Desalination and Water Treatment
www.deswater.com
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doi: 10.1080/19443994.2012.719469

50 (2012) 198–205
December

Taylor & Francis
Taylor & Francis Group

Electrochemical determination of copper(II) using modified glassy carbon electrodes

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Received 30 November 2011; Accepted 27 June 2012

ABSTRACT

Electrochemical modification of glassy carbon (GC) electrode surface via electrochemical oxidation of 1-aminoindan in acetonitrile including 100.0 mM of tetrabutylammonium tetrafluoroborate and applicability of electrode modified in this way for electrochemical determination of copper(II) (Cu(II)) were reported in this study. Electrochemical surface modification was performed by cyclic voltammetry in the potential range between +0.9 and +1.5 V vs. Ag/Ag$^+$ (10.0 mM of $AgNO_3$) at the scan rate of 100 mV/s by 30 potential cycles. The modified electrode surface was characterized by cyclic voltammetry, electrochemical impedance spectroscopy and contact angle measurement. The characterization results were compared with the characterization results of bare GC electrode. The results of the amperometric measurements of the modified GC electrode towards Cu(II) ions were investigated. It was determined that the modified electrode surface had electrochemical responses towards Cu(II) ions with high sensitivity, good selectivity, stability, reproducibility and repeatability. According to the results, it is believed that it will be possible to find an application area for this new surface in any industrial fields.

Keywords: Heavy metal; Copper; Electrochemical treatment; Metal determination; Glassy carbon

1. Introduction

In the last 50 years, environmental pollution and human exposure to heavy metals have dramatically surged because of their increasing use in industrial processes. Some metals are key constituents of metallo-proteins and their accumulation leads to various systemic diseases with nervous and/or other ways [1]. For this reason, environmental contamination by trace metals is a serious problem not only for ecosystem, but also for human health [2]. Especially heavy metals such as copper, mercury, lead, zinc, and cadmium or their compounds in environment have been of special concern because they are non-degradable and therefore persistent. From this point of view, in recent years with population increment and industrial development, determination of heavy metal ions has attracted attention [3–5].

On the other hand, among these heavy metals, copper is an essential element in the nutrition of plants, animals and moreover it is also fundamental in many metabolic processes since it is the third most abundant trace element in biological systems [6]. And even chronic deficiency of copper causes anemia of a microcytic type [7]. However, excess of copper may also cause symptoms of gastroenteritis with nausea, hypercupremia, vomiting, myalgia and hemolysis [7].

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For this reason, determination of concentration of copper ions during environmental monitoring is important. Several methods have been proposed for the detection of heavy metals in aqueous solution such as atomic absorption spectrometry (AAS) [8], UV–vis spectroscopy [9], colorometric analysis [10], ion chromatography [11], inductively coupled plasma mass spectrometry [12] and electroanalytical techniques [13]. However, in recent years, determination of these ions with low detection limits has been carried out by electrochemical methods because of their simplicity, simultaneous determination, low-cost, accurateness, sensitivity and high stability when compared to instrumental analysis [4,14]. For this reason, modification of electrode surfaces has been an important area of research in electrochemistry and material science. Especially, covalently modified carbon electrodes for catalytic, analytical and biotechnological applications have garnered interest, since carbon-based substrates have advantages such as chemical inertness, broad useful potential range, low residual current, low cost, easy modification and great versatility [15].

From this point of view, this study was based on the electrochemical determination of copper(II) (Cu (II)) ions in aqueous solutions through the electrochemical modification of glassy carbon (GC) electrode by 1-aminoindan (1AIn) in non-aqueous media. The bare and modified electrode surfaces were characterized by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and contact angle measurement. The approvals for the layer formation on the GC electrode surface through the sensitivity of the surface towards the Cu(II) ions were investigated by amperometry technique. According to our best knowledge, this study is the first successful application of 1AIn in the preparation of new surfaces for the electrochemical determination of metal ions in aqueous solutions.

2. Experimental

2.1. Chemicals and instruments

All chemicals needed for the experiments were purchased from Merck, Riedel and Sigma-Aldrich companies and were of reagent grade. 1AIn used for surface modification was purchased from Acros (New Jersey, USA) and 10.0 mM solution of 1AIn was prepared in acetonitrile (CH_3CN) including 100.0 mM of tetrabutylammonium tetrafluoroborate (TBATFB).

The electrode modification experiments were performed in both aqueous and non-aqueous media. In the aqueous media experiments, Britton–Robinson (BR) buffer solutions with different pH values (2.0, 7.0 and 12.0) were used while in non-aqueous media experiments, CH_3CN including 100.0 mM of TBATFB was being used. All chemicals for preparation of BR buffer solution were of extra pure grade and were obtained from Merck Ltd (Darmstadt, Germany).

The electrochemical techniques used for modification and characterization of electrode surfaces were applied by a traditional three-electrode cell system with potentiostat/galvanostat PCI4/750 from Gamry Instruments (Warminster, USA), which was equipped with a C3 cell stand. BAS model MF-2012 GC electrode was used as working electrode with a geometric area of 0.071 cm^2. The reference electrode was used as Ag/AgCl in saturated KCl ($Ag/AgCl/KCl_{sat}$) for aqueous media and as Ag/Ag^+ (10.0 mM of $AgNO_3$) ($Ag/Ag^+/AgNO_3$) for non-aqueous media. The Pt wire was used as an auxiliary electrode. The amperometric measurements for the determination of Cu(II) ions were carried out in an electrochemical cell including BR buffer solution, pH 7.0, combined with a three-electrode configuration system using an Autolab PGSTAT 30 Potentiostat/Galvanostat operated by the GPES software Eco Chemie (Utrecht, Netherlands). In amperometric measurements $Ag/AgCl/KCl_{sat}$ and Pt wire were used as the reference and the auxiliary electrodes, respectively while 1-aminoindan-modified GC (1AIn/GC) electrode was being used as working electrode. All experiments were carried out inside a Faraday cage at room temperature (at 25˚C). All solutions used for the voltammetric measurements were deaerated with argon (99.999%) at least 5 min before the electrochemical treatment.

2.2. Electrode preparation, modification and characterization procedures

In order to avoid contamination of oxidation products and to obtain a clean renewed electrode surface, the GC electrode surfaces were pretreated as reported previously [3,4,16]. The electrochemical modification of the pretreated bare GC electrode surface was performed by CV using PHE 200 software of Potentiostat/Galvanostat PCI4/750 from Gamry Instruments (Warminster, PA, USA). The process was carried out in CH_3CN including 10.0 mM of 1AIn and 100.0 mM of TBATFB. The prepared electrode was named as 1AIn/GC electrode and it was prepared for each step freshly just before the experiments.

The bare and modified GC electrodes were characterized by CV, EIS and contact angle measurement. The characterization with CV was carried out in the presence of 1.0 mM of $K_3[Fe(CN)_6]$ ($Fe(CN)_6^{3-}$) in BR buffer solution, pH 2.0 and 1.0 mM of ferrocene in CH_3CN including 100.0 mM of TBATFB as redox active molecules by the same software used for the electrochemical modification of the GC electrode surface. The characterization with EIS was carried out by EIS 300 software of the same electrochemical analyser used for the electrochemical modification and characterization of bare and modified GC electrode surfaces. The EIS experiments were performed in 100.0 mM of KCl containing 1.0 mM of equiv-molar ratio of $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ ($Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$) redox couple at the frequency range 0.05–75.000 Hz at 10 mV oscillation amplitude and at constant electrode potential of 0.215 V. The contact angle measurements were performed with a contact angle measuring system, CAM 200 (KSV Instruments Ltd, Helsinki, Finland) at 25℃. The sessile drop method was used to measure the contact angle and the water drop on the bare and modified GC electrode surfaces was formed by manual micro-syringe. Both the average values of the left and right contact angles, standard deviations of multiple measurements and drop dimension parameters were automatically calculated from the digitalized image.

2.3. Analytical application of modified GC electrode

In order to present an application area for the new electrode and also to approve the presence of the layer on the modified electrode surface differently from bare GC, the applicability of the modified electrode was investigated for the electrochemical determination of Cu(II) ions in aqueous solutions. For this aim, amperometric signal dependence on varied Cu (II) concentrations was studied in an electrochemical cell including BR buffer solution, pH 7.0, at –400 mV vs. $Ag/AgCl/KCl_{sat}$ and the responses were presented as plots representing changes in current vs. metal ion concentration.

Some additional experiments were performed for the investigation of the modified electrode for its stability, repeatability, reproducibility and selectivity. In order to check the stability of 1AIn/GC electrode, the 1AIn/GC electrode was kept over the BR buffer solution, pH 7.0, at room temperature for 2, 8, 16, 24 and 48 days. Then all of them were used for the determination of 0.1 nM of Cu(II) ions. The reproducibility of 1AIn/GC electrode was investigated by the determination of 0.1 nM of Cu(II) ions with different 1AIn/GC electrodes. The repeatability of the 1AIn/GC electrode was investigated by multiple determinations of 0.1 nM of Cu(II) ions by the same 1AIn/GC electrode. On the other hand, the selectivity of 1AIn/GC electrode for the determination of 0.1 nM of Cu(II) ions was investigated in the presence of Cd(II), Ni(II), Pb (II) and Zn(II) ions. At least five independent electrodes were prepared for each measurement and the results were evaluated by statistical analysis.

AAS was applied as the reference method, and it was performed by AAS spectrophotometer (Unicam 929, Cambridge, UK).

3. Results and discussion

The present work reports the preparation of electrochemically modified carbon electrode surface and possibilities for its application in daily life. Electrochemical modification was performed by electrochemical oxidation of amine group in the structure of the main compound via potential cycling. The interaction of modified electrode with Cu(II) ions was investigated by amperometry technique. The results in each step were presented and also discussed in the following sections with all details:

3.1. Modification of GC electrode

In order to determine an ideal solvent for the electrochemical modification process of GC electrode surface, 10.0 mM stock solutions of 1AIn were prepared in both aqueous and non-aqueous media. For aqueous media, BR buffer solutions in different pH values, pH 2.0, 7.0 and 12.0, were used while CH_3CN including 100.0 mM of TBATFB solution was being preferred for non-aqueous media. However, 1AIn did not solve in BR buffer solution in any pH values, for this reason there had no possibility to perform electrochemical modification process for carbon surface in aqueous media. Because of this, experiments for electrochemical surface modification were performed only in non-aqueous media. From this point of view, surface modification of polished and cleaned GC electrodes was performed with 10.0 mM solution of 1AIn in CH_3CN containing 100.0 mM of TBATFB by potential cycling between +0.9 and +1.5 V at the scan rate of 100 mV/s. Fig. 1 shows the modification voltammogram of GC electrode surface with 1AIn vs. $Ag/Ag^+/AgNO_3$.

As it is seen from Fig. 1 that irreversible oxidation peak was registered at approximately +1250 mV at the first potential cycle. This irreversible anodic peak was attributed to the oxidation of amine group in the structure of 1AIn. The peak current decreased by increasing number of potential cycles and it practically reached the steady-state conditions even in the second cycle. This can be attributed to the fast formation of relatively dense layer on the carbon surface which is not permeable for grafting more 1AIn

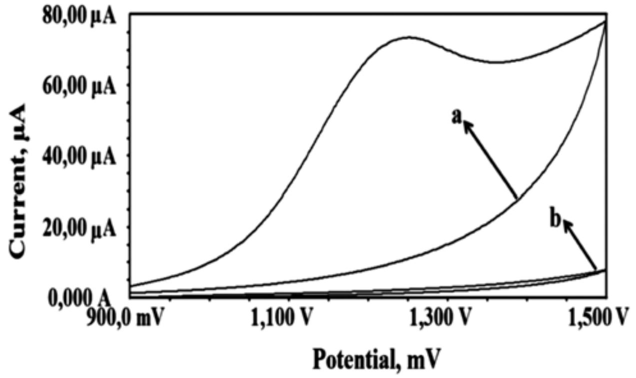


Fig. 1. Cyclic voltammograms of 10.0 mM of 1AIn and 100 mM of TBATFB in CH_3CN at the bare GC electrode: (a) 1st and (b) 30th cycles. The scan rate was 100 mV/s vs. $Ag/Ag^+/AgNO_3$.

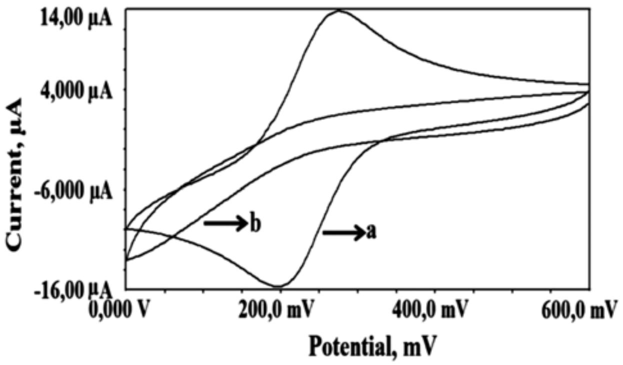


Fig. 2. The cyclic voltammograms of 1.0 mM of $Fe(CN)_6^{3-}$ in BR buffer solution, pH 2.0, at the (a) bare GC and (b) 1AIn/GC electrodes. The scan rate was 100 mV/s vs. Ag/AgCl/ KCl_{sat}.

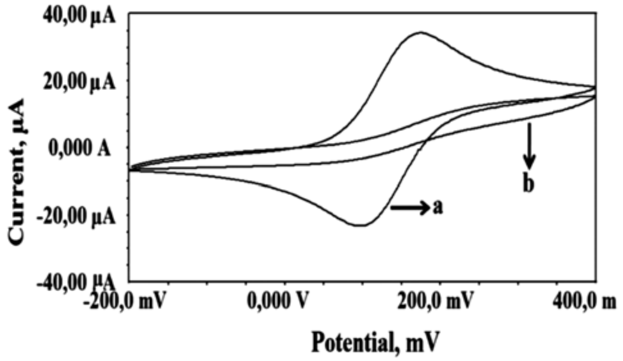


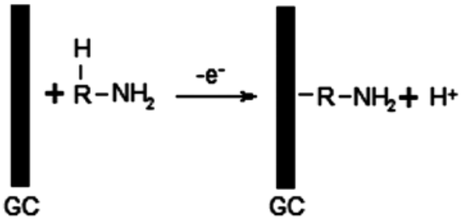
Fig. 3. The cyclic voltammograms of 1.0 mM of ferrocene in CH_3CN containing 100 mM of TBATFB at the (a) bare GC and (b) 1AIn/GC electrodes. The scan rate was 100 mV/s vs. $Ag/Ag^+/AgNO_3$.

molecules, in another way further oxidation of 1AIn on 1AIn/GC electrode surface. This idea is based on the similar proposed offers in many studies performed with the compounds including amine groups in their structure: e.g. Oztekin et al. have performed the electrochemical polymerization of 4-nitroaniline in which irreversible peak at the first potential cycle was registered at approximately +1050 mV [16]. Another example can be the study of Zhao et al. in which cyclic voltammograms were recorded through the oxidation of amine groups in the structure of 2-amino-4-thiazoleacetic acid for the modification of GC electrode surface in 0.5 M H_2SO_4 solution and an oxidation peak was observed at +1105 mV [17].

3.2. Characterization of bare and 1AIn/GC electrodes

The characterization of bare GC and 1AIn/GC electrodes was realized by CV, EIS and contact angle measurement. In order to characterize the formation of 1AIn layer on GC electrode surface, the cyclic voltammograms were registered in the presence of redox active compounds: 1.0 mM of $Fe(CN)_6^{3-}$ in BR buffer solution, pH 2.0, and 1.0 mM of ferrocene in CH_3CN containing 100.0 mM of TBATFB. Figs. 2 and 3 show the cyclic voltammograms of $Fe(CN)_6^{3-}$ and ferrocene at the bare and modified GC electrode surfaces, respectively. As it is seen from Figs. 2 and 3, oxidation/reduction reaction of redox probes was completely blocked at the 1AIn/GC electrode, while well-defined reversible redox peaks were being observed at the bare GC electrode. The blockage for oxidation/reduction reaction of redox probe is a reliable indication of grafting of guest molecule to the GC surface. Here presented results are in harmony with the study presented by Oztekin et al. in which the similar blockage effects for the electron transfer of the redox probes at the phenanthroline-modified GC electrode were observed [5]. However, the contrary situation also could be possible as mentioned in the same study such as the activation effect for the electron transfer of the redox probes including amine groups [5].

Substituting groups on the modified surfaces may markedly affect the electrochemical responses of the surfaces if they are reacted with redox probes when compared with the bare surfaces. Moreover the values of acidity constants of the layers significantly can differ the surfaces from each other [16]. For this reason, the cyclic voltammograms of $Fe(CN)_6^{3-}$ as a redox probe in different pH values (2.0; 4.0; 6.0; 7.0; 9.0; 11.0) of BR buffer solution at the 1AIn/GC electrode surface were recorded in order to determine the surface properties of the new electrode. Previously discussed results in Section 3.1. demonstrated that 1AIn could be grafted to the bare GC electrode surface via the electrochemical oxidation of amine groups (Fig. 1). The electrochemical characterization results in the presence of redox probes approved this idea in the formation of the layer (Figs. 2 and 3). However, during this electrochemical characterization process, the mechanism of grafting was not clarified. Whereas there were just two main possibilities: (i) The amine group of 1AIn structure could be free on the carbon surface after modification and (ii) the amine group could not be free because of the formation of C–N bond between 1AIn molecule and carbon surface after amine oxidation during modification process. If 1AIn was not grafted to the GC surface through amine oxidation and if amino groups were free (Scheme 1), at relatively high pH values of BR buffer solution ($pH >> pK_a$), the amine group of 1AIn dissociated and charged negatively and the oxidation/reduction peaks of $Fe(CN)_6^{3-}$ should gradually diminish because the increase of negative charge on the layer of 1AIn/GC electrode lead to electrostatic repulsion of $Fe(CN)_6^{3-}$. On the other hand, at low pH values of buffer solution ($pH << pK_a$), the 1AIn on the layer should be protonated. So 1AIn/GC electrode surface was positively charged and $Fe(CN)_6^{3-}$ ions were attracted by 1AIn layer, through this interaction $Fe(CN)_6^{3-}$ ions were able to access the underlying GC surface and attend at oxidation/reduction process via the demonstration of a well-defined redox peaks. The cyclic voltammograms illustrating oxidation/reduction behaviour of $Fe(CN)_6^{3-}$ at 1AIn/GC electrode vs. pH are presented in Fig. 4. As it is seen from Fig. 4 that at any pH value, the electron transfer for $Fe(CN)_6^{3-}$ was blocked so it was thought that there was not any functional group (e.g. amine groups) on the modified surface. This simple electrochemical characterization proved the proposed idea about the amine oxidation process in the grafting of GC electrode surface described more in details in Section 3.1. Due to these explanations, the mechanism for the electrochemical layer formation on the GC electrode surface was proposed as presented in Scheme 2.



Scheme 1. Proposed mechanicsm for layer formation through the ring.

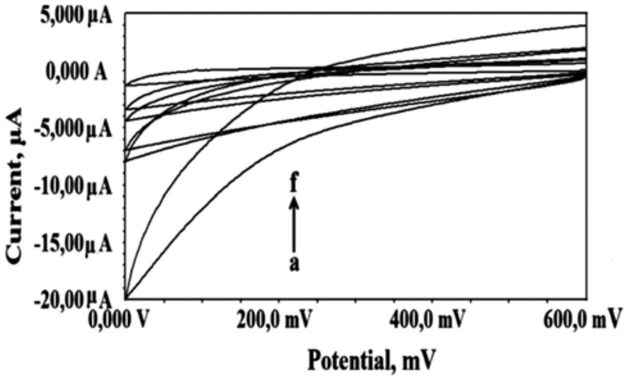
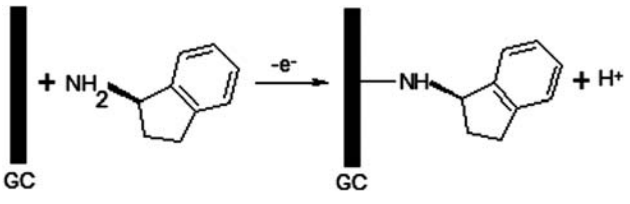


Fig. 4. Cyclic voltammograms of 1.0 mM of $Fe(CN)_6^{3-}$ in BR buffer solutions of various pH values at the 1AIn/GC electrode. Corresponding pH values are: (a) 2.0, (b) 4.0, (c) 6.0, (d) 7.0, (e) 9.0 and (f) 11.0. The scan rate was 100 mV/s vs. Ag/AgCl/ KCl_{sat}.



Scheme 2. Proposed mechanicsm for layer formation through amine oxidation.

The EIS was applied as another characterization technique for the investigation of the changes in the surface properties of GC electrode after its modification by 1AIn. Fig. 5(A) and (B) represent typical Nyquist plots of bare and 1AIn/GC electrodes in 100.0 mM of KCl containing 1.0 mM of equiv.-molar ratio of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$. They can be presented in two frequency region: (i) at high frequency, the semicircle part represents the charge transfer resistance that limits the electron transfer process. The intercept with real axis at high frequencies corresponds to the electrolyte resistance and (ii) at lower frequency, the linear part is an electrochemical characteristic of a mass diffusion limited electron transfer process, which is represented by Warburg impedance [18]. Fig. 5(C) shows the overlay plots of EIS of bare and modified GC electrodes. As it is seen from Fig. 5 (C) Nyquist plot of bare GC electrode represents a straight line at low frequency with a very small semicircle at high frequency region, the Nyquist plot of 1AIn/GC electrode represents a semicircle at high frequency region, implying that modified GC surface shows a blocking ability for electron transfer reaction. The main parameter values obtained from the equivalent circuit elements with EIS spectra of the bare and 1AIn/GC electrodes were given in Table 1. The

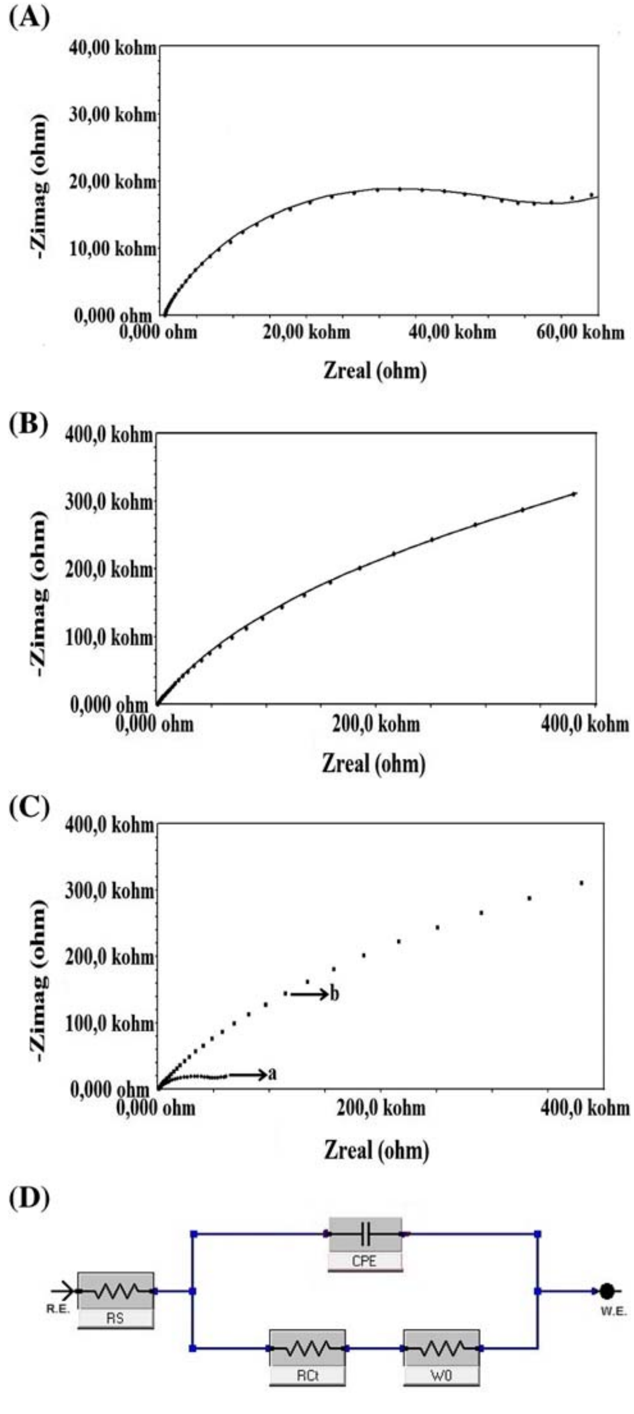


Fig. 5. (A) Fitting of impedance spectrum of 1.0 mM of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ in 100 mM of KCl at the bare GC electrode. (B) Fitting of impedance spectrum of 1.0 mM of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ in 100 mM of KCl at the 1AIn/GC electrode. (C) Nyquist plots of 1.0 mM $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ solution in 100 mM of KCl at the (a) bare and (b) 1AIn/GC electrodes. Frequency range was from 0.05 to 75,000 Hz, the modulation amplitude was 10 mV, working electrode potential was +0.215 V vs. Ag/AgCl/KCl_{sat}. (D) Randles-type equivalent circuit of the 1AIn/GC electrode.

electron transfer resistance of the bare GC electrode (54.72 Ω) was calculated as lower than for 1AIn/GC electrode (610.00 Ω) which confirms the fact that the electron transfer is very fast at bare GC electrode. These results are in agreement with previously published results [16,18,19]. The equivalent circuit was presented in Fig. 5D, including the solution resistance (R_s), the charge transfer resistance (R_{ct}), the Warburg resistance (W_o) and the constant phase element (CPE). In order to calculate the electron transfer rate constant, k°, for $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ at different surfaces, Eq. (1) can be used to evaluate the high frequency part of EIS spectra which was presented with all details in Table 1.

$$R_{ct} = \frac{RT}{(nF)^2 A k^\circ C} \tag{1}$$

where A is the electrode area; n is number of electrons requested for oxidation/reduction of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ system, C is the molar concentration of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$; R is ideal gas constant, T is temperature in Kelvin degree; F is Faraday constant. Values for k° were calculated as 1.79×10^{-4} and 1.61×10^{-5} cm/s for bare and 1AIn/GC electrodes, respectively. The covered electrode area was also calculated according to Eq. (2).

$$\theta = 1 - (R^\circ_{ct}/R_{ct}) \tag{2}$$

where R°_{ct} is the charge transfer resistance of the bare GC electrode and R_{ct}, is the charge transfer resistance of the 1AIn/GC electrode; Q is the area that is modified with 1AIn. The R_{ct} is the value of each electrode surface, which is obtained with fitting of Nyquist plot of related electrode surfaces. It was calculated that EIS signal is equivalent to 91.02% coverage of the GC surface.

Table 1
The main parameters of EIS circuit for 1.0 mM $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ solution in 100 mM of KCl at the bare and 1AIn/GC electrodes. Frequency range is from 0.05 to 75,000 Hz with 10 mV of wave amplitude at a formal potential of 0.215 V, R_s: solution resistance, α-CPE expontet, W_d: Warbug diffusion impedance, R_{ct}: charge transfer resistance, Y_0: constant value of CPE

Simulation data	Bare GC	1AIn/GC
R_s (Ω)	500.0	709.0
Y_0	3.350×10^{-6}	2.609×10^{-6}
α (m)	720.0×10^{-3}	728.9×10^{-3}
W_d (Ω)	79.10×10^{-6}	5.802×10^{-6}
R_{ct} (Ω)	54.72×10^3	610.0×10^3

The contact angle measurement was employed as additional characterization technique for the comprassion of the properties of bare and 1AIn/GC electrodes since the variation of the wetting force is extremely sensitive to the surface modification. The contact angle values for water on bare GC and 1AIn/GC electrodes were measured as 85.09° ± 2.3° and 36.26° ± 4.7°, respectively. The results showed that the bare GC electrode surface lost its hydrophobic properties after modification by the 1AIn. The differences between the contact angles of both surfaces approved that through the electrochemical modification of GC electrode, the surface gained new properties as reported also in previous literatures [15,16].

3.3. *Analytical application for 1AIn/GC electrode*

In order to find an application to the new surface, the interaction between Cu(II) ions and modified surface was investigated by the addition of varied concentrations of Cu(II) ions (0.001–10 nM) to the electrochemical cell including BR buffer solution, pH 7.0. Fig. 6 shows the current change of the bare and 1AIn/GC electrodes towards the increasing amount of Cu(II) ions. The current change for the bare GC electrode was not significant with a linear response (Fig. 6, curve a). It attributed to the insensitivity of the surface through the Cu(II) ions. However the 1AIn/GC electrode exhibited a good sensitivity with a hyperbolic dependence on Cu(II) concentration (Fig. 6, curve b). It can be attributed to the complex formation between the film formed on the GC electrode and metal ions. This showed the greatly enhanced sensitivity and decreased the lowest detectable concentration of Cu(II) ions with 1AIn/GC electrode. Here can be presented several examples for the modification of electrode surfaces with their applicability in determination of Cu(II) ions [20,21]. However through this modified electrode, the detection limit (0.1 pM) was calculated lower than most of the previously published literatures.

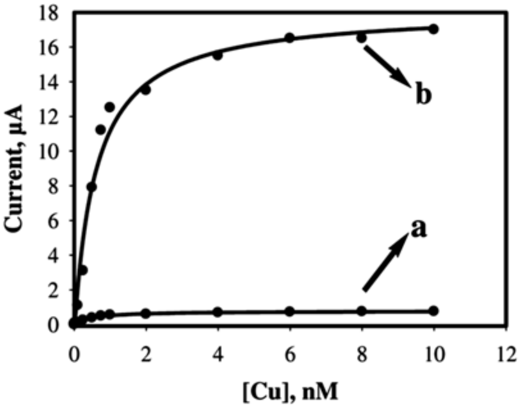


Fig. 6. Amperometric responses of the (a) bare and (b) 1AIn/GC electrodes at –400 mV vs. Ag/AgCl/KCl$_{sat}$ upon successive addition of 0.001–10 nM of Cu(II).

In addition to the highest sensitivity of the modified electrode for the determination of Cu(II) ions, the properties in the point of reproducibility, repeatability, selectivity and stability of the modified electrode were also investigated in order to evaluate its performance. The reproducibility of the 1AIn/GC electrode was investigated by successively determining 0.1 nM Cu(II) with five independently prepared electrodes, and the relative standard deviation (RSD) was calculated as 1.9%, demonstrating a good reproducibility. The repeatability of the 1AIn/GC electrode was evaluated by examining the amperometric responses five times with the same electrode and the RSD was calculated as 3.1%. The 1AIn/GC electrode had good stability since the 1AIn/GC electrode had a decreased value of over 45% for the ΔI_{max} after 48 days. Selectivity of 1AIn/GC electrode was investigated through the influence of Cd(II), Ni(II), Pb(II) and Zn(II) ions as interfering ions for the amperometric detection of Cu(II) ions. The results showed that there was no significant change in the amperometric response of the 1AIn/GC electrode up to 1000 times higher concentration of interferences than Cu (II) ions. AAS was selected as reference method to prove electrochemically obtained results. The statistical evaluation of electrochemical and AAS-based determinations showed acceptable precision of the proposed electrode.

4. Conclusion

In this paper, the preparation of new electrode through the electrochemical modification of carbon surface with 1AIn and its application were reported. The 1AIn/GC electrode was very stable and it exhibited high sensitivity towards Cu(II) ions. Selective determination of Cu(II) ions by the 1AIn/GC electrode was based on the interaction between the 1AIn layer on the GC electrode and Cu(II) ions. It is believed that for the future, the 1AIn/GC electrode will be applied for the determination of Cu(II) ions in different samples and/or further determinations.

Acknowledgements

This study was supported by the Selcuk University Research Foundation under the project number of 10201153. The authors would like to thank them for their financial support.

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