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The Synergistic Effect of Nitroprusside and CuNiDH as Electrocatalyst with High Performance for Electro-Oxidation of Sodium Sulfide in Alkaline Media

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Abstract- Due to the importance of sulfide removal from wastewater and waste streams, in this study, eight cost-effective electrocatalysts were designed and prepared by electrochemical technique and their performance was evaluated in the presence of a high concentration of sodium sulfide. According to the results, among the prepared electrocatalysts, CuNiDH-NP@G electrode (modified graphite with nitroprusside (vasodilator drug) and CuNi-double hydroxide) had the highest efficiency in sulfide electro-oxidation. Then, to improve the performance of the CuNiDH-NP@G electrode its structure was optimized and investigated by field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), and energy-dispersive X-ray spectroscopy (EDS). Based on the results of electrochemical analyzes, in the presence of sulfide the process is controlled by diffusion. The diffusion coefficient, heterogeneous electron transfer rate constant and electron transfer coefficient for sulfide electrochemical oxidation were determined 2.85×10^{-5} cm^2/s, 3.126 $cm.s^{-1}$ and 0. 72 respectively. The use of non_noble metals as the electrocatalyst for sulfide electro-oxidation, the very easy, affordable, and fast preparation of the introduced electrode and high performance of it demonstrate important items for the use of this procedure and electrode in the subsequent investigation of a different material.

Keywords- Sulfides electro-oxidation; Sodium nitroprusside; Electrocatalyst; Modified electrode; CuNi-double hydroxide

1. INTRODUCTION

Hydrogen sulfide is produced in domestic and industrial processes. Sulfide in wastewater, especially industrial wastewater that has a higher sulfide content, not only pollutes the environment and has a high cost for its removal but also has caused significant damage to the industry by corrosion. Therefore, sulfide removal and separation are of great interest to researchers.

Zaman & Chakma [1] investigated the possibilities and limitations of different technologies for the production of hydrogen and sulfur from hydrogen sulfide.

However, none of these methods are used today and from the industrial point of view, the CLAUS process is used to remove hydrogen sulfide from fuels, which has its disadvantages and is only affordable on a large scale [2]. An alternative is an electrochemical method [3,4]. The final oxidation products can be a mixture of S^0, polysulfides, (SO_4^{-2}) sulfate, and thiosulfate ($S_2O_3^{-2}$). The oxidation products depend on the electrode materials used and the reaction conditions such as concentration of sulfide, pH, anodic potential, and convection [5].

When S^0 is produced by direct oxidation it precipitates on the anode surface acts as a high-strength insulator and reduces the active surface area of the electrode. As a result, we need to increase the anode potential. This high potential also causes adverse reactions such as oxygen oxidation and eventually the entire surface of the poisoned electrode is covered.

Different electrode materials have been used for sulfide electro-oxidation. Carbon materials [6,7] are low cost and although they can produce S^0 which can be recovered but need to be replaced because of poisoning.

Non-carbon materials such as titanium oxide [8], platinum [9], and nickel [10] have also been used for sulfide electro-oxidation, whose surface is not only accumulated of S^0 after some time [11] but also a sulfide-metal film is formed [9,10], which disables the electrode.

Strategies have been proposed to solve this problem: a) Changing electrode materials to avoid the sulfur formation and production of Oxyanions Sulfur. [12,13], b) Production of polysulfides by the use of an alkaline anolyte [7,10,14–22], c) Using an organic solvent to extract anodic sulfur [23], d)Use of surfactant. [24,25], e)Using pulse current. [26], f) Reactivation of the anode surface by mechanical movement of a cylindrical rotary electrode through different potential regions. [5,27,28] and other works [16,29].

Despite all the research and studies, finding an effective way to overcome the passivation of sulfur on the anode surface is still very attractive. Accordingly, due to the importance of sulfide oxidation in various fields, in this study, the graphite electrode was modified with sodium nitroprusside, which is a drug substance, and nickel-copper hydroxides and used as an effective electrocatalyst for electro-oxidation of sodium sulfide in alkaline media.

2. EXPERIMENTAL

2.1. Materials and solution

All the utilized chemicals were analytical grade and used without any prior purification. nickel (II) sulfate hexahydrate ($NiSO_4.6H_2O$) iron (II) sulfate heptahydrate ($FeSO_4.7H_2O$), copper (II) sulfate pentahydrate ($CuSO_4.5H_2O$) and sodium pentacyanonitrosylferrate (Sodium nitroprusside ($Na_2Fe(CN)_5NO.2H_2O$)) were used for manufacture of electrodes. Sodium hydroxide (NaOH) was used for preparing of electrolyte, and sodium sulfide (Na_2S) was used as electroactive material. all were purchased from Merck chemical companies. In all solutions were used of deionization water.

2.2. Apparatus

An electrochemical cell with a three-electrode configuration was used. A bar graphite (0.38 cm^2) rod and modified graphite (0.05 cm^2) rod were used as counter and the working electrode, respectively. All potentials were recorded respect to Ag/AgCl-saturated KCl reference electrode (E=0.2 V). Studies were accomplished by an electrochemical system comprising of EG&G model 273A potentiostat/galvanostat. The system was run by a PC through M270 and M398 commercial software via a GPIB interface. The surface morphology of the working electrode was investigated by field emission scanning electron microscopy (FESEM) model SIGMA VP (ZEISS company of Germany) also the energy dispersive X-ray spectroscopy (EDS) and Mapping detector was made by Oxford Instrument company of England. X-ray diffraction (XRD) study was performed by X-ray diffractometer model X' Pert Pro (Panalytical company). All experiments were performed at room temperature.

2.3. Preparation of electrode

The graphite rods (Sony brand) were used as the working electrode. The method of cleaning and preparing graphite electrodes is described in detail in our previous article [4]. The deposition of nickel, copper, iron and their alloy on the bar graphites was performed by an electrochemical procedure.

3. RESULTS AND DISCUSSION

Graphite electrodes modified with Ni, Cu, Fe, Fe-Ni, Cu-Ni, Fe-Cu, Cu-Ni-Fe and finally Cu-Ni-NP were made based on the solutions listed in Table 1. Then metal hydroxides and oxyhydroxides of Ni, Cu and Fe were formed on these electrodes by cyclic voltammetry in the potential range of 0 to 1 V vs (25 cycles) from a solution of 1 M NaOH [30].

$$Ni(OH)_2 + OH^- \rightleftharpoons NiOOH + H_2O + e$$

$$Cu(OH)_2 + OH^- \rightleftharpoons CuOOH + H_2O + e$$

$$CuOOH + OH^- \rightleftharpoons CuO_2 + H_2O + e$$

$$Fe(OH)_2 + OH^- \rightleftharpoons FeOOH + H_2O + e$$

Table 1. Electrochemical coatings solution composition

Order	Metal layer	Sodium nitroprusside (SNP)	$FeSO_4.7H_2O$	$CuSO_4.5H_2O$	$NiCl_2.6H_2O$	Potential range	Number of Cycle
1	Fe	-	5 ml 1 M	-	-	-0.6 _ -1.5	10
2	Ni	-	-	-	5 ml 1 M	0 _ -1	10
3	Cu	-	-	5 ml 1 M	-	0 _ -1	10
4	Fe-Ni	-	2.5 ml 1 M	-	2.5 ml 1 M	0 _ -1	10
5	Fe-Cu	-	2.5 ml 1 M	2.5 ml 1 M	-	0 _ -1	10
6	Cu-Ni	-	-	2.5 ml 1 M	2.5 ml 1 M	0 _ -1	10
7	Cu-Ni-Fe	-	2.5 ml 1 M	2.5 ml 1 M	2.5 ml 1 M	0 _ -1	10
8	Cu-Ni-NP	2.5 ml 1 M	-	2.5 ml 1 M	2.5 ml 1 M	0 _ -1	10

Finally, modified electrodes were investigated in sodium hydroxide electrolyte 1 M in the presence and absence of sodium sulfide.

By studying voltammograms of graphite electrodes modified with $Ni(OH)_2$, $Cu(OH)_2$, FeNiDH (FeNi-double hydroxide), CuNiFeTH (CuNiFe-ternary hydroxide) in the presence of different concentrations of sodium sulfide, it was found these electrodes are not appropriate for use as electrocatalysts in this field of study. This can be due to their surface poisoning by the product of electro-oxidation reaction such as sulfur or formation of sulfide-metal.

Graphite electrodes modified with $Fe(OH)_2$, FeCuDH, CuNiDH, and CuNiDH-NP all exhibited good sensitivity and performance to sodium sulfide addition and concentration change in the electrolyte also there were no signs of surface poisoning.

As can be seen in Figure 1, with the addition of sodium sulfide to the electrolyte, a marked change in the anodic current is observed which caused by sulfide electro-oxidation by modified electrodes. It should be noted, however, the iron-modified electrode was sensitive to the presence of sulfide in the electrolyte and there were no signs of poisoning, but its electrocatalytic performance was even lower than that of graphite electrode.

Among these electrodes, the best performance was obtained with CuNiDH-NP modified graphite electrode (CuNiDH-NP@G), which showed the highest electro-oxidation efficiency and there was no intruder peak (Figure 2). It should be noted, according to all available sources

in the field of research, in addition to producing S^0, the production of polysulfides, (SO_4^{-2}) sulfate and thiosulfate ($S_2O_3^{-2}$), are inevitable [5,31,32].

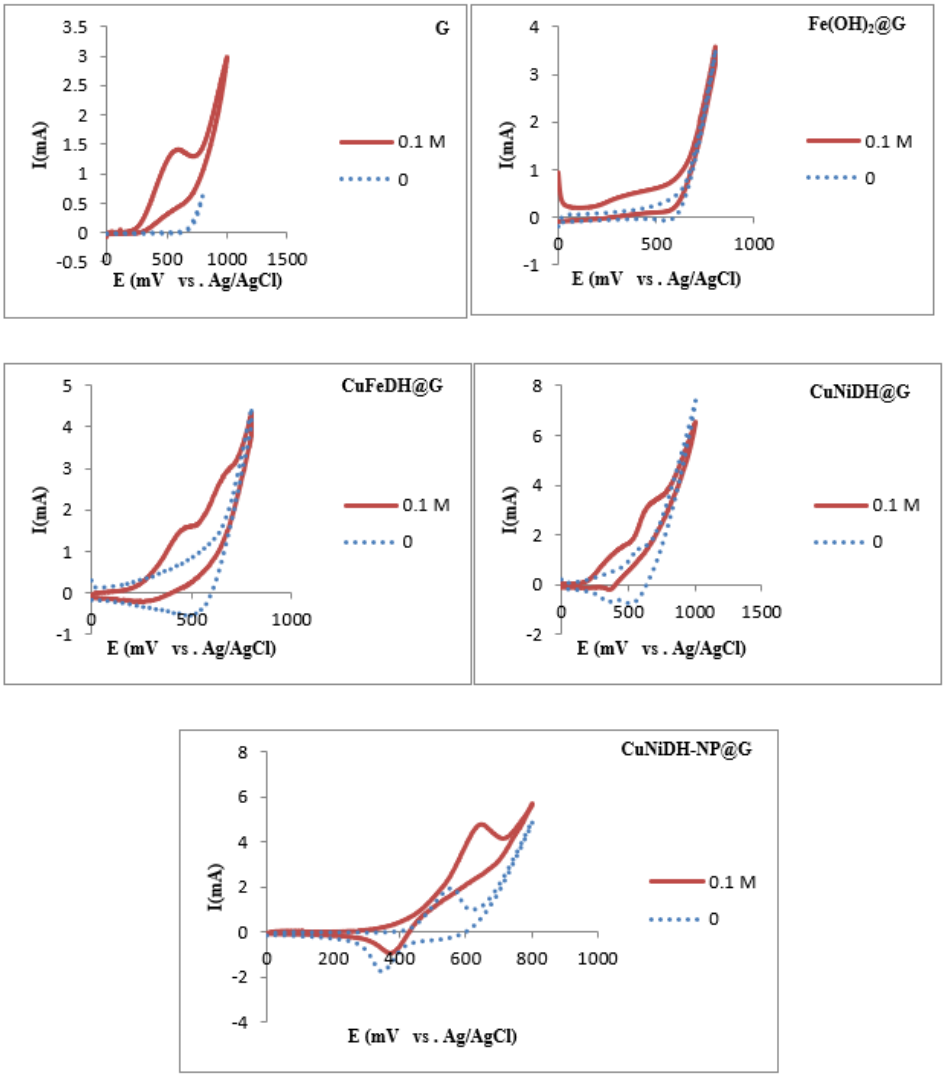

Figure 1. Performance evaluation of graphite (G), $Fe(OH)_2$@G, FeCuDH@G, CuNiDH@G, and CuNiDH-NP @G electrodes in the absence and presence of 0.1 M sodium sulfide in 1 M sodium hydroxide solution (scan rate = 100 mV/s)

Since the graphite electrodes modified with CuNiFeTH@G and CuNiDH-NP @G differ only in the iron salt type to further investigate the cause of its good performance experiments were designed.

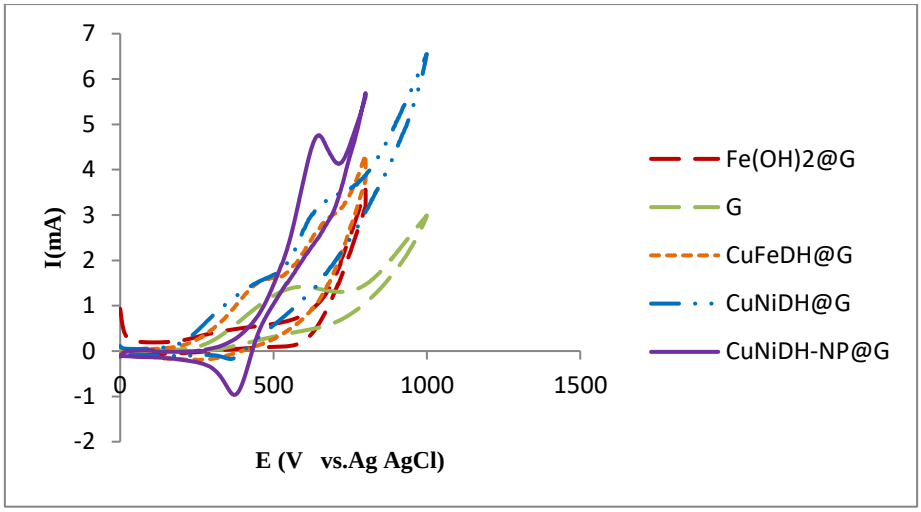

Figure 2. Voltammetric treatment of (G),$Fe(OH)_2$@G, FeCuDH@G, CuNiDH@G, and CuNiDH-NP @G electrodes in the presence of 0.1 mol/L sodium sulfide concentrations in 1 M sodium hydroxide (scan rate = 100 mV/s)

Firstly, for more assurance of synergistic effect among the metals present on the modified graphite surface, in an experiment, the graphite electrode was modified by $CuSO_4.5H_2O$ and NP to fabricate the $Cu(OH)_2$NP@G electrode and in another experiment modified with $NiCl_2.6H_2O$ and NP to produce $Ni(OH)_2$NP@G and its performance as an electrocatalyst was investigated. As can be seen in Figure 3(a), these two electrodes do not perform significantly in the absence of the third metal. In addition, in the presence of 0.2 M sodium sulfide the performance of $Cu(OH)_2$NP@G and $Ni(OH)_2$NP@G electrodes is even lower than that of graphite (Figure 3(b)).

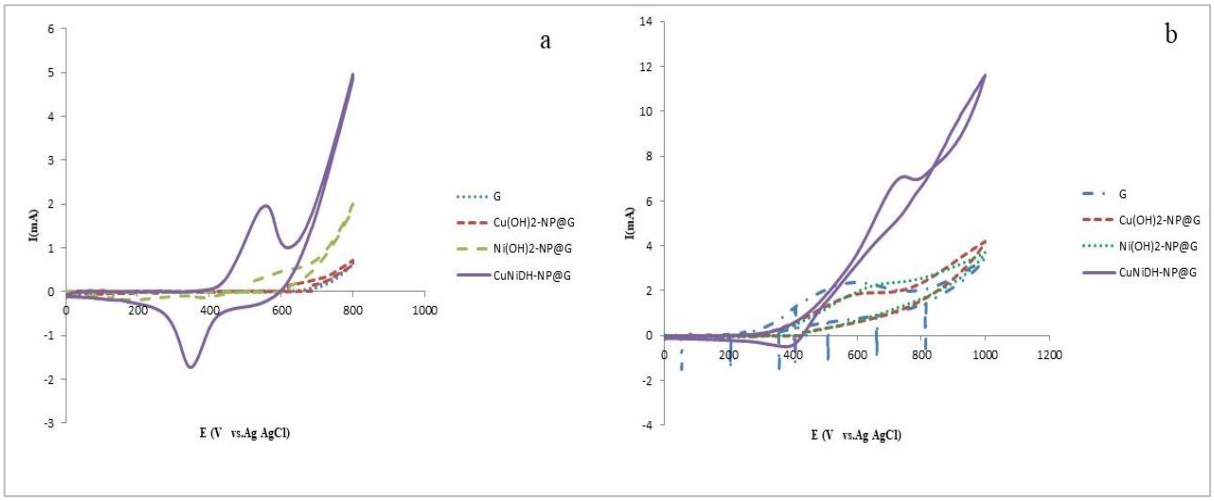

Figure 3. Cyclic voltamograms of G, $Cu(OH)_2$NP@G, $Ni(OH)_2$NP@G and CuNiDH-NP@G electrodes in 1 M sodium hydroxide solution a) in the absence and b) presence of 0.2 M sodium sulfide (scan rate = 100 mV/s)

Therefore; it is quite clear that the presence of all three salts of $CuSO_4.5H_2O$, $NiCl_2.6H_2O$, and NP in the electrode solution and in fact the presence of all three metals; Ni, Cu, and Fe together have a high synergistic effect.

In the next step, it was necessary to carry out further experiments to determine the exact cause of the high performance of the electrocatalyst introduced. As SNP releases NO and CN^- in the body during metabolism, some assumptions were made [33]:

The first hypothesis: The CN^- in the newly formed structure derived from SNP salt can be effective in electrocatalytic performance. In fact, CN^- is oxidized and reduced along with Ni and Cu as electrocatalysts.

To test this hypothesis, graphite modified with a mixture of (1 M) $NiCl_2.6H_2O$ and $CuSO_4.5H_2O$ (1 M) and (1 M) $K_4Fe(CN)_6$ was used to investigate the performance of CN^- in the structure. As can be seen in Figure 4(a), this electrode does not perform well and does not exhibit good sensitivity to the presence of sulfide. So, this hypothesis was invalidated.

Second hypothesis: The NO in the newly formed structure derived from SNP salt can be effective in electrocatalytic performance. In fact, NO is oxidized and reduced along with Ni and Cu as an electrocatalyst.

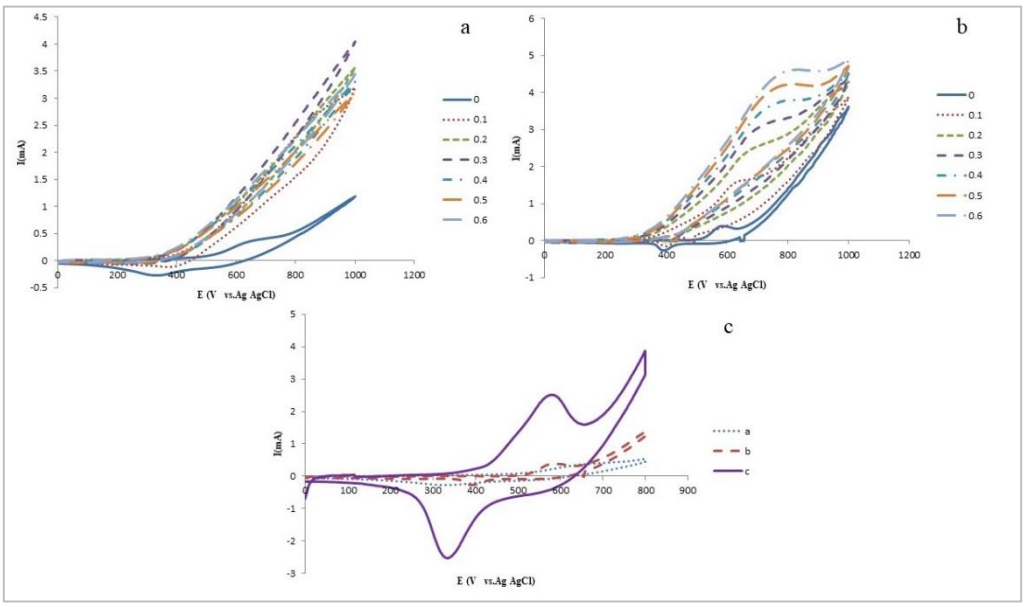

Figure 4. Voltammetric treatment of graphite electrode modified with mixtures of a) $NiCl_2.6H_2O$ (1 M), $CuSO_4.5H_2O$ (1 M) and $K_4Fe(CN)_6$ (1 M) b) $NiCl_2.6H_2O$ (1 M), $CuSO_4.5H_2O$ (1 M) and $Fe(NO3)_3$. $9H_2O$ (1 M) at concentrations of 0.0-0.6 M sodium sulfide in 1 M sodium hydroxide solution (scan rate = 100 mV/s); c) Comparison of the performance of the modified graphite electrode with a mixture of a)$NiCl_2.6H_2O$ (1 M), $CuSO_4.5H_2O$ (1 M), $K_4Fe(CN)_6$ (1 M) b) $NiCl_2.6H_2O$ (1 M), $CuSO_4.5H_2O$ (1 M), $Fe(NO3)_3.9H_2O$ (1 M) c) $NiCl_2.6H_2O$ (1 M), $CuSO_4.5H_2O$ (1 M), SNP (1 M) in 1 M sodium hydroxide solution (scan rate = 100 mV/s)

To test this hypothesis, graphite modified with a mixture of (1 M) $NiCl_2.6H_2O$ and $CuSO_4.5H_2O$ (1 M) and (1 M) $Fe(NO_3)_3.9H_2O$ to was used investigate the performance of NO in the structure. As can be seen in Figure 4(b) & (c), this electrode does not perform as well as the main electrode but is sensitive to the presence of sulfide and responds to it.

Based on the results obtained, the NP trapped in the crystal structure of the electrode at the deposition stage is a significant factor in the high performance of the CuNiDH-NP@G electrode [34]. The presence of NP not only plays a role in the crystal structure, but also the NO^+ in it has the ability to oxidize and reduce [35] which is vital in the electrocatalytic process.

$$[Fe^{II}(CN)_5(NO)]^{2-} + e \quad \longleftrightarrow \quad [Fe^{II}(CN)_5(NO)]^{3-}$$

To achieve the electrode with maximum efficiency, the NP content in CuNiDH-NP@G electrode was optimized. Therefore, plating solutions in different amounts SNP were used (Table 2). Based on the results of cyclic voltammograms (Figure 5). The best performance was related to the electrode which was made of 0.2 M SNP solution. Other electrochemical studies were performed using optimized electrodes.

Table 2. Electrochemical coatings solution composition

Number of Cycle	Potential range	SNP	$CuSO_4.5H_2O$	$NiCl_2.6H_2O$	Metal layer	order
10	0 _ -1	2.5 ml 0.05 M	2.5 ml 1 M	2.5 ml 1 M	CuNiDH-NP $_{0.05}$@G	1
10	0 _ -1	2.5 ml 0.1 M	2.5 ml 1 M	2.5 ml 1 M	CuNiDH-NP $_{0.1}$@G	2
10	0 _ -1	2.5 ml 0.2 M	2.5 ml 1 M	2.5 ml 1 M	CuNiDH-NP $_{0.2}$@G	3
10	0 _ -1	2.5 ml 0.5 M	2.5 ml 1 M	2.5 ml 1 M	CuNiDH-NP $_{0.5}$@G	4
10	0 _ -1	2.5 ml 1 M	2.5 ml 1 M	2.5 ml 1 M	CuNiDH-NP $_{1}$@G	5

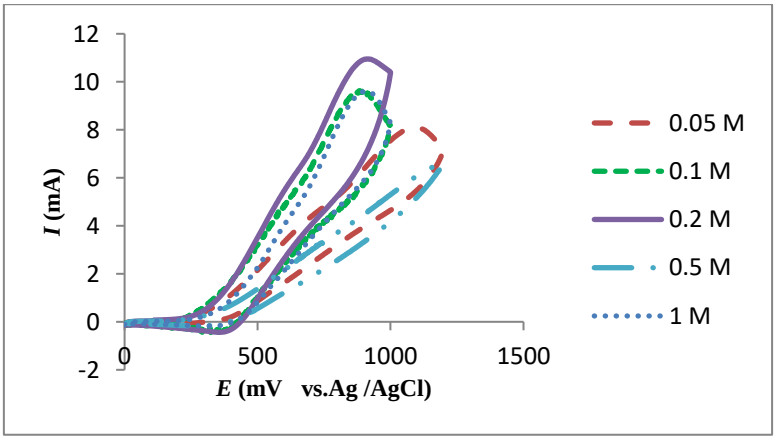

Figure 5. Investigation of CuNiDH-NP@G electrodes made by different concentrations of SNP salt in the electroplating solution (Table 2) (scan rate = 100 mV/s); The concentration of sodium sulfide: 0.5 M; The concentration of sodium hydroxide solution: 1 M

3.1. Investigation of XRD spectra and FESEM images

Figure 6 shows the X-ray diffraction (XRD) patterns of the CuNiDH-$NP_{0.2}$@G and CuNiDH-$Fe_{0.2}$@G (which results from the use of salt mixtures $NiCl_2.6H_2O$, $CuSO_4.5H_2O$, and $FeSO_4.7H_2O$ for modification of graphite electrode) electrodes. In the Figure 6(a), the presence of Fe, Cu, and Ni peaks is evidence of the successful formation of metal particles on the graphite electrode surface.

Based on the Shearer equation (Eq. 1), the size of the crystals of CuNiDH-NP0.2 on the graphite electrode was calculated as 27.76 nm.

$$\tau = \frac{K\lambda}{\beta \mathrm{Cos}\theta} \qquad \text{(Eq. 1)}$$

τ: size of the crystals

K: dimensionless shape factor (0.9)

λ: X-ray wavelength (0.154 nm)

β: line broadening at half the maximum intensity (FWHM) (0.00540 rad)

θ: Bragg angle (21.73 °)

Based on the two XRD spectra, different iron salts has created different morphologies on the surface of the graphite electrode. Since the crystal structure of the electrodes is very effective in the operation of electrochemical systems, the crystal structure resulting from the use of NP salt will have a large contribution to the high performance of this electrocatalytic system.

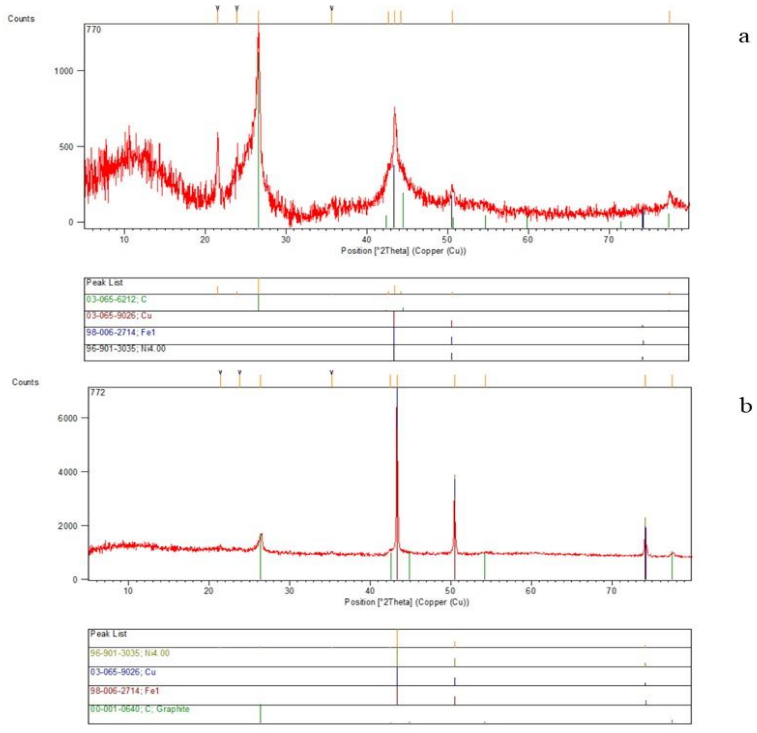

Figure 6. XRD patterns of a) CuNiDH-$NP_{0.2}$@G and b) CuNiDH-$Fe_{0.2}$@G electrodes

FESEM images of CuNiDH-$NP_{0.2}$@G electrode at different magnifications and its EDS spectrum and Map image are shown in Figure 7(a). Likewise, FESEM images of CuNiDH-$Fe_{0.2}$@G electrode (The G/Cu-Ni-$Fe_{0.2}$ electrode is the same as the G/Cu-Ni-Fe electrode, which is described in Table 1 with the difference that the concentration of $FeSO_4.7H_2O$ in the electrode manufacturing solution is 0.2 molar) and its EDS spectrum and Map image are shown in Figure 7(b). As can be seen in the figures, the two electrodes have a different crystalline structure, and the EDS spectrum also shows a different weight percentage of the elements in each electrode. The most different weight percent (wt%) is related to the copper element. In the CuNiDH-$NP_{0.2}$@G electrode, wt% of copper is 56.7% and in CuNiDH-Fe $_{0.2}$@G electrode, it is 77.1% that this issue is also important in the different performance of the two electrodes.

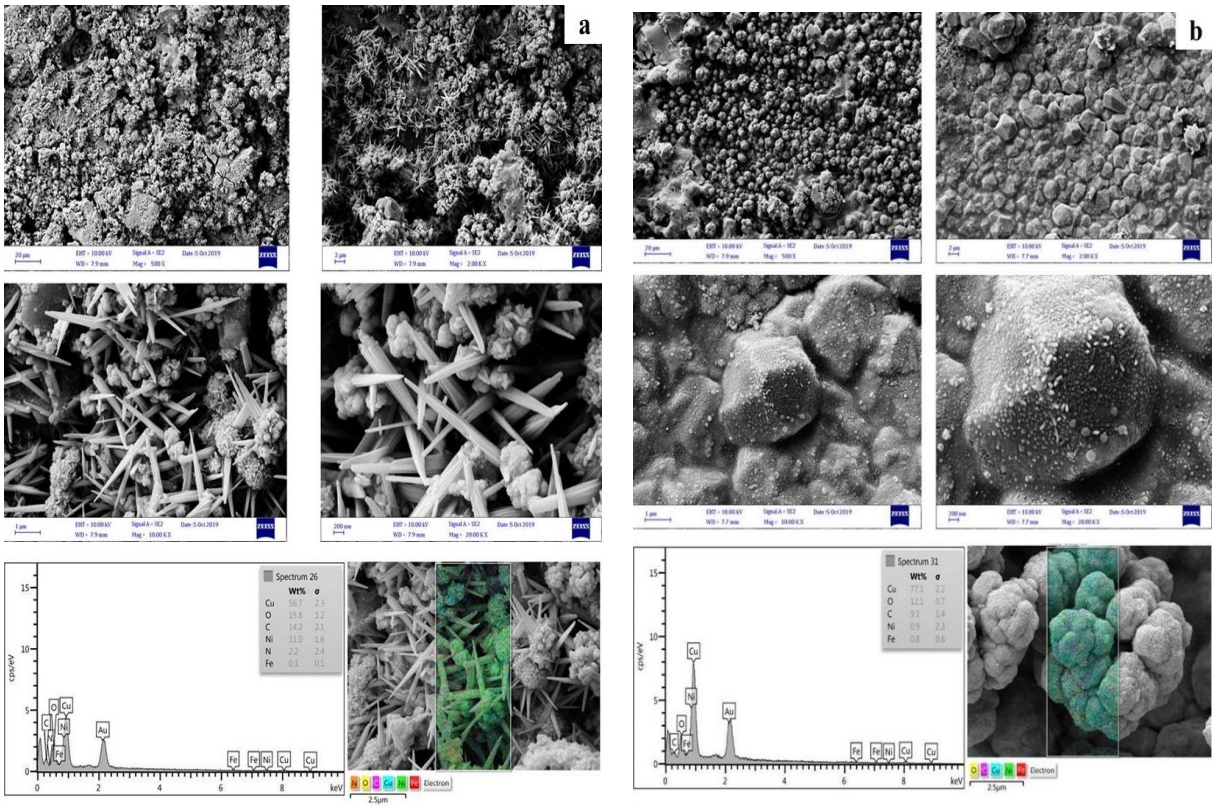

Figure 7. SEM images (in different magnifications: 20 µm, 2 µm, 1 µm, and 200 nm), EDS Spectrum and Map Image of a) CuNiDH-$NP_{0.2}$ @G and b) CuNiDH-$Fe_{0.2}$ @G electrodes

3.2. Effect of sodium sulfide concentration

Figure 8 shows the electrochemical behavior of CuNiDH-$NP_{0.2}$@G electrode in the presence of different concentrations of sodium sulfide (0- 0.5 M) at the scan rate of 100 mV/s. As the sulfide concentration increases, a noticeable increase is observed in the peak anodic current of the electrode, which confirms the high performance and sensitivity of the electrode. It should be noted, most research on sulfide removal has not paid much attention to techniques such as cyclic voltammetry. However, the electro-oxidation currents reported in the literature are in the micro-ampere range [35,36] ,in contrast to our project that the electro-oxidation

current is in the milli-ampere range. This noticeable difference in electrooxidation current compared to other papers is evidence of high performance of introduced electrode. As the electrocatalyst formed on the electrode surface participates in the sulfide electrooxidation process, the peak of cathodic current decreases with increasing sodium sulfide concentration. In fact, in the first step, the electrocatalyst is oxidized with increasing potential and in the second stage oxidized electrocatalyst is reduced by sodium sulfide oxidation. As a result, this issue reduces the cathodic peak current.

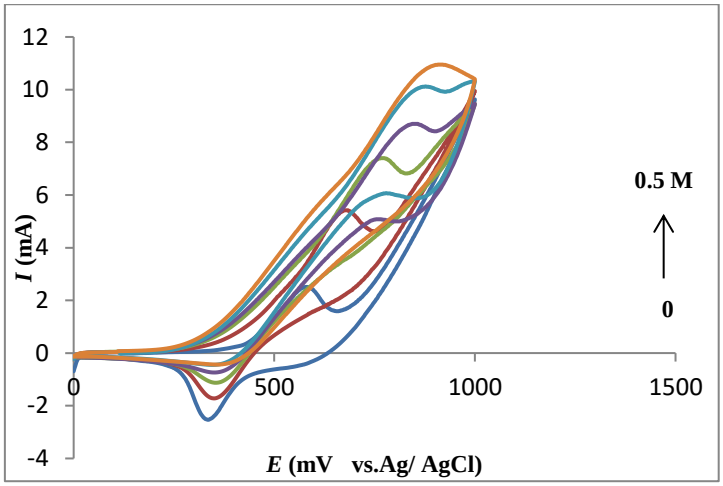

Figure 8. Voltammetric treatment of the CuNiDH-NP$_{0.2}$@G electrode in the alkaline media (1 M NaOH) at 0-0. 5 mol/L sodium sulfide concentrations (scan rate = 100 mV/s)

3.3. Investigation of fractal dimensions of the modified electrode

To complete the study of the CuNiDH-NP$_{0.2}$@G electrode surface, its fractal dimension [34] was also measured. Figure 9(a) shows the voltammogram of CuNiDH-NP$_{0.2}$@G electrode in 1 M sodium hydroxide solution. A pair of electrocatalyst peak oxidation and reduction is clearly seen in the figure.

By plotting the peak current logarithm versus the scan rate logarithm (Figure 9(b)), the alpha parameter (α) (that is slop of this plot) is obtained. As a result, by using it and the equation 2 surface fractal dimension (D_f) was equal to 2.1 [37,38].

$$\alpha = \frac{D_f - 1}{2} \qquad \text{(Eq. 2)}$$

3.4. Classical analysis

In order to obtain kinetic data, the effect of the scan rate was investigated. The effect of the scan rate on the cyclic voltammograms of the CuNiDH-NP$_{0.2}$@G electrode in the attendance of 0.2 mol/L sodium sulfide at 298 K is shown in Figure 10(a). As Figure 10(a) shows with the increase of the scan rate, the anodic current increases also because of shifting the anodic peak to a more positive potential, an irreversible reaction is taking on the CuNiDH-NP$_{0.2}$@G

electrode. Based on literature for an irreversible reaction, $\left|E_{\mathrm{p}} - E_{\mathrm{p}/2}\right|$ is proportional to the square root of the scan rate. From the intercept of this plot (Figure 10 (b)) and using [39]:

$$\left|E_p - E_{p/2}\right| = \frac{47.7}{n\alpha} \text{ mV at } 25\ ^{\circ}C \qquad \text{(Eq. 3)}$$

The value of $n\alpha$ was calculated as 0. 72, where E_{p} is anodic peak potential and $E_{\mathrm{p}/2}$ is potential in half of the anodic peak current, α is electron transfer coefficient and n is the number of the transferred electron.

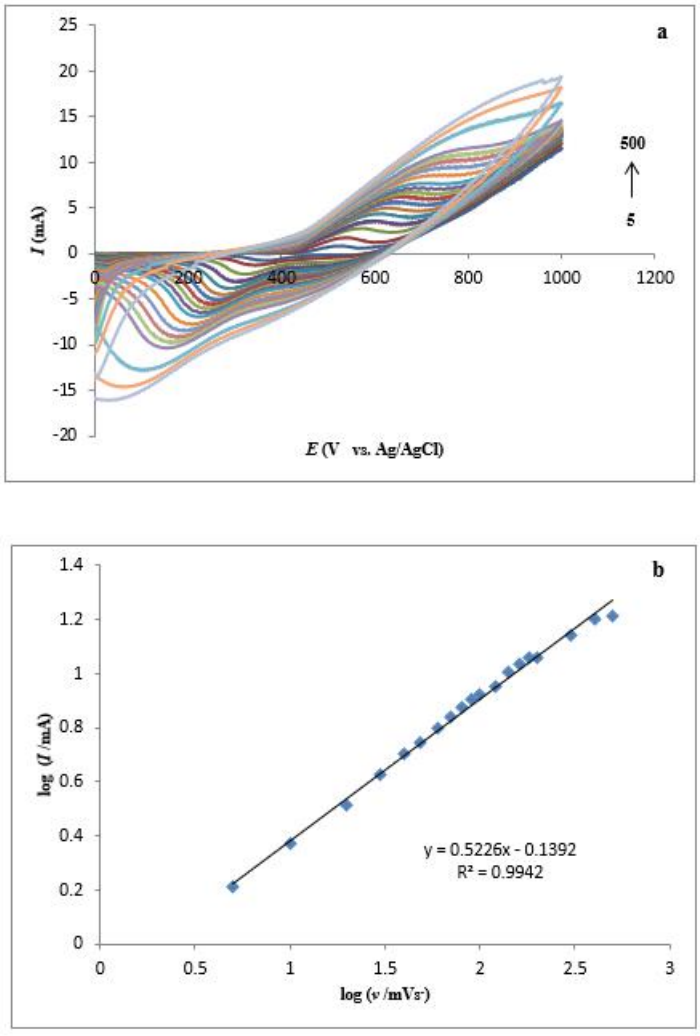

Figure 9. (a) Voltammetric treatment of the CuNiDH-NP $_{0.2}$@G electrode in the alkaline media (1 M NaOH) at the scan rate of 5 - 500 mV/s. (b) The relation of the anodic peak current logarithm with the logarithm of the scan rate

Also according to [39]:

$$i_{\mathrm{p}} = 2.99 \times 10^5 (n\alpha)^{1/2} A C_0^* D_0^{1/2} v^{1/2} \qquad \text{(Eq. 4)}$$

at 25 °C for an irreversible reaction, i_p is proportional to the square root of scan rate, from the slop of this plot at the scan of 0 to 30 mV/s (Figure 10(c)), The value of diffusion coefficient (D_0) was determined as 2.85×10^{-5} cm^2/s, where i_p is the anodic peak current, A is the surface area of the electrode, ν is scan rate, C_0 is the concentration and α is the electron transfer coefficient.

For an irreversible process, the heterogeneous electron transfer rate constant (k_{et}) can be earned from Laviron equation [40]:

$$E_{pa} = E^0 + \frac{RT}{(1-\alpha)nF} \ln\left(\frac{(1-\alpha)nF}{RTk_{et}}\right) + \frac{RT}{(1-\alpha)nF} \ln \nu \qquad \text{(Eq. 5)}$$

According to this equation, the slope of the plot of anodic peak potential (E_{pa}) versus the logarithm of the scan rate (Figure 10(d)) gives (1-α) n and k_{et} can be earned from the intercept of this plot. Finally, k_{et} was calculated as 3.126 $cm.s^{-1}$.

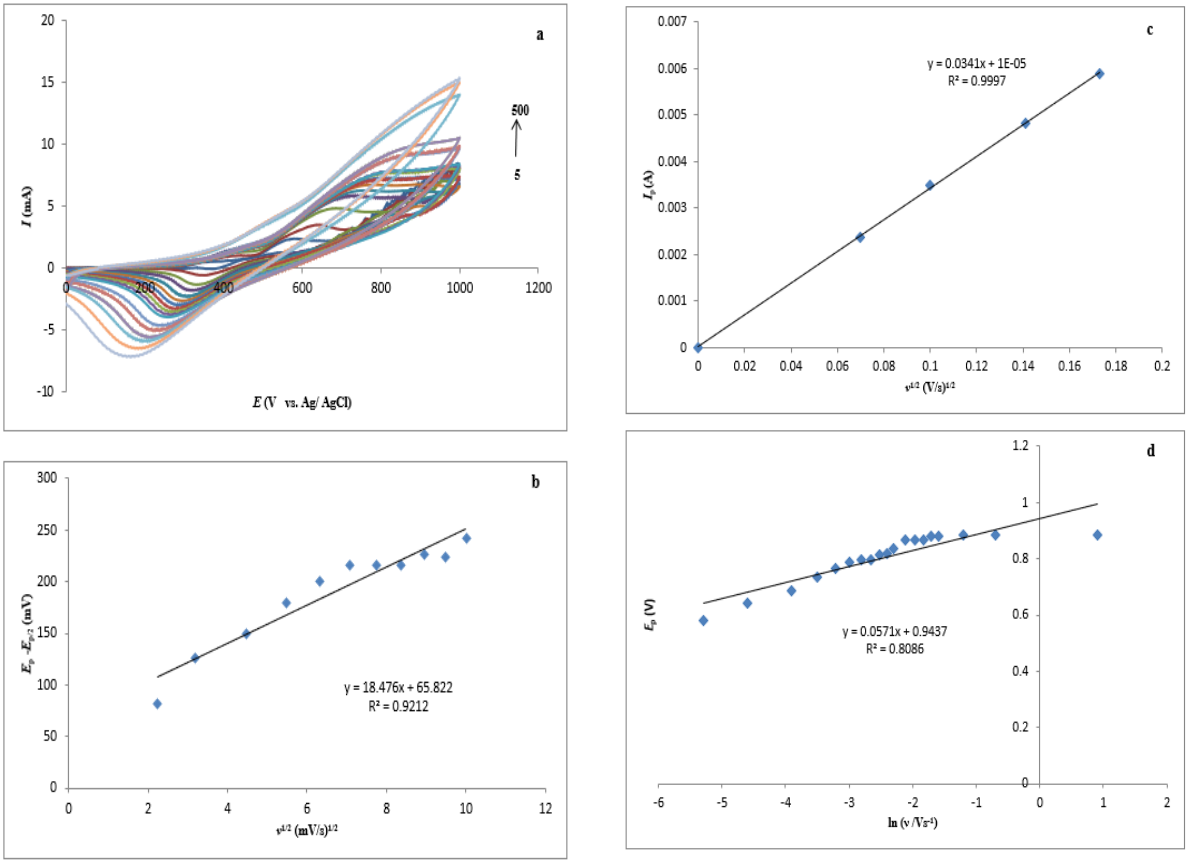

Figure 10. (a) Voltammetric treatment of the CuNiDH-NP $_{0.2}$@G electrode in the alkaline media in the presence of 0. 2 M sodium sulfide at the scan rate of 5 - 500 mV/s. (b) The relation of the $E_p - E_{p/2}$ with the square root of the scan rates. (c) The relation of the anodic peak currents with the square root of the scan rates (0–30 mV/s). (d) The relation of the anodic peak potential with the logarithm of the scan rate

3.5. Investigation of chronoamperometry curves

Figure 11(a) is the chronoamperometry curves obtained at different concentrations of sodium sulfide. The currents obtained at different concentrations are due to sulfide electro-oxidation, which confirms the results of the voltammograms. Figure 11(b) shows the current obtained from the chronoamperometry curve at a concentration of 0.2 M sodium sulfide versus the $t^{-0.5}$. The linearity of this graph indicates that the process is controlled by diffusion.

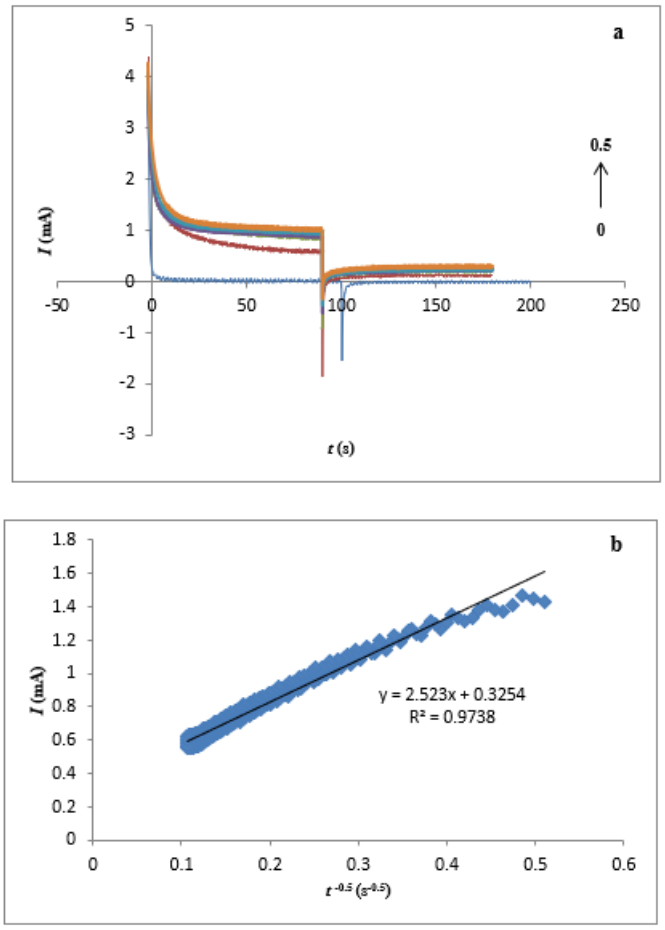

Figure 11. (a) Chronoamperograms of the CuNiDH-NP $_{0.2}$@G electrode in the alkalin media at 0 - 0. 5 M sodium sulfide concentrations (potential step1: 0.58 V and potential step 2: 0.33 V). (b) The diagram of current of the CuNiDH-NP $_{0.2}$@G electrode in 0.2 M sodium sulfide vs. $t^{-0.5}$

3.6. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy technique was used to confirm the previous results. The nyquist diagrams of the bare graphite electrode and CuNiDH-NP$_{0.2}$@G electrode and also equivalent circuit of CuNiDH-NP$_{0.2}$@G electrode can be seen in the Figure 12. The reduction in diameter of the CuNiDH-NP$_{0.2}$@G electrode nyquist compared to the bare graphite electrode is due to the reduction of charge transfer resistance.

R_s: resistance of the electrode and solution

R_{Ct}: charge transfer resistance

C_{dl}: double layer capacitance

C_{ads} and R_{ads}: related to the adsorbtion of electrolyte ions on the electrocatalyst

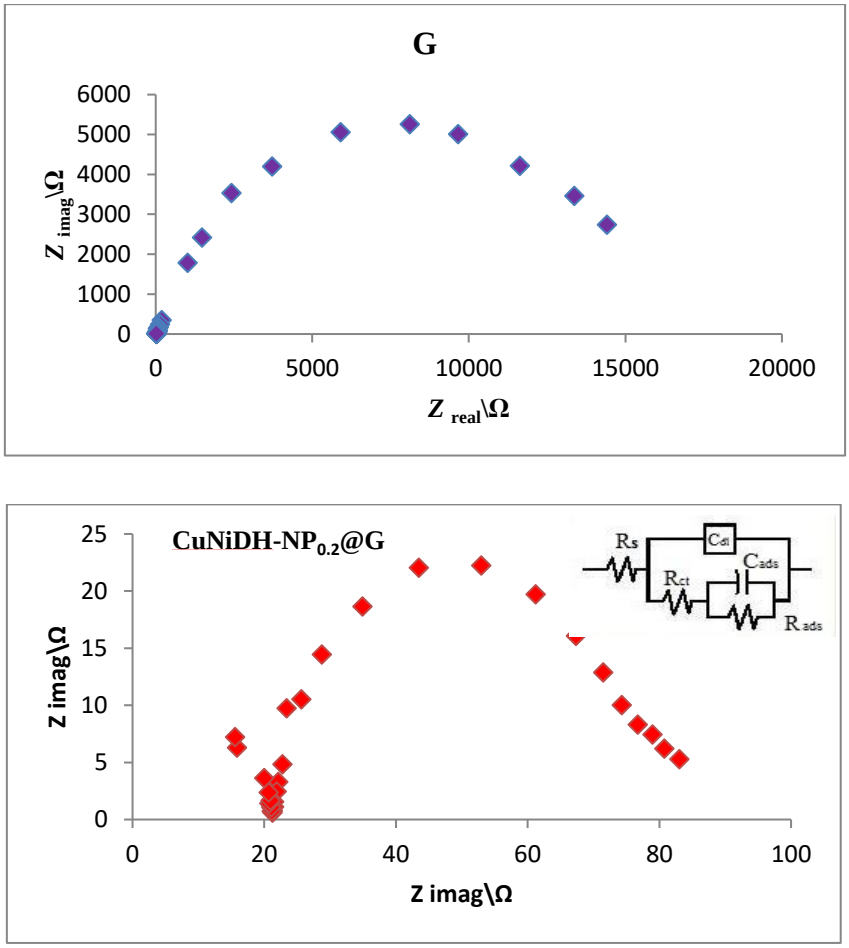

Figure 12. Nyquist diagrams of G and CuNiDH-$NP_{0.2}$@G electrodes (in addition of CuNiDH-NP $_{0.2}$@G electrode equivalent circuit) in NaOH 1 M at 0.58 V Ag/AgCl dc potential

3.7. Verification of contaminated surface of the electrode

To evaluate the stability of the electrode in the long-term use, the performance of the CuNiDH-$NP_{0.2}$@G electrode was studied before and after applying 500 cycles in the 0.2 M sodium sulfide solution (Figure 13). For this study, 0.1 M $K_4Fe(CN)_6.3H_2O$ solution was used and the performance of graphite electrode and CuNiDH-$NP_{0.2}$@G electrode before and after 500 cycles in 0.2 M sodium sulfide solution was investigated.

As can be seen in the Figure 14, the anodic current of the modified electrode decreased after 500 cycles, but the entire surface of the electrode was not poisoned, and the anodic current of the modified electrode was still higher than that of graphite.

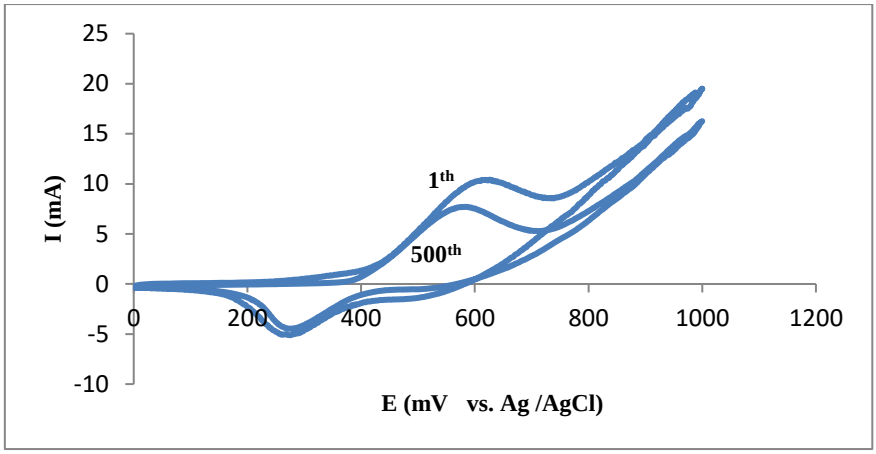

Figure 13. Voltammetric treatment of the CuNiDH-$NP_{0.2}$@G electrode for the first cycle and 500^{th} cycle in the alkaline media (1 M NaOH) at 0.2 mol/L sodium sulfide (scan rate = 100 mV/s)

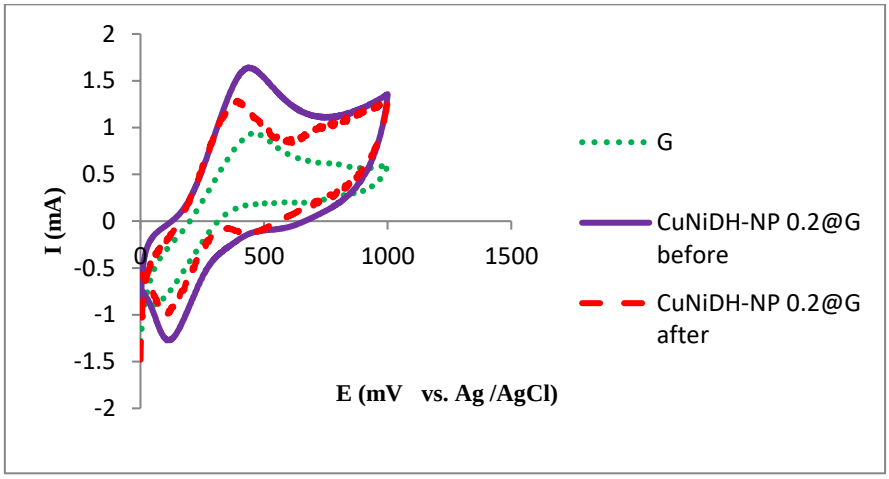

Figure 14. Voltammetric treatment of the G electrode and CuNiDH-$NP_{0.2}$@G electrode in 0.1 M $K_4Fe(CN)_6.3H_2O$, before and after 500 cycles in the alkaline media (1 M NaOH) at 0.2 mol/L sodium sulfide (scan rate = 100 mV/s)

4. CONCLUSIONS

In this study, the electro-oxidation of sodium sulfide in the alkaline media was successfully accomplished by the CuNiDH-$NP_{0.2}$@G electrode as a novel electrocatalyst**.** The introduced electrode was prepared by an electrochemical technique. Based on the results, this electrocatalyst has a high performance for electro-oxidation of sulfide. Accordingly, the NP, Ni and Cu have a synergistic effect. It was also concluded that NO existed in the electrocatalyst structure can be effective in electrocatalytic performance. In fact, NO is oxidized and reduced along with Ni and Cu as an electrocatalyst. The different crystal structure obtained due to the use of sodium nitroprusside salt can not be ignored in the good performance of the electrode. It should be noted that the introduced electrode has good stability for a long time of use.

high performance of CuNiDH-$NP_{0.2}$@G electrode and the simplicity of preparation of the electrode demonstrate great factors for using this procedure and electrode in the subsequent study of sulfides.

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Conflict of interest

The authors declare that they have no conflict of interest.

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