with 663 VA Autolab (Metrohm, Herisau, Switzerland), using a standard cell with three electrodes. The CPE-AuNPs-Cys-MWCNTs was the working electrode. An Ag/AgCl/3M KCl as a reference electrode and platinum electrode was auxiliary. Software NOVA 1.8 (Metrohm, Herisau, Switzerland) was used for data evaluation. Prior to each measurement, approximately 0.1 mm of CPE-AuNPs-Cys-MWCNTs was wiped on a filter paper to obtain a new surface. The parameters of the measurement were as follows: initial potential of −1.3 V, end potential +0.3 V, deposition time 90 s, deposition potential −1.3 V, voltage step 5 mV, amplitude 25 mV, frequency 200 Hz and equilibration time 5 s. As supporting electrolyte was used acetate buffer pH 5.5.

3. RESULT AND DISCUSSION

In the **Figure 1** shows the structure of composite material AuNPs-Cys-MWCNTs. There is a detailed view of the structure of MWCNTs on which AuNPs are attached. The average particle size of AuNPs was estimated to be 60 nm.

An optimal ratio of the individual components in the paste electrode was determined. The electrochemical sensor (CPE-AuNPs-Cys-MWCNTs) was optimized for simultaneous detection of Zn(II), Cd(II), Pb(II) and Cu(II). The electrochemical method SqWASV was optimalized with respect to deposition time and potential, amplitude and frequency. The calibration curves for metals and the equation coefficient of the calibration curves with the coefficients of determination r^2 are shown in **Figure 2.** The detection limits were found to be 4.5 µg/L for Zn(II), 9.8 µg/L for Cd(II), 8.0 µg/L and 4.0 µg/L for Pb(II) and Cu(II) respectively. In addition, solution of AuNPs-Cys-MWCNTs were applied to the surface of the SPEs. The modified SPEs were successfully tested for Zn(II), Cd(II), Pb(II) and Cu(II) detection.

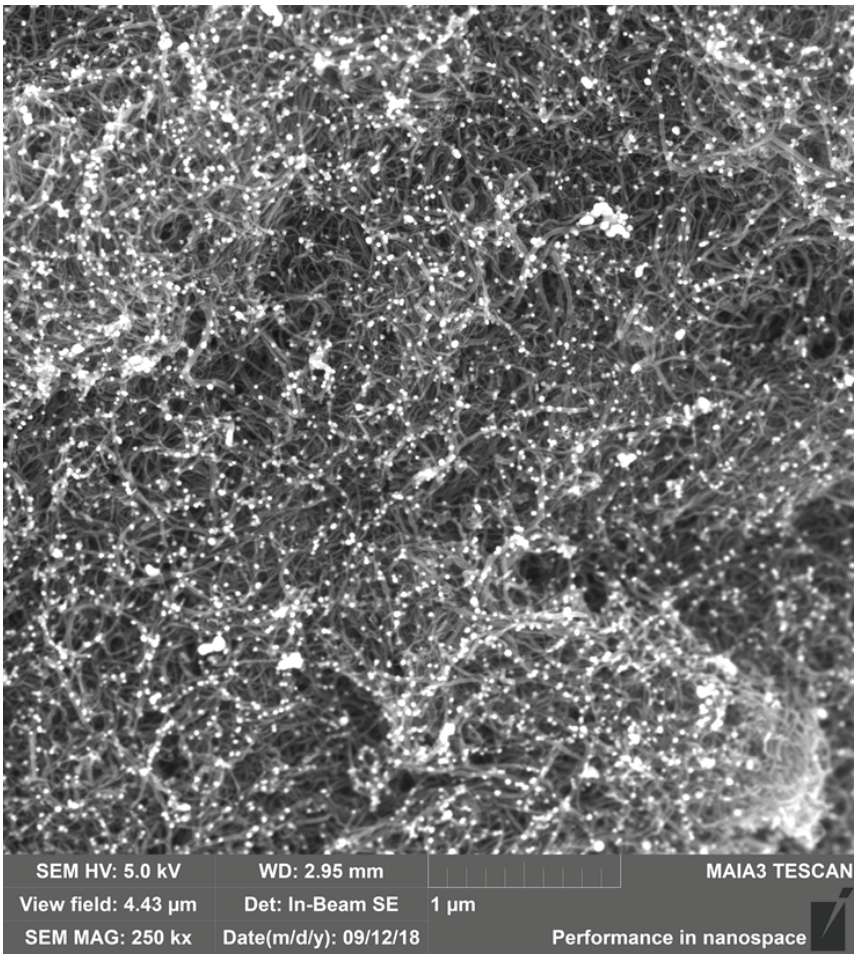

Figure 1 SEM characterization of AuNPs-Cys-MWCNTs

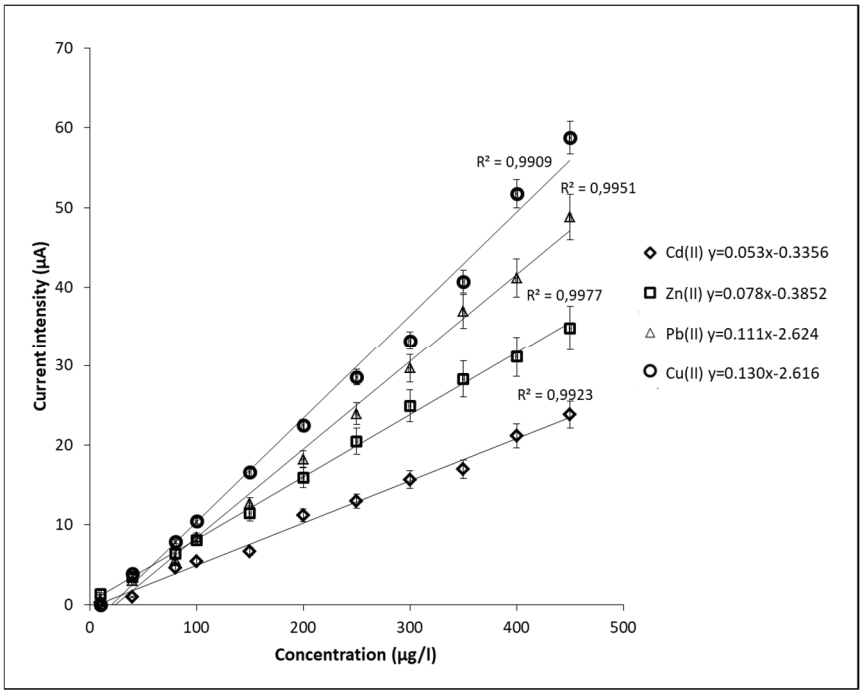

Figure 2 The determined calibration curves for Cd(II), Pb(II), Cu(II) and Zn(II)

4. CONCLUSION

In conclusion, we have developed a new modification for the CPE, which could potentially be used to determine the trace amounts of heavy metals in the aquatic environment. The materials used in this study (AuNPs, MWCNTs, cystein) are nontoxic, environmentally friendly substances, so they are not other potential threat to the environment. The electrochemical potential of this composite material has been demonstrated for the use of SPEs surface modification.

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