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Electrochemical determination of Cu(II) ions using glassy carbon electrode modified by some nanomaterials and 3-nitroaniline

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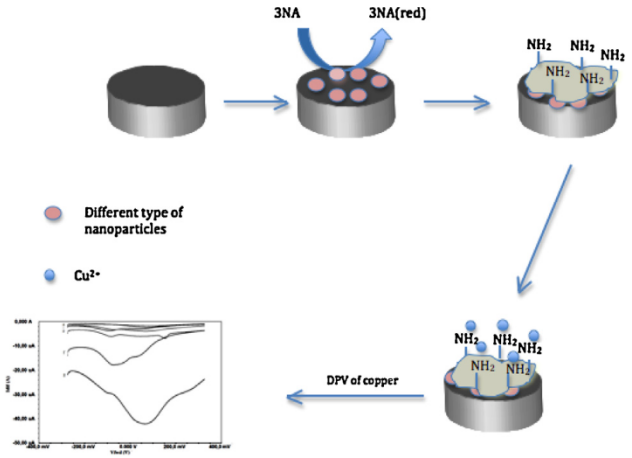
HIGHLIGHTS

- Glassy carbon (GC) electrodes were initially modified by several nanomaterials.
- Then these electrodes were electrochemically modified by poly-3-nitroaniline (poly-3NA).
- Modified electrodes were sensitive for Cu(II) ions.
- Differential pulse voltammetry was applied for determination of Cu(II) ions.
- GC electrode modified with MWCNTs and poly-3NA was the most sensitive toward Cu(II).

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this research was to investigate the effect of the several nanomaterials in electrochemical determination of Cu(II) ions. For this aim, firstly the deposition of graphene oxide (GO), graphene, magnetite (Fe_3O_4), gold-chitosan (AuChts) or multilayer carbon nanotubes (MWCNTs) on the glassy carbon (GC) electrode surface was performed. Then the electrochemical modification of electrode by poly-3-nitroaniline (poly-3NA) was performed by 100 potential cycles in the range between +0.9 V and +1.4 V vs. $Ag/AgNO_3$ at the sweep rate of 100 mV/s. For electrochemical reduction of nitro groups present on modified GC electrode surface, potential cycling was performed in 100 mM HCl between −0.1 V and −0.8 V vs. $Ag/AgCl/(KCl_{sat.})$ at the sweep rate of 100 mV/s. Nanomaterial and poly-3NA modified electrodes were applied in the determination of Cu(II) ions by differential pulse voltammetry. It was determined that GC electrodes consecutively modified with MWCNTs, poly-3NA and then by electrochemical reduction of nitro groups were the most sensitive towards Cu(II) ions with detection limit of 0.5×10^{-9} M.

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1. Introduction

Some heavy metals at particular concentrations are known to be essential for human metabolism due to formation of metallo-proteins and metallo-enzymes and their importance in transcriptional events [1,2]. Copper in the form of Cu(II) ions is one of the most important heavy metal for living species and according to distribution in human organism among the other heavy metals it takes the third place after iron and zinc ions [3]. However with the increasing human activities such as metal plating, application of fertilizers, mining, development and usage of electrical devices, laptops, mobile phones, batteries and pesticides, large quantities of copper is released into the environment [4–6]. Aqueous solutions containing Cu(II) ions are used and/or produced and they are potential pollutants. In many industrial countries, soil contaminated by a variety of heavy metals such as copper is found in hazardous waste sites, which could be a result of illegal or inappropriate drainage of waste water. Copper compounds tends to accumulate in the living organisms and through edible plants and animals, copper compounds can enter into human food chain or into beverages [7]. Long-term exposure to excess of Cu(II) ions can increase the risk of many diseases including gastrointestinal disturbance, liver or kidney damage, neurodegenerative diseases, amyotrophic lateral sclerosis, cancer, Alzheimer's disease, etc [8,9]. Cu(II) ions are especially toxic for microorganisms, such as algae, fungi, bacteria and viruses [10]. Based on above mentioned facts there has been always huge interest in the development of simple and fast methods suitable for Cu(II) ion determination [11–13].

In the most natural samples the amount and/or concentration of Cu(II) ion is relatively low, therefore, effective measurements for the determination of Cu(II) ion traces are highly desired. Most of the copper analysis have been performed by conventional methods such as atomic absorption/emission spectroscopy [14], graphite furnace atomic absorption spectroscopy [15], inductively coupled plasma mass spectrometry [11,16], inductively coupled plasma optical emission spectroscopy with solid phase extraction [17,18], X-ray fluorescence [19,20], colorimetric analysis [21], chemiluminescence based detection [22,23] and neutron activation analysis [12]. Each of the mentioned analysis has its own distinct advantages, but also there are some limitations related to practical application of these techniques, including inconvenient and time-consuming procedures, requirement of expensive equipment and sophisticated maintenance, etc. As a consequence, there is a growing interest in the development of electrochemical sensors, which would be suitable for the determination of Cu(II) ion concentration. Such sensors should be robust, sensitive, compact, simple, low cost, reliable, easily adaptable and selective [13,24–28].

Solid state electrodes, such as gold, platinum or carbon have superior electrochemical properties, but various carbon forms are preferred because of being electrochemically inert and having wide potential window suitable for electrochemical detection, good conductivity and resistance to environmental and chemical hazards [29]. Due to these facts all carbon based electrodes seem very promising for electrochemical analytical systems [30]. To enhance and/or to extend carbon electrode properties some modifications of the surfaces are applied [31]. Recently, there has been increasing interest in electrodes' surface modification with some conductive/non-conductive polymers, organic and inorganic molecules due to their ability to bind various metal ions [9,13,27,28,32,33]. Moreover, for certain electroanalytical requirements in order to detect various analytes as individual, selective or simultaneous detection, the carbon electrodes have been modified with various nanomaterials (NMs). Main advantages of the application of a NMs-modified electrode when compared to others: high effective surface area, mass transport, catalysis and control over local microenvironment. The electrochemical sensors based on unmodified/modified nanostructured carbon materials could be applied in sensors suitable for the detection of chemical and biochemical analytes [34,35].

In this study new electrode for Cu(II) ion detection by stripping voltammetry is suggested and evaluated. In order to increase analytical characteristics of this electrode glassy carbon electrode was modified with graphene oxide (GO), graphene, magnetite (Fe_3O_4), gold-chitosan (AuChts) or multilayer carbon nanotubes (MWCNTs) in order to increase electrochemically active surface and then electrodes were modified with electrochemically reduced 3NA to obtain electrochemically active area for Cu(II) ion detection.

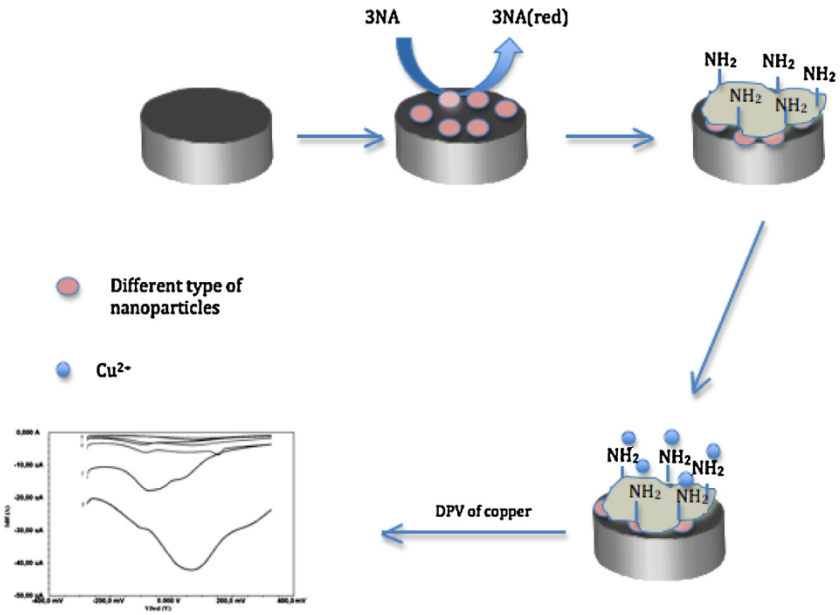
2. Experimental

All chemicals used in this study were of analytical grade and were purchased from Merck, Riedel and Sigma–Aldrich companies. All NMs except MWCNTs were synthesized using the purest available chemicals, which were additionally purified by procedures described in other references [36–39], while MWCNTs was purchased from Sigma–Aldrich.

Electrochemical measurements were performed using a Gamry Reference 750 Potentiostat/Galvanostat from Gamry Instruments (PA, USA) equipped with a C3 cell stand. Glassy carbon electrodes of 0.071 cm^2 geometric area were used as working electrodes. Platinum wire was used as a counter electrode. Ag/AgCl in saturated KCl (Ag/AgCl/($KCl_{sat.}$)) was applied as a reference electrode for the experiments, which were performed in aqueous media; or a Ag/Ag^+ in 10 mM $AgNO_3$ ($Ag/AgNO_3$) was applied for the experiments, which were performed in non-aqueous media. All experiments were carried out inside a Faraday cage at a room temperature. In order to avoid contamination and to obtain a clean renewed electrode surface: the surface of the bare GC electrode was hand-polished as described before [40,41].

Electrochemical modification of GC electrode surface was performed with Gamry PCI4/750 potentiostat controlled by PHE 200 software. Modification protocol was carried by using 3NA and performed by 100 reversible potential cycles between +0.9 V and +1.4 V in acetonitrile (CH_3CN) including 100 mM tetrabutylammoniumtetrafluoroborate (TBATFB). After the modification of the GC electrode, the surface of obtained GC/3NA electrode was carefully washed with pure water. Electrochemical reduction of nitro groups on the GC/3NA surface to amino groups was performed by 100 potential cycles in 100 mM HCl solution in the potential range between −0.1 V and −0.8 V at scan rate of 100 mV/s [28]. Deposition of nanomaterials on bare, modified and/or reduced electrodes' surfaces was performed by dropping twice 5 μL drops of NMs prepared in pure water as 1 mg/mL solution. Subsequently, it was dried in the air. Modification procedures are schematically depicted in Scheme 1.

In order to investigate the effect of selected nanomaterials to the electrochemical determination of copper (II) ions by modified GC electrode surfaces previously described by our research group [28], in this study, several different types of electrodes were designed and evaluated: (I) bare GC; (II) GC/3NA; (III) GC/3NA(red); (IV) several GC electrodes differently modified with selected nanomaterials and 3NA. For copper determination all electrodes were immersed in aqueous 1 mM Cu(II) ions containing solutions prepared in Britton–Robinson (BR) buffer solution, pH 5.0, for five minutes. After immersion electrode was carefully washed with pure water and stable potential (STB POT) was applied for Cu(II) ions reduction into metallic copper (1). This process then was followed by differential pulse voltammetry (DPV), which was performed in the range of −0.3 V to +0.3 V vs. Ag/AgCl/KCl_{sat} with a pulse amplitude of 50 mV, pulse time of 0.1 s, pulse period (interval) of 1 s and a voltage step of 2 mV in BR buffer solution, pH 5.0. During this



Scheme 1. Schematic presentation of electrode modification and evaluation procedure.

stage copper is being oxidized back to its preliminary state (2). All results were compared with that obtained using bare GC electrode, GC/3NA and GC/3NA(red) electrodes.

$$Cu^{2+} + 2e^- \rightarrow Cu \quad (1)$$

$$Cu - 2e^- \rightarrow Cu^{2+} \quad (2)$$

In order to investigate proposed electrodes' selectivity for Cu(II) ions test was performed in the presence of the 1 mM interfering Zn(II), Cd(II), Pb(II), Mn(II), Co(II), Fe(III) metal ions together with 1 mM Cu(II) ions in BR buffer solution, pH 5.0. Stability test was performed by storing prepared electrode in argon (Ar) atmosphere at +4 °C in refrigerator for 0, 1, 4 and 14 days. Reproducibility test was performed using three different GC electrodes, which were prepared in exact same conditions. Moreover, repeatability test was performed using same electrode for copper detection multiple times. Between detections, electrode was washed with pure water and ethylenediamine tetraacetic acid (EDTA). For all experiments STB POT and DPV analysis were applied.

3. Results and discussion

Adsorption and electrochemical deposition followed by reduction of functional groups on the modified GC electrodes' surface were combined for electrochemical detection of Cu(II) ion. The interaction mechanism of the Cu(II) ions and the amino groups can be explained by interaction of amino groups and Cu(II) ions and formation chelate complex (Fig. 1), which is taking place on modified electrode surface. On the other hand, the efficiency of 3NA modified surfaces was enhanced by nanomaterials, which were applied in this research. For this aim, number of differently modified electrodes was prepared by the deposition of NMs before or after electrochemical modification with 3NA; the electrodes were classified into several groups: (I) bare GC; (II) GC modified with 3NA (GC/3NA); (III) GC modified with electrochemically reduced 3NA (GC/3NA(red)); (IV) GC/3NA additionally modified with nanomaterial (GC/3NA/NMs); (V) 3NA(red)/GC additionally modified with nanomaterial (GC/3NA(red)/NMs), (VI) GC modified with nanomaterial (GC/NMs) and then modified with 3NA (GC/NMs/3NA); (VII) GC modified with nanomaterial and then modified with electrochemically reduced 3NA (GC/NMs/3NA(red)). Then these electrodes were applied for the electrochemical determination of Cu(II) ions. Firstly GO and 3NA/GO modified electrodes were evaluated. DPV results, which are shown in Fig. 2, illustrate that the highest DPV peak was observed at −0.06 V towards Cu(II) ions with GC/NMs/3NA(red) electrode.

Dependently on oxidation reduction process and oxidation state copper ions have several reduction potentials for various reduction processes $Cu^{2+} + 2e^- \rightarrow Cu$ of +0.34 V, $Cu^{2+} + e^- \rightarrow Cu^+$ +0.15 V, $Cu^+ + e^- \rightarrow Cu$ + 0.52 V vs. hydrogen electrode at standard conditions (at partial pressure of 1 atmosphere and at 25 °C (298 K) temperature when concentrations of initial Cu-ion solutions are 1 M). However, under different experimental conditions (e.g., ion concentration, electrode material, reference electrode, etc.) this potential can vary [42,43]. GC electrode modified by electrochemically reduced poly-4NA (GC/4NA(red)) has been already investigated by Oztekin et al. [28] and this electrode has been found suitable for Cu(II) determination. But differently from the previous article present research

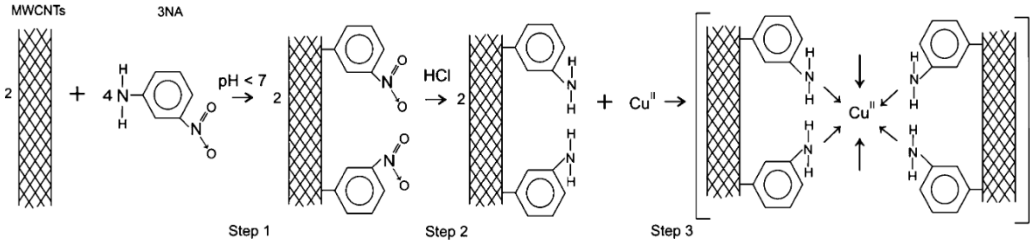


Fig. 1. Reaction scheme of (1) 3NA electrochemical modification on MWCNTs, (2) nitro group electrochemical reduction to amino groups and (3) Cu(II) reduction.

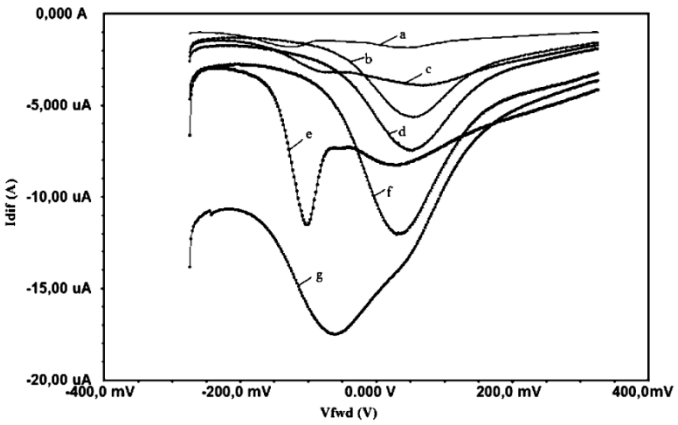


Fig. 2. Differential pulse voltammograms of copper at Bare GC (a); GC/3NA (b); GC/3NA(red) (c); GC/3NA/GO (d); GC/3NA(red)/GO (e); GC/GO/3NA (f); GC/GO/3NA(red) (g) electrodes recorded in BR buffer solution, pH 5.0 vs. $Ag/AgCl/KCl_{sat}$.

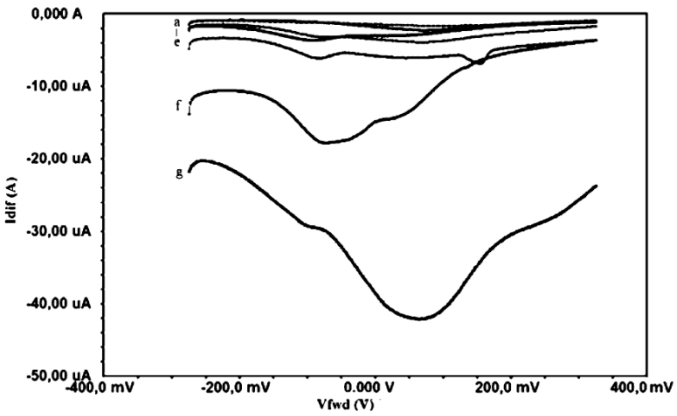


Fig. 3. Differential pulse voltammograms of copper at GC/NPs/3NA(red) electrodes: Bare GC (a); GC/3NA(red) (b); GC/Fe_2O_3/3NA(red) (c); GC/AuChts/3NA(red) (d); GC/Graphene/3NA(red) (e); GC/GO/3NA(red) (f); GC/MWCNTs/3NA(red) (g) recorded in BR buffer solution, pH 5.0 vs $Ag/AgCl/KCl_{sat}$.

showed that GC/GO/3NA(red) electrode is 5 times more sensitive compared to GC/3NA(red) electrode. The reason of this advanced sensitivity is related to larger electrochemically active surface, which has been increased by GO. Other researches also noticed some advantages of electrodes modified by carbon nanomaterials [44,45].

As it is understood from Fig. 2, the modification of GC by GO before electrochemical modification procedures enhances current responses compared with that of GC/3NA and GC/3NA(red)/ electrodes. Therefore, another step of this research was to determine nanomaterials which are the most efficient in electrochemical determination of Cu(II) ion. Five different nanomaterials were chosen for this aim: GO, graphene, Fe_3O_4, AuChts and MWCNTs and five different electrodes (GC/Fe_2O_3/3NA(red), GC/AuChts/3NA(red), GC/Graphene/3NA(red), GC/GO/3NA(red) and GC/MWCNTs/3NA(red)) were prepared for this part of research and their electrochemical responses towards Cu(II) ions were compared with bare GC and GC/3NA(red) electrodes.

DPV results (Fig. 3) showed that analytical signal registered by GC/MWCNTs/3NA(red) at +0.05 V electrode increases twice when compared with that registered with GC/GO/3NA(red). This effect is related to properties of MWCNTs. Since the MWCNTs can adsorb ions and molecules, exhibit strong adsorptive ability towards other species and increase their surface concentration [46]. In this way, it can provide large area for electrochemical modification by poly-3NA, which leads to significantly larger electrochemically active surface available for Cu(II) ion binding [47]. On the basis of above-mentioned factors Cu(II) ion binding efficiency on the GC/MWCNTs/3NA(red) electrode is much higher in comparison with that of electrodes, which are modified by the other nanomaterials used in this research. Therefore further experiments were carried using GC/MWCNTs/3NA(red) electrode.

The characteristics of the sensing systems such as selectivity, repeatability, reproducibility and stability are important as much as sensitivity. For this reason all further experiments were performed and the results were evaluated while applying statistical analysis. The investigation of sensitivity of the GC/MWCNTs/3NA(red) electrode towards binding of Cu(II) ions was carried out in the presence of other interfering metal ions (Zn(II), Cd(II), Pb(II), Mn(II), Co(II), Fe(III)). When other ions were presented at the same concentration as Cu(II) ions, their interfering effect decreased in following order: Co(II) > Mn(II) > Fe(III) > Cd(II) > Pb(II) > Zn(II). Here presented interfering metal ions at 1 mM concentration reduced the current peak from 14 to 37%. When all these metal ions at 1 mM concentrations were applied simultaneously and together with Cu(II) ions the interference towards Cu(II) ions determination increased up to 40%. Also no additional peaks were visible in related potential range, which would clearly indicate interfering effect. Takeuchi et al. have published research based on DPV results of Cu(II) detection, which are consistent with the results presented here. Addition of interfering metal ions reduces Cu(II) ion peak current and no other peaks have been observed in potential range between −0.3 V and +0.3 V. However in that research authors have also expanded the potential range and interfering metal peaks appeared outside −0.3 V and +0.3 V potential range [48]. In order to perform exact determination of interfering metals that are present in the sample together with Cu(II) ions it is essential to know the potentials of current peaks of interfering ions (Table 1).

During the investigation of the stability of GC/MWCNTs/3NA(red), electrode was kept at +4 °C temperature for 0, 1, 5 and 14 days in closed vessel with Ar gas and their sensitivity towards Cu(II) ions has been investigated using DPV. It has been noticed that the stability of analytical signal of electrode was decreasing gradually and after 5 days it became stable. After 14 days of incubation GC/MWCNTs/3NA(red) remained at 50% level of its' original electrochemical response towards Cu(II) ions (Fig. 4). In our previous research the stability of GC electrode modified with poly-4NA for Cu(II) ion determination has been analyzed within 4 days and

Table 1
Interference of various metal ions to DPV-based analytical signal of GC/MWCNTs/3NA electrode registered in BR buffer, pH 5.0 vs. Ag/AgCl/KClsat.

Ions	Concentration (mM)	DPV peak curent (μA)	Relative difference from 1 mM Cu^{2+}
Cu^{2+}	1	−42.12	0
All metals	1	−25.38	40%
Co^{2+}	1	−26.63	37%
Mn^{2+}	1	−27.71	34%
Fe^{3+}	1	−31.50	25%
Cd^{2+}	1	−33.60	20%
Pb^{2+}	1	−32.22	27%
Zn^{2+}	1	−36.13	14%

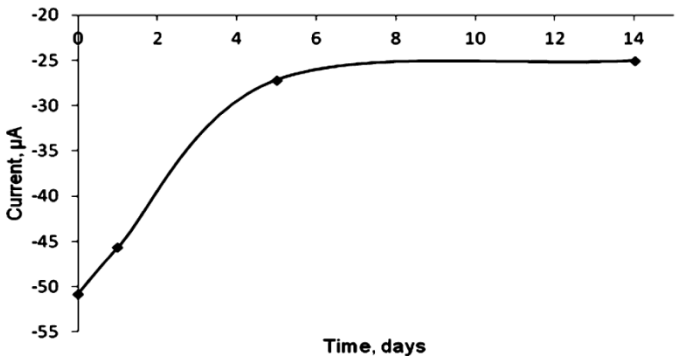


Fig. 4. Stability of DPV-based analytical signal of GC/MWCNTs/3NA(red) electrode in BR buffer solution, pH 5.0 vs. Ag/AgCl/KCl_{sat}.

the results of this test have demonstrated that analyzed electrode remained stable after mentioned period [28]. In other research by Fu et al. glassy carbon electrode, which was dedicated for copper determination, was modified with single-walled carbon nanotubes, gold nanoparticles and immobilized with L-cysteine self-assembled monolayers after 30 days still retained 82% of their initial analytical signal [49].

Compared to the electrodes analyzed in other researches, GC/MWCNTs/3NA(red) electrode showed relatively good storage stability, because after 5 days of incubation still 50% of initial analytical signal remains and later no decrease of analytical signal was observed, when the last stability test was performed after 14 days. Repeatability of differently modified electrodes in Cu(II) ion detection was tested using three similar electrodes prepared at same conditions. Relative standard variation (R.S.V.) of this test was 6.4%. R.S.V. of the reproducibility test was 1.4%. Between measurements for reproducibility electrode was regenerated using EDTA, which is known to be able to form complexes with heavy metals including Cu(II) ions. Zhuang et al. have analyzed the applicability of gold microelectrode for Cu(II) detection and their R.S.V. of reproducibility and repeatability is 5.1% and 3.2%, respectively [50]. In other research, which has been performed by Mohadesi et al., platinum electrode modified with overoxidized polypyrrole doped with Nitroso-R, which was applied for Cu(II) detection, their repeatability R.S.V. test results were in the range of 1.1–1.8% depending on Cu(II) concentration [51]. Another electrode, which has been analyzed for Cu(II) detection by Wang et al., was glassy carbon electrode modified with graphene and gold nanoparticles. R.S.V. for this electrode was calculated as 5.8% [42]. After the evaluation of repeatability and reproducibility results obtained by various electrodes applied in Cu(II) detection, which have been reported in some other researches and comparing them with the results of repeatability and reproducibility that were obtained in the frame of this article, it was determined that here reported GC/MWCNTs/3NA(red) electrode can compete in the determination of Cu(II) ions with other electrodes, which were reported to be suitable for Cu(II) determination [50,51].

Finally, only the GC/MWCNTs/3NA(red) electrode was evaluated for the limit of detection (LOD) value towards Cu(II) ions. The determination of Cu(II) ions was performed for three times and standard deviation values were calculated for all of the concentration values and for each differently modified electrode. Although the GC/MWCNTs/3NA(red) was the most sensitive (0.5×10^{-9} M) electrode for Cu(II) ions out of all electrodes, which were evaluated in this study, however it is still not the best sensitivity because the LOD value reported for the NTA/Reduced-P4NA/GC electrode was 0.5×10^{-12} M [28]. Another electrochemical Cu(II) ion sensor, which showed better sensitivity than our electrode, has been developed by Yang et al. and its detection limit was below 0.2×10^{-12} M. In this sensor analyte-recognizing element has been formed by a covalent attachment of the tripeptide Gly-Gly-His to self assembled monolayer of 3-mercaptopropionic acid formed on the gold electrode [52]. There are some more reports, which showed similar results with sensor presented in recent research, e.g.: Niu et al. have studied the electrochemical Cu(II) determination with a self-assembled monolayer of penicillamine formed on gold electrode that has limit of detection at 4.0×10^{-7} M [9]; Zeng et al. have reported the electrochemical determination of Cu(II) on gold electrode surface by stripping techniques with LOD at 1.0×10^{-10} M [53]; Betelu et al. have reported Cu(II) determination on 4–carboxyphenyl–grafted screen printed electrode with the limit of detection at 5.0×10^{-9} M by using square wave voltammetry [54]; Bai et al. have reported cysteine–modified mercury film electrode suitable for the Cu(II) determination at 5.0×10^{-10} M level by using stripping potentiometry [55].

4. Conclusions

In this research we have presented improved, low cost, easy fabrication, low-time consuming and sensitive method for Cu(II) by electrode based on MWCNTs deposited on GC electrode and then electrochemically modified with 3NA. The resulting GC/MWCNTs/3NA(red) electrode demonstrated that accurate determination of copper by DPV method is possible even in the presence of some interfering metal ions. Advanced analytical characteristics of here evaluated electrode shows great potential for the construction of electrochemical Cu(II) ion sensors and they open a new avenue for the development of sensing systems suitable for industrial application.

Disclaimer

This manuscript has not been published by other articles or simultaneously submitted to other articles for publishing.

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