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Electrochemical Evaluation of Binding Copper and Copper Histidine Complex on Histidine Modified Gold Electrode

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Histidine monolayer was adsorbed on the surface of the gold electrode in aim to investigate electrochemical behavior of Cu^{2+} ion and Cu-His complex. Formation of the layer on the gold surface was investigated with cyclic voltammetry with *p*-benzoquinone/hydroquinone redox pair. Interaction between the modified electrode and Cu^{2+} and Cu-His was characterized with cyclic voltammetry and adsorptive anodic stripping voltammetry. Coupling of the Cu^{2+} and Cu-His onto the modified electrode was successfully done for a wide range of tested concentrations. Electrode response was linearly proportional to log $c(Cu^{2+})$ and log c(Cu-His) with correlation coefficient $R^2 = 0.9945$ and $R^2 = 0.9807$ respectively.

Keywords: Gold electrode, Histidine, Adsorptive anodic stripping voltammetry, Quartz crystal microbalance

1. INTRODUCTION

Understanding the nature of biomolecules interactions is fundamentally important in the domain of biotechnology. Synergy between biomolecules, metal surfaces and cationic species can provide interfaces with required performance which can enable fabrication of new biomaterials for medical and pharmaceutical research and sensors/biosensor design.

Histidine (His) is essential amino acid for humans [1] and has significant role in metabolism and wide range of physiologocal processes [2]. Copper is essential trace element and it’s deficiency and excess can trigger number of diseases [3]. It is known that Cu^{2+} can be coordinated to hisitidine between carboxyl group and primary and secondary amine groups in imidazole ring, forming very stable compound.

Numerous chelators self assembled on the surface of a metal electrode are used for complexation of different cations. The most studied compounds include penicillinamine [4], meso 2,3-dimercaptosuccinic acid [5] and reduced glutathione [6]. Recently, thiol-based SAM functionalized by a carboxyl group responsible for complexation of Zr^{4+}, UO_2^{2+}, Pb^{2+} and Cu^{2+} [7-10] were prepared.

Liedberg *et al*. [11] described one oxygen coordination between the carboxyl group of histidine and gold surface while Marti *et al*. [12] suggested that the both oxygen atoms of the carboxyl group coordinate to gold. Regardless of whether histidine binds to gold through one or both oxygen atoms the remaining unbound amino group and imidazole nitrogen atom emerge as possible binding sites for additional complexation for metal cations. Histidine and Cu^{2+} cation can form monodentate [13], bidentate [14, 15] or tridentate [16] complexes. Coordination number for copper histidine complex can be 1 or 2. Higher stability was determined for 2:1 histidine to copper ratio [17]. This capability of Cu-His (1:1) complex to produce a stable complex in coordination with another histidine was tested in this study. Analytical methods for determination of histidine have been developed, particularly in food samples, such as chemiluminiscence [18], capillary electrophoresis [19], HPLC [20], potentiometric [21] and recently amperometric [22] method.

Among many different methods for determination of metal cations coordinated to a self assembled ligand, adsorptive stripping voltammetry is often used. Adsorptive stripping voltammetry is based on preconcentration of metal cation and stripping of accumulated metal ions. Adsorption transfer stripping voltammetry (AdTSV) is a variation of the anodic and cathodic stripping voltammetry. The distinction of AdTSV is in accumulation step which is accomplished during a process of adsorption [23].

Quartz crystal microbalance (QCM) is sensitive weight measuring device based on the piezoelectric effect. Sauerbrey first recognized the possibilities in application of QCM technology [24] and from then on QCM was used for numerous objectives.

In the present work we investigated formation of His layer on the surface of the gold electrode (Au/His). The main method was the cyclic voltammetry (CV) but complementary QCM measurements were also performed. Following the layer formation, AdTSV was used for the evaluation of binding Cu^{2+} and Cu-His complex on Au/His modified electrode.

2. EXPERIMENTAL

2.1. Chemicals and solutions

All the reagents used were of analytical grade. L-histidine (His) was obtained from Sigma-Aldrich (St. Louis, USA). *P*-benzoquinone (PBQ) was purchased from Fluka (Buchs, Switzerland). Sodium dihydrogen phosphate, sodium hydrogen phosphate, potassium chloride, copper(II) nitrate, acetic acid, sodium acetate and sodium perchlorate were from Kemika (Zagreb, Croatia). Hydroquinone (H_2Q) was from Merck (Darmstadt, Germany). 0.1 M phosphate buffer solution, pH = 7.7 (PB) and 0.1 M acetate buffer pH = 4.6 (AB) both containing 0.1 M sodium perchlorate were used. Redox probe solutions were prepared daily. All solutions were prepared with deaerated double deionized water from Millipore-MilliQ system (USA).

2.2. Preparation of Au/His electrode

Gold disc electrodes were prepared by pressing gold wire (purity 99.999%, 1.00 mm diameter, Aldrich, USA) into Teflon rod. Electric contact was made by copper wire at one end of the rod. The gold surface was polished with SiC powder of different mesh (240, 800, and 1200) and with Al_2O_3 powder (1 and 0.25 μm). After polishing, the electrode was sonicated in ultrapure water for 5 min followed by immersing in Piranha solution ($v(H_2O_2$, conc.): $v(H_2SO_4$, conc.) = 1:3) for 5 min. Then the electrode was rinsed with ultrapure water, sonicated in methanol and electrochemically polished in 0.1 M $HClO_4$ between 0 and 1.5 V until stable voltammogram was obtained. The scanning of final voltammogram was finished at 0 V. The real electrode surface area was calculated from the integration of reduction peak at 0.84 V *vs*. reference electrode assuming 482 $\mu C/cm^2$ for AuO reduction [25]. A roughness factor was calculated as the ratio of real and geometric area and was in range 1.4 - 1.6. Modification of the gold electrode was performed in 100 mM His water solution for approximately 2 h at room temperature. After removal from His solution the electrode was rinsed with ultrapure water to eliminate physically adsorbed species. Surface coverage (Γ) was calculated from peak current (Fig. 2) according to equation (1) [26]:

$$I_p = \frac{n^2 \cdot F^2 \cdot A \cdot \Gamma \cdot v}{4 \cdot R \cdot T} \qquad (1)$$

where Γ is the amount of adsorbed His, v is the scan rate, A is the surface of the electrode, I_p is the peak current and *n*, *F*, *R* and *T* have their common meanings and was 19.85 $nmol/cm^2$.

2.3. Sample preparation

Accumulation of Cu^{2+} was carried out under open circuit potential by immersion of the Au/His electrode into 5 mL of stirred Cu^{2+} solution for 10 min. Standard solutions were prepared in the range between 10^{-8} and 10^{-3} M. After accumulation the Au/His/Cu^{2+} electrode was rinsed with ultrapure water to eliminate physically adsorbed ions before electrochemical measurements. A 20 mM solution of Cu-His complex was prepared in deinoized water by mixing equimolar concentrations of $CuNO_3$ and His and successive dilution to the range between 10^{-8} and 10^{-4} M. Accumulation of Cu-His complex was carried out under open circuit potential by immersion of the Au/His electrode into 5 mL of stirred Cu-His solution for 15 min. After accumulation the Au/His/Cu-His electrode was rinsed with ultrapure water to eliminate physically adsorbed species before electrochemical measurements.

2.4. Instrumentation

Cyclic voltammetry (CV) and adsorption transfer stripping voltammetry (AdTSV) were carried out on Potentiostat 264 A (Princeton Applied Research, USA) coupled to a computer by ED410 e-corder (eDAQ-Australia) for data collecting and analysis. The CV and AdTSV measurements were performed using Chart & Scope software (eDAQ-Australia). All electrochemical measurements were carried out in a three-electrode cell. The gold disc electrode was used as the working electrode, while platinum wire and Hg|Hg_2Cl_2|KCl saturated (SCE) electrode were used as the counter and reference electrode, respectively. Measurement solutions were deaerated with nitrogen gas for 10 min before measurements. All measurements were performed at room temperature. The applied potential scan rate in CV was 50 mV/s.

Quartz crystal microbalance measurement was performed on Quartz Crystal Digital Controller, QCM200 (Stanford Research Systems, USA) connected to a computer by LabVIEW.

Cu-His complex formation was tested by recording the spectra in the range between 400 and 800 nm using UV-VIS spectrophotometer DMS-80, Varian, USA (data not shown).

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry of Au and Au/His electrodes

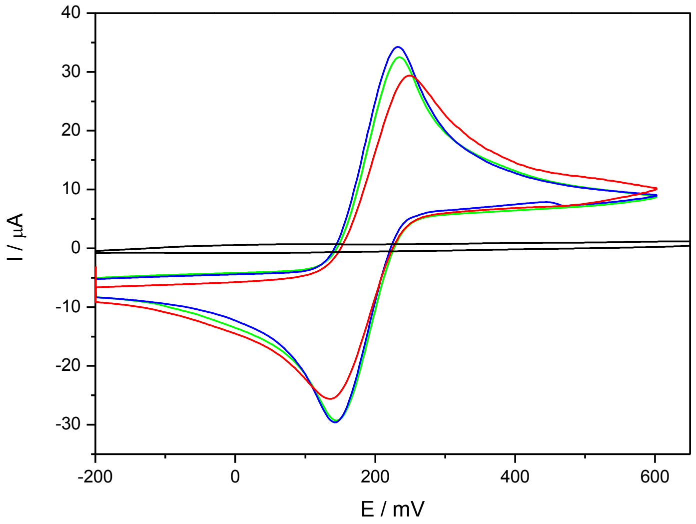

Figure 1. Cyclic voltammogram of Au in 0.1 M AB pH = 4.6 containing 0.1 M $NaClO_4$ (black), in 0.1 M AB pH = 4.6 containing 0.1 M $NaClO_4$ with 1 mM His (black), in 0.1 M AB pH = 4.6 containing 0.1 M $NaClO_4$ with 5 mM PBQ/H_2Q (green) and of Au/His in 0.1 M AB pH = 4.6 containing 0.1 M $NaClO_4$ with 5 mM PBQ/H_2Q (red) and of Au/His electrode after acid treatment in 0.1 M $HClO_4$ (blue). Scan rate 50 mV/s.

In order to electrochemically characterize Au and Au/His electrodes cyclic voltammetry experiments were employed. Au electrode did not demonstrated response (Fig. 1) in tested potential range in 0.1 M AB pH = 4.6 containing 0.1 M $NaClO_4$ (black) nor did in the same buffer with addition of 1 mM His (black). Identical electrode in AB with 5 mM PBQ/H_2Q (green) exhibited well defined voltammogram with anodic and cathodic peak at 234 mV and 143 mV, respectively (ΔE_p = 90 mV). Following the His adsorption on the Au electrode cyclic voltammogram of Au/His electrode was recorded in 0.1 M AB pH = 4.6 containing 0.1 M $NaClO_4$ with 5 mM PBQ/H_2Q (red). Changes on the electrode surface can be investigated via electron transfer reactions of the reversible redox pair on the modified and unmodified surface [27]. Assembly of the monolayer on the electrodes slows electron transfer reactions causing reduction in measured peak current (I_p) and increase in peak-to-peak separation (ΔE_p) [28]. It is evident that cyclic voltammogram (red) exhibited decrease in peak current (~ 5 µA) and enlargement peak-to-peak separation (ΔE_p = 114 mV) relative to bare Au as a result of His adsorption on the gold surface. Blue curve corresponds to Au/His electrode subsequent to treatment in 1 M perchloric acid for 5 min. The response of the modified electrode after treatment in highly acidic environment became almost the same as green curve due to protonation of carboxyl group of His. The protonated carboxyl group has lost capability of binding to Au surface and His was released into the solution. This is in agreement with Liedberg's [11] and Marti's [12] conclusion on the contribution of the carboxyl group of His for adsorption to gold.

Fig. 2 illustrates cyclic voltammogram of Au and Au/His electrodes in 0.1 M PB pH = 7.7 containing 0.1 M $NaClO_4$. It is evident that Au and Au/His modified electrode displayed no response in buffer solution (black). After Au and Au/His electrode immersion in 4 mM $CuNO_3$ solution for 10 min, green and red voltammgrams were recorded. Green curve refers to Cu^{2+} physically adsorbed onto Au (Au/Cu^{2+}) and was observed at 190 mV while red curve refers to Cu^{2+} complexly bound on Au/His (Au/His/Cu^{2+}) and was noticed at 178 mV. The recording of voltammogram started at negative potential (-200 mV), at which Cu^{2+} reduces to Cu. Increase of the potential resulted in appearance of anodic peaks corresponding to oxidation of copper to Cu^{2+}. Cathodic waves correspond to Cu^{2+} reduction. Decrease in cathodic current, due to diffusion of Cu^{2+} ions from the surface to the solution is evident.

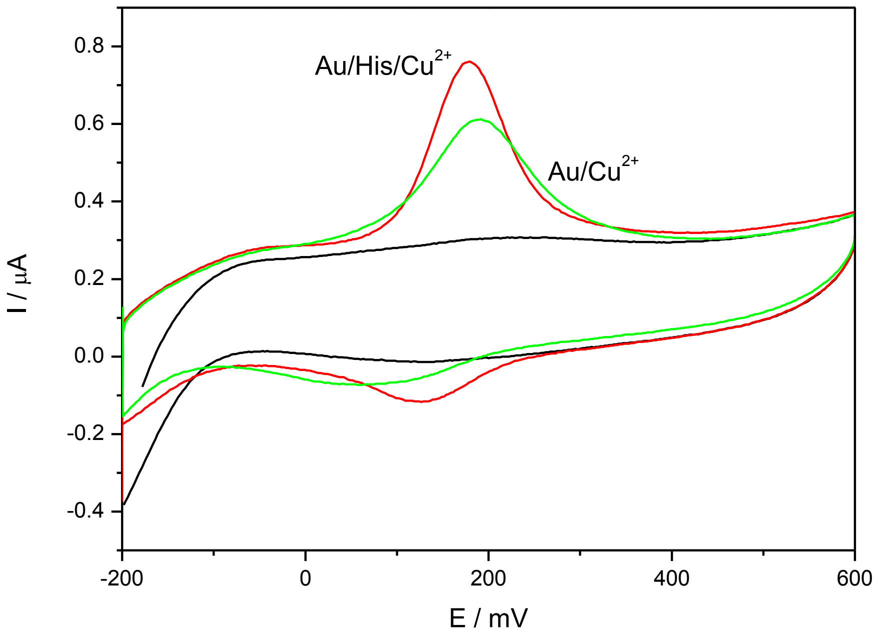

Figure 2. Cyclic voltammogram of Au and Au/His (black) in 0.1 M PB pH = 7.7 containing 0.1 M $NaClO_4$ and of Au (green) and Au/His (red) in 0.1 M PB pH = 7.7 containing 0.1 M $NaClO_4$ after accumulation in 4 mM $CuNO_3$ for 10 minutes. Scan rate 50 mV/s.

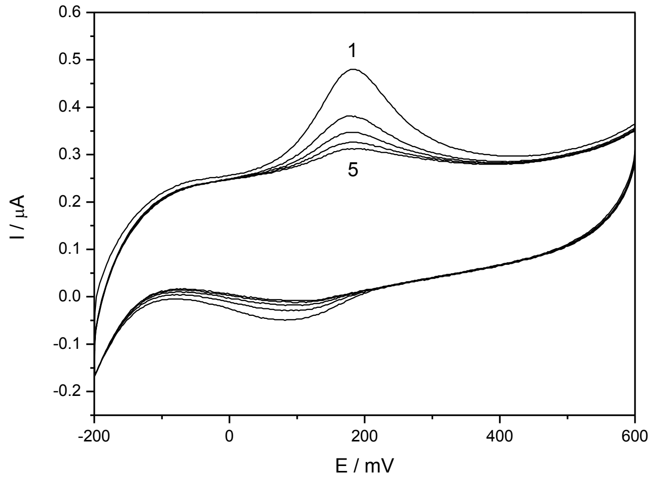

Figure 3. Consecutive cyclic voltammograms of Au/His electrode coordinated by Cu^{2+} recorded in 0.1 M PB pH = 7.7 containing 0.1 M $NaClO_4$. 1 - first cycle, 5 - final cycle.

There has been a debate in scientific community concerning the electrochemistry of Cu^{2+} on the modified surfaces. Previous investigations attributed the behavior to Cu^{2+}/Cu^{+} [29-32] but recent findings demonstrated that the performance is due to Cu^{2+}/Cu^{0} process where copper is underpotential deposited on

gold when electrochemically reduced [33].Fig. 3 presents consecutive cyclic voltammograms of Au/His electrode coordinated by Cu^{2+} recorded in 0.1 M PB pH = 7.7 containing 0.1 M $NaClO_4$. It is apparent that successive potential scanning decreased anodic and catodic peaks and finally, after 5 cycles, both peaks disappeared. After each cycle Cu^{2+} was released from Au/His and removed to solution. The clean Au/His electrode could then be used for new complexation from another test solution.

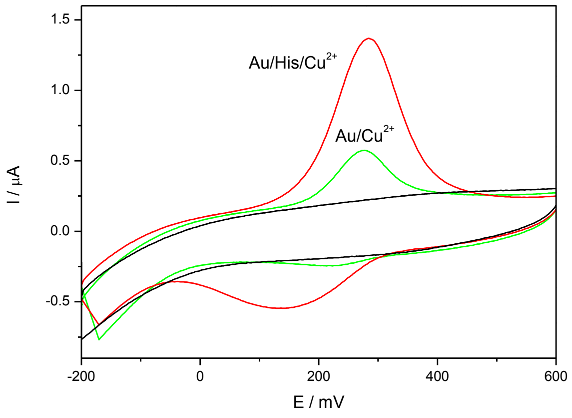

Figure 4. Cyclic voltammogram of Au and Au/His (black) in 0.1 M AB pH = 4.6 containing 0.1 M $NaClO_4$ and of Au (green) and Au/His (red) in 0.1 M AB pH = 4.6 containing 0.1 M $NaClO_4$ after accumulation in 4 mM $CuNO_3$ for 10 minutes. Scan rate 50 mV/s.

Results presented in Fig. 4 highlight the importance of measuring medium. The measurement was carried in 0.1 M AB pH = 4.6 containing 0.1 M $NaClO_4$ and all other experimental conditions were the same as in Fig. 2. In buffer solution, no electrochemical activity was detected for Au or Au/His electrodes (black). Following the accumulation of Cu^{2+} from 4 mM $CuNO_3$ solution (10 min) green and red curves were recorded. Anodic peaks on both curves corresponding to copper oxidation at Au and Au/His electrodes and were observed at 275 mV and 286 mV, respectively. Green curve refers to Cu^{2+} physically adsorbed onto Au (Au/Cu^{2+}) and red curve refers to Cu^{2+} complexly bound on Au/His (Au/His/Cu^{2+}). The anodic peak current for Au has the same value as in Fig. 2. The anodic peak for Au/His at pH = 4.6 has almost two times higher value than that at pH = 7.7. Acidic medium results in protonation of His groups responsible for ion complexsation which facilitates release of Cu^{2+}. The effect of protonation at pH = 4.6 was also confirmed by peak shifts to higher potentials. Reducing the pH to low values increases decomplexation efficiency however at very low pH values protonation of carboxyl His group can destroy the formed His monolayer. Therefore pH = 4.6 was chosen as a compromise between high Au/His electrode response and the stability of prepared surface and used for further AdTSV experiments.

3.2. Quartz crystal microbalance

Complementary QCM measurements were also performed to additionally describe the formation of His layer on the Au electrode. The measurement (Fig. 5) was performed on AuQCM gold electrode in 0.1 M AB pH = 4.6 containing 0.1 M $NaClO_4$ (base frequency 0). Upon injection of 1 M His the change in frequency (~ 80 Hz) is evident. After 10 min solution of His in the measuring cell was replaced with buffer. Thus that final change in the frequency (slightly less than 80 Hz) can be attributed to the His adsorbed on the AuQCM electrode.

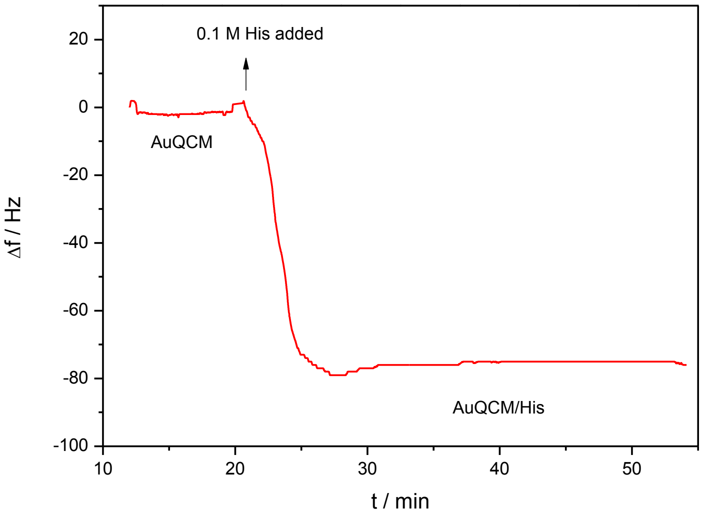

Figure 5. Time dependence of frequency change for AuQCM electrode after addition of 0.1 M His solution in 0.1 M AB pH = 4.6 containing 0.1 M $NaClO_4$.

3.3. Adsorption transfer stripping voltammetry

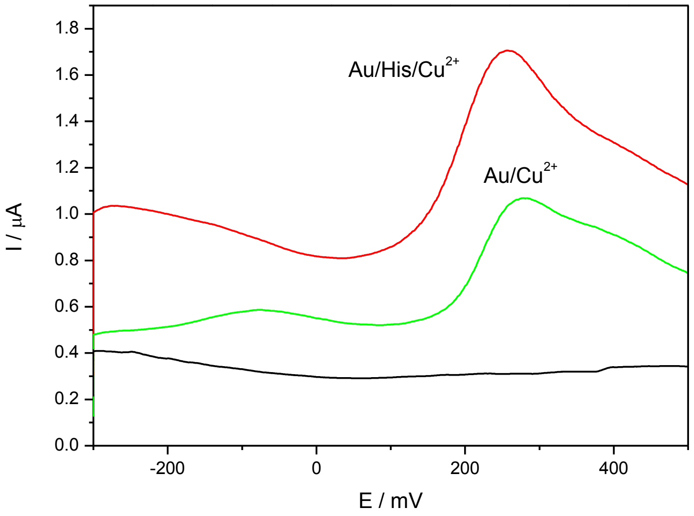

Figure 6. AdTSV voltammograms of Au and Au/His without Cu^{2+} accumulation (black), Au (green) and Au/His (red) after Cu^{2+} accumulation recorded in 0.1 M AB pH = 4.6 containing 0.1 M $NaClO_4$. Accumulation time 15 min, reduction time 15 s, reduction potential -300 mV, pulse height 25 mV, scan rate 20 mV/s, $c(Cu^{2+})$ = 10 µM.

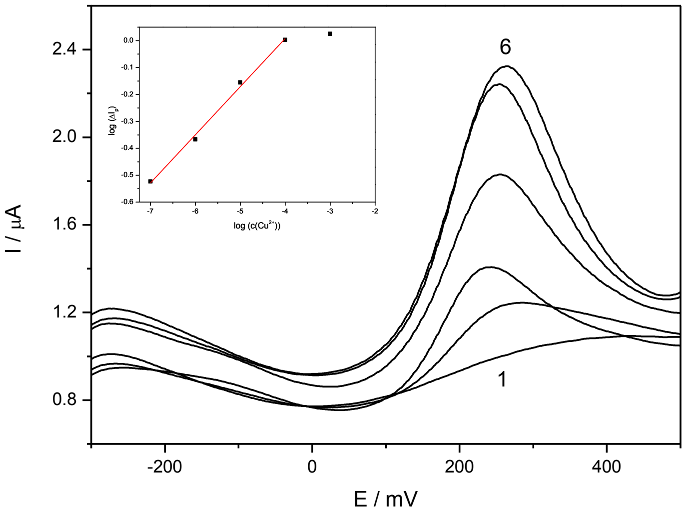

Figure 7. AdTSV voltammograms of Au/His electrode after Cu^{2+} accumulation. Experimental conditions were the same as in Fig. 6. $c(Cu^{2+}) = 10^{-8}$ (1) to 10^{-3} M (6). Inset: Calibration curve.

Black curve in Fig. 6 corresponds to Au and Au/His electrodes behavior without Cu^{2+} accumulation recorded in 0.1 M AB pH = 4.6 containing 0.1 M $NaClO_4$. Green and red curves were recorded after Cu^{2+} accumulation in 10 µM $CuNO_3$ solution for 15 min on Au and Au/His respectively.

Other experimental conditions were the same as proposed by Mohadesi and Taher [34]. The modified electrode demonstrated almost twice the response (ΔI_p = 0.8 μA) in comparison to unmodified electrode (ΔI_p = 0.47 μA). These results confirmed the capability of His modified electrode for efficient Cu^{2+} complexation and were in agreement with previously described cyclic voltammetric measurements.

Capability of prepared Au/His electrode for Cu^{2+} complexation was tested in the wide concentration range (10^{-8} to 10^{-3} M). The Au/His was immersed into stirring aqueous solutions of Cu^{2+} for 15 min. Following the accumulation step the electrode was transferred to electrochemical cell with 0.1 M AC pH = 4.6 containing 0.1 M $NaClO_4$. The electrode was and polarized at -300 mV *vs.* reference electrode for 15 s. Polarization initiated a reduction of Cu^{2+} which was then anodically oxidized and the current response was measured in the range from -300 to 600 mV. Then the electrode was transferred into 0.1 M EDTA for 3 minutes to remove residual copper from the surface. The results of measurement are displayed in Fig. 7.

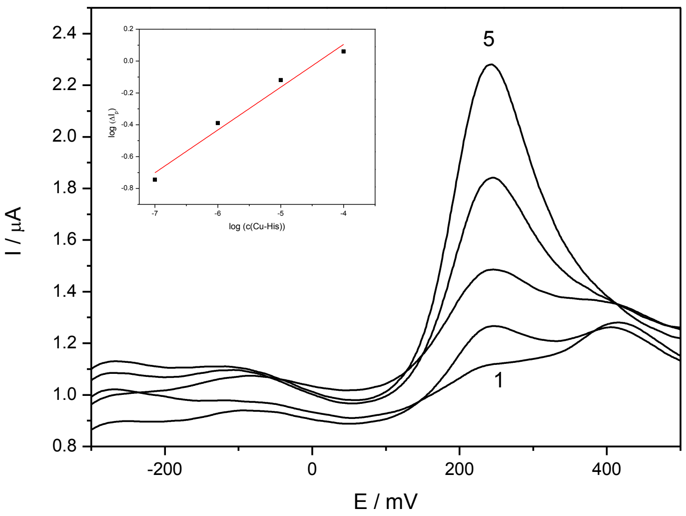

Figure 8. AdTSV voltammograms of Au/His electrode after Cu-His complex accumulation. Experimental conditions were the same as in Fig. 6. *c*(Cu-His) = 10^{-8} (1) to 10^{-4}M (5). Inset: Calibration curve.

It can be seen that complexation in 10^{-8} M Cu^{2+} solution is almost negligible under the applied experimental conditions (AdTSV voltammogram 1, Fig. 7). However the stripping peak current at higher concentration revealed proportional increase with concentration up to 10^{-4} M. Accumulation in 10^{-3} M Cu^{2+} did not result in further proportional current increase due to complete saturation of His monolayer. Relation between log ΔI_p (ΔI_p - difference between peak current determined at peak potential and current obtained at base line *i.e.* line drown between the initial and final points of the wave) *vs.* log $c(Cu^{2+})$ exhibits linear relationship and regression equation is:

$$\log\left(\Delta I_p / \mu A\right) = (1.92 \pm 0.16) + (0.24 \pm 0.03) \cdot \log\left(c\left(Cu^{2+}\right)/M\right),\ R^2 = 0.9945$$

Fig. 8 demonstrates Au/His electrode response to Cu-His concentration in the range between 10^{-8} to 10^{-4} M. Experimental conditions were same as in Fig. 7. Response of electrode was linearly proportional to Cu-His concentration and can be described by equation:

$$\log \Delta I_{\mathrm{p}} = (2.42 \pm 0.14) + (0.33 \pm 0.03) \cdot \log c(\mathrm{Cu-His}),\ R^2 = 0.9807$$

Stability constant for Cu-His complex is $pK_a = 10.1$ [17] which means that the concentration of unbound copper is very small compared to Cu-His concentration, hence the response (Fig. 8.) is due to complex bounding Cu-His on Au/His electrode and not due to physical adsorption of Cu^{2+} on to Au.

Furthermore the response (Fig. 8.) is not due to physical adsorption of His on Au because concentration of free His is also insignificant. In aqueous solution His makes monodetant [13] bidentante [14, 15] or tridentate [16] complexes, coordinating copper by carboxyl group and primary or secondary amine group, consequently possible interference arising from physically adsorbed Cu-His on Au is negligible due to copper coordination to carboxylic group *i*.e. the group responsible for bonding to gold. The slope obtained for measurement of Cu-His has higher value than one obtained for Cu^{2+}. This may be a consequence of higher stability of $\mathrm{Cu-(His)}_2^{2+}$ complex ($pK_a = 17.5$ [17]) which is formed by coupling Cu-His on the Au/His surface, compared to Cu-His. This confirms the possibility for determination of His or His modified proteins.

4. CONCLUSION

His has an ability to bind to the gold which presents a drawback in electrochemical measurements with gold electrodes. In this research preparation and characterization of His modified Au electrode was described. The capability of the electrode prepared for Cu^{2+} complexation was tested by cyclic voltammetry and adsorptive anodic stripping voltammetry. The same method was used to describe interaction between modified Au/His electrode and Cu-His complex. The prepared electrode can be used for His or his-tag protein determination.

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