Chapter VI

Electrochemical sensor for Guanine using Cobalt Hexacyanoferrate/Al

The electrocatalysis of slow electron transfer reactions is perhaps the most important feature of chemically modified electrodes (CMEs). Such electrodes enhance the rate of electron transfer by reducing the overpotential associated with a reaction. Therefore, such electrocatalysis enables a high current density (i.e. increased sensitivity) to be obtained for a poor kinetic reaction at a potential close to the equilibrium potential. The electrocatalytic properties of many modified electrodes have already been studied by different authors, and valuable reviews have been published [1-4]. Among the various compounds used as electrode surface modifiers, the hexacyanoferrates of transition elements are very important. This may be due to the presence of two sets of redox couples, i.e. $\text{Fe(CN)}_6^{3+/4-}$ and $M_{\text{ox}}/M_r$ in some of the hexacyanoferrates which appear during the variation of potential. Such a characteristic favours the use of some hexacyanoferrates as electron transfer mediators in the preparation of CMEs. The first attempt in this domain was preparation of iron(III) hexacyanoferrate (Prussian Blue, PB)-coated electrodes by V.D. Neff [5].

Metal hexacyanoferrates are an important class of insoluble mixed-valence polynuclear compounds extensively used to prepare chemically modified electrodes (CMEs) [6-17]. Because, they can produce well characterized electroactive films with properties in common not only with redox and ion-exchange polymers but also with intercalation compounds. Studies on metal hexacyanoferrates have mainly been focused on transition metal compounds, including prussian blue [6], cadmium
hexacyanoferrate (CdHCF) [7]. zinc hexacyanoferrate (ZnHCF) [8], copper hexacyanoferrate (CuHCF) [9], cobalt hexacyanoferrate (CoHCF) [10], nickel hexacyanoferrate (NiHCF) [11], indium hexacyanoferrate (InHCF) [12], vanadium hexacyanoferrate (VHCF) [13], lanthanum hexacyanoferrate (LaHCF) [14], palladium hexacyanoferrate (PdHCF) [15], manganese hexacyanoferrate (MnHCF) [16], and also hybrid hexacyanoferrates, for example copper and cobalt hexacyanoferrate (CuCoHCF) [17]. The electrode surfaces can be modified with metal hexacyanoferrate by different ways such as electrodeposition, adsorption, entrapping into a polymer matrix, electroless deposition, mechanically attaching the insoluble metal hexacyanoferrate or by the reaction between metal hexacyanoferrate with self-assembled monolayer of an organosulfur compound on a gold electrode [18-23].

Among the transition metal hexacyanoferrates, cobalt hexacyanoferrate is considered as attractive material to modify the electrode surfaces due to its excellent reversible redox behavior [24, 25]. The structure and electrochemical properties of CoHCF have been reported in the literature [26, 27]. Recently, with the micro dialysis sampling technique, morphine was detected in rat brain by using HPLC on a cobalt hexacyanoferrate chemically modified electrode [28]. Cobalt hexacyanoferrate-modified glassy carbon electrodes have also been shown to be useful for electrocatalytic oxidation of NADH [19], ascorbic acid [27], dopamine [24] and hydrazine [29]. Cobalt, nickel and indium hexacyanoferrate films have shown catalytic activity towards electrooxidation of SO$_3^{2-}$ and S$_2$O$_5^{2-}$ ions [12].

A great number of works deal with electrocatalytic oxidation or reduction of solution species at CoHCF modified electrodes, and applications of these reactions for electrochemical sensors and biosensors. But fabrication of a sensor using
hexacyanoferrate modified Al electrode has not been reported. So present chapter
describes the electrochemical oxidation of guanine using CoHCF modified
aluminum electrode. Optimization studies such as scan rate, pH, supporting
electrolyte, thickness of CoHCF were studied. Sensitivity and detection limit were
studied using different concentrations of guanine by differential pulse voltammetry.
Probable analytical applications were also studied.

In order to optimize the conditions for getting better coatings, electroless
deposition of cobalt hexacyanoferrate (CoHCF) on aluminium electrode was carried
out at various times. Thickness of CoHCF film on aluminium was measured from
the mass measurements. The influence of anodizing parameters on the surface
properties of the oxide film are discussed in detail

6.1 Electrode modification conditions

The electroless preparation of the CoHCF/Al modified electrode was carried
out in two steps involving the deposition of metallic cobalt on the aluminum surface
and then derivatization of the deposited cobalt to give CoHCF. Preliminary
experiments showed that by dipping the aluminum surface in the Co\(^{2+}\) solution, no
chemical deposition of metallic cobalt on the aluminum surface is occured. It was
found that the redox reaction between metallic aluminum and Co\(^{2+}\) can be performed
in the presence of F\(^{-}\) ions. In detail, in the presence of F\(^{-}\): (1) the apparent standard
potential of the Al\(^{3+}/Al\) system (E\(_0\)) is decreased, which favors the redox reaction to
form metallic cobalt on the electrode, and (2) the Al\(_2\)O\(_3\) deposited on the electrode is
dissolved by complexing the Al\(^{3+}\) ions as AlF\(^{4-}\) to provide the surface conditions for
the metallic cobalt deposition on the aluminum.

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The optimization of the CoCl₂ and NaF concentrations in the plating solution is very important in this step. An extensive study led us to use a 2 M CoCl₂ solution, saturated with NaF (plating solution). On the other hand, preliminary experiments showed that the chemical derivatization of metallic cobalt to give CoHCF film on the electrode can be performed even in the absence of any deliberately added oxidizing agent. In this step, the kind of electrolyte, its concentration, as well as the concentration of Fe(CN)₆³⁻ are important. It has been found that a 0.25 M solution of Fe(CN)₆³⁻ containing 0.25 M KCl (derivatization solution) is suitable. This parameter is optimized based on thickness of the CoHCF film on aluminium by electroless method.

6.1.1 Effect of thickness

The thickness of CoHCF film was optimized based on the peak current (Ip). The thickness of the CoHCF film depends on the immersing time of the electrode in the plating bath and derivatizing solutions. In the present work, the plating time was varied from 2 to 7 min and the derivatizing time from 2 to 30 min, respectively depending on the desired film thickness. It was have found that the optimized film thickness of CoHCF was 5 µm of the anodic peak current for five CoHCF film preparations (Figure 6.1). This might be associated with a oxidation in the actual working surface area of the electrode that results from excess deposition when larger volumes of CoHCF film become aggregated on the electrode surface. In light of this possibility, the thickness of the film was selected as 5 µm for further sensor optimization and studies.
6.1.2 Effect of supporting electrolyte

The redox peaks are dependent on the nature of the cation of the supporting electrolyte. This behaviour clearly indicates that the electrolyte cation should be responsible for maintaining the electroneutrality of the electrode surface, thus allowing redox reactions. Six media, namely KCl, phosphate buffer, Britton-Robinson buffer, acetate buffer, sulphuric acid and nitric acid were tested as supporting electrolytes. It was found that KCl and phosphate buffer were outstanding in terms of peak current and sensitivity. Among these two, the best peak was obtained in phosphate buffer. When the concentration of phosphate buffer was 0.25 M, the highest peak was obtained. Thus 0.25 M phosphate buffer was chosen as supporting electrolyte.
6.2 Electrochemical behavior of the modified electrode

In order to morphologically stabilize the crystal lattice of the films, the freshly prepared electrode was cycled between 0 and 1.0 V for about 30 cycles with a scan rate of about 50 mV s\(^{-1}\). To sustain the electroneutrality of the modified film throughout the electrochemical process, ions usually enter into or escape from the immobilized film. Therefore, ions have an extensive effect on the electrochemical performance of the modified electrodes. Since the Co\(^{2+}\) cations in the modifying film are not expected to be electroactive in the potential range examined, 0.0-1.0 V, the two redox couples can be explained as proposed by Kulesza and co-workers [30] by assuming the existence of two possible stoichiometries for CoHCF, namely NaCo\(^{II}\)\(_{1.5}\)Fe\(^{II}\)(CN)\(_{6}\) and Na\(_{2}\)Co\(^{II}\)Fe\(^{II}\)(CN)\(_{6}\). Therefore, it is likely that two redox couples including Co\(^{II}\)\(_{1.5}\)Fe\(^{III}\)(CN)\(_{6}\)/NaCo\(^{III}\)\(_{1.5}\)Fe\(^{II}\)(CN)\(_{6}\) and NaCo\(^{II}\)Fe\(^{III}\)(CN)\(_{6}\)/Na\(_{2}\)Co\(^{II}\)Fe\(^{II}\)(CN)\(_{6}\) and an alkali metal cation is necessary for doping of the film to provide charge neutrality within the film. The cyclic voltammogram (Fig. 6.2) exhibits two sets of reversible redox peaks with formal potentials (E\(^\circ\) [\((E_{p,a} E_{p,c})/2\)] of about 0.43 and 0.83 V, which have been attributed to the transformations between Fe(II) and Fe(III) in NaCo\(^{II}\)\(_{1.5}\)-Fe\(^{II}\)(CN)\(_{6}\) and Na\(_{2}\)Co\(^{II}\)Fe\(^{II}\)(CN)\(_{6}\), respectively. Therefore, it is likely that two redox couples, including Co\(^{II}\)\(_{1.5}\)Fe\(^{III}\)(CN)\(_{6}\)/NaCo\(^{II}\)\(_{1.5}\)Fe\(^{II}\)(CN)\(_{6}\) and NaCo\(^{II}\)Fe\(^{III}\)(CN)\(_{6}\)/Na\(_{2}\)Co\(^{II}\)Fe\(^{II}\)(CN)\(_{6}\), can be expected.
Electrochemical cyclic voltammograms of cobalt hexacyanoferrate adsorbed on an aluminium electrode at various potential scan rates: 10-100 mV/s⁻¹.

Fig. 6.2 shows the cyclic voltammograms corresponding to the response of an aluminium electrode modified with adsorbed cobalt hexacyanoferrate complex in a 0.25 M phosphate buffer solution at various scan rates over a range of 10 - 100 mV/s. The anodic and cathodic peak currents are directly proportional to the scan rate in the range below 100 mV/s, as shown in Fig. 6.3 for the second well-defined redox couple. The ratio of anodic to cathodic peak currents obtained at low scan rates is almost unity. The peak-to-peak potential separation (ΔEp) is small (~20 mV for scan rate 10 mV/s⁻¹). Also, the formal potential $E^\circ = (E_{pa} + E_{pc})/2$ is approximately independent of the potential scan rate for sweep rates below 100 mV/s⁻¹, suggesting facile charge transfer kinetics over this range of sweep rate and a transfer coefficient (α) of ~0.5. However, for sweep rates above 100 mV/s⁻¹, the peak separations begin to increase, emphasizing a limitation arising from charge-
transfer kinetics. At higher sweep rates, the plot of peak current versus scan rate deviates from linearity and the peak current becomes proportional to the square root of the sweep rate, indicating diffusional behavior in charge transport at these sweep rates. The surface coverage can be evaluated from the equation,

\[ \Gamma = \frac{Q}{nFA} \]

where \( Q \) is the charge obtained by integrating the anodic peak under the background correction (at a low scan rate of 10 mV/s\(^{-1} \)) and other symbols have their usual meanings. In the present case, by assuming the involvement of one electron in the process, the calculated value of \( \Gamma \) is \( 5.73 \times 10^{-9} \) mol cm\(^{-2} \).

![Graph](image)

Fig. 6.3. Plot of anodic and cathodic peak currents of the second well-defined redox couple of CoHCF versus scan rate
6.3 Electrocatalytic oxidation of guanine at the surface of CoHCF – modified electrode aluminium electrode

The electrochemical reduction and oxidation of natural nucleic acids are irreversible and occur at highly negative and positive potential, respectively. This nucleic acid shows well-defined oxidation peak at 0.9-1.0 V at the different modified electrodes. [31]

The oxidation peak of guanine is close to the second well-defined oxidation peak potential of CoHCF that appears in the buffer (pH = 7) medium. Therefore, we expected an electrocatalytic mechanism initiated by electrochemical oxidation of the reduced form of the complex exist at the surface of the electrode and then completed by chemical oxidation of guanine, which also serves to regenerate the reduced form of the CoHCF. To reveal the electrocatalytic activity of CoHCF toward the oxidation of guanine, the voltammetric behaviour of guanine was investigated at the surface of bare and CoHCF-modified aluminium electrodes. Fig. 6.4 shows the cyclic voltammograms of CoHCF-modified Al in a 0.25 M phosphate buffer solution (a) and in the presence of 0.5 μM guanine (b). The anodic peak current of the CoHCF complex increased due to the presence of guanine, whereas cathodic peak current of this complex decreased accordingly. The peak current of 1.3 mA was obtained at 0.75 V. Therefore, an enhancement of peak current is achieved in this system, which clearly demonstrates the occurrence of an electrocatalytic process. Since the current measurement with modified electrode may be perturbed by the current from the possibly of direct oxidation of guanine. In figure 6.4, we have subtracted the current of the oxidation of guanine at the surface of the bare electrode from the currents at the surface of CoHCF-modified aluminium electrode.
Fig. 6.4. Cyclic voltammograms of modified electrode (a) in the absence and (b) in the presence of 0.5 μM guanine in 0.25 M phosphate buffer solution.

6.3.1 Effect of preconcentration (accumulation) time

Several reports have revealed that guanine can be adsorbed on the surface of modified electrodes at open circuit condition [11, 29, 41, 42]. However, in many accumulation steps, potential and time may significantly affect the sensitivity of the determination by changing the amount of the adsorbed species at the electrode surface. Therefore, the effect of accumulation time (t) was investigated for 0.5 μM of guanine in various accumulation times under the foregoing optimal operating conditions. For 0.5 μM of guanine, before reaching the saturation condition (beyond ~210 s (fig. 6.5.), the peak current increases on increasing the accumulation time. However, for 0.5 μM concentrations, the responses are linear up to 400 s after reaching the saturation conditions (i.e. 220 s). Apparently, lower concentrations of
the analytes require longer accumulation time, meaning that the choice of accumulation time is dictated by the desired sensitivity. To avoid saturation of the electrode surface and to account for a reasonable sensitivity, an accumulation time of 240 s was used for the further studies.

![Graph](image_url)

Fig. 6.5 Effect of accumulation time versus current for 1 µM of guanine on the surface of the CoHCF/Al in 0.1 M PBS of pH 7.

6.3.2 Effect of scan rate

Useful information involving the electrochemical mechanism usually can be acquired from the relationship between the peak current and scan rate. Fig. 6.6 shows the cyclic voltammograms of 0.5 µM guanine in phosphate buffer of pH = 7, recorded at different scan rates. It can be seen that with the increase of the scan rate, the oxidation peak currents increased gradually.
Fig. 6.6. Cyclic voltammograms of 0.5 \( \mu \text{M} \) guanine in PBS pH = 4 obtained at different scan rates: 10-100 mVs\(^{-1}\).

As shown in figure 6.6, the anodic peak current intensities due to guanine oxidation increases linearly with the scan rate in the range of 10-150 mV/s, demonstrating that the oxidation of guanine on CoHCF/Al is an adsorption-controlled process. Further, some deviation from linearity was observed at higher scan rates, and the associated anodic peak current vary directly with the potential scan rate square root employed, indicating that the kinetics of the overall process are controlled by the rate of mass transport of guanine from the bulk solution to the electrode surface at these scan rates. In addition, the catalytic oxidation peak potential (\( E_p \)) shifts to more positive values with increasing the scan rate. A linear dependence was observed between the peak potential and the logarithm of scan rate (figure 6.7), \( \log (v) \) as described by the regression equation:
Ep = 741.25 + 33.286 log ν \quad R^2 = 0.9952

The slope of this plot is equal to 33.83 mV/decade\(^1\) and also by considering a two-electron mechanism, it can be demonstrated that, the transfer coefficient, \(\alpha\), is equal to 0.62. The results are in good agreement with those cited in the literature [32].

Fig. 6.7. Effect of scan rate on peak current in buffer solution containing 0.5 µM guanine at CoHCF/Al.

6.3.3 Effect of pH

It was noted that pH has a profound effect on the oxidation current of guanine at the modified aluminium electrode, while the electrochemistry of the redox system itself is pH independent. The pH of the electrolyte solution was adjusted by adding a 0.10 M NaOH or HCl solution to PBS. Fig. 6.8. shows the
effect of pH on peak current at CoHCF modified Aluminium electrode in 0.25 M PBS buffer solution. As illustrated in trace in Figure 6.8 & 6.9, only a gradually increase in the oxidation current of guanine with increasing pH from 3.50 to 6.0 is observed at the modified electrode. When the pH was 4, the oxidation current of guanine at the modified electrode increases sharply, and decreases slowly with increasing pH upto 6.

![Graph showing the effect of pH on peak current at CoHCF modified Aluminium electrode in 0.25 M PBS buffer solution.](image)

Fig. 6.8. Effect of pH on peak current at CoHCF modified Aluminium electrode in 0.25 M PBS buffer solution.

As we know, the oxidation potential of guanine is pH dependent and the $E_{pa}$ vs pH plot indicates that the oxidation peak potential, $E_{pa}$ varies linearly with pH as expressed by the equation:

$$E_p (3.5 < pH < 6.0) = -0.339pH + 1.07686$$
which indicates a $2H^+, 2e^-$ transfer mechanism as it was also reported in a number of previously proposed guanine oxidation mechanisms [33, 34].

![Graph showing the effect of pH on peak potential at CoHCF modified aluminium electrode in 0.25 M PBS buffer solution.]

**Fig. 6.9.** Effect of pH on peak potential at CoHCF modified aluminium electrode in 0.25 M PBS buffer solution.

Based on these observations, an electrocatalytic mechanism for the oxidation of guanine by CoHCF can be expected and the catalyst is regenerated (Eq. (3))

\[
2\text{Na}_2\text{Co}^{II}\text{Fe}^{II}(\text{CN})_6 \rightarrow 2\text{Na}\text{Co}^{III}\text{Fe}^{III}(\text{CN})_6 + 2e
\]

\[
(\text{guanine})_R + 2\text{Na}_2\text{Co}^{II}\text{Fe}^{III}(\text{CN})_6 \rightarrow (\text{guanine})_{ox} + 2\text{Na}_2\text{Co}^{I}\text{Fe}^{II}(\text{CN})_6
\]
6.4 Detection Limit

Fig. 6.10. Differential pulse voltammograms of various concentrations of guanine over range of 10-110 µM guanine at the surface of a CoHCF modified aluminium electrode in 0.25 M PBS buffer solution

Differential pulse voltammograms were recorded for various guanine concentrations at the CoHCF modified Al electrode and given in Fig 6.10. It shows a linear variation of the peak current intensity with guanine concentration in the range of $10 \times 10^{-6}$ M to $110 \times 10^{-6}$ M in phosphate buffer (pH = 4.0). Fig. 6.11 shows the calibration plot and the linear regression equation was expressed as:

$$I_{pa}(\mu A) = 0.078C_{\text{guanine}} (\mu M) + 0.0396 \quad R^2 = 0.9991$$
Ten repeat voltammetric experiments were carried out at the lowest guanine concentration and the standard deviation (s) of the measured currents was calculated. By interpolating a current value of intercept ±3 s (corresponding to an S/N certainty of 99.8%) into the calibration equation given in Fig. 6.11 we obtained a detection limit of 52 nM guanine. Hence, it can be concluded that the CoHCF modified aluminium electrode show excellent sensitivity and lower detection limit for guanine,

The detection limit, linear calibration range and sensitivity of modified electrode for guanine detection are comparable and even better than those obtained by using other modified electrodes (Table 6.1). In addition, CoHCF|Al showed higher stability for differential pulse voltammetry measurements of guanine.

![Fig. 6.11. Calibration curve obtained from the DPV voltammogram.](image_url)
6.5 Analytical applications

![Graph](image)

Fig. 6.12. Differential pulse voltammograms of various concentrations of ss-DNA guanine over range of 5-50 μM guanine at the surface of a CoHCF modified aluminium electrode in 0.25 M PBS buffer solution

Practical utilization of the CoHCF modified Al electrode was assessed in a real sample by measuring the guanine concentration in ss-DNA. The sample was prepared according to the process reported elsewhere. In short, native calf thymus dsDNA samples were dissolved in water, and then the solution was heated in a boiling-water bath (100 °C) for about 10 min. Finally, the solution was rapidly cooled in an ice bath. Generally, thermal denaturation involves the rupture of hydrogen bonds, the disturbance of stacking interaction, but not any breakage of a covalent bond. So, thermally denatured dsDNA may act as ss-DNA. The obtained
solution was diluted to an appropriate concentration daily using phosphate buffer solution (pH 4). Fig. 6.12 shows DPV of various concentration of ss-DNA. Well-defined peaks were observed at CoHCF modified aluminum electrode. This is due to the oxidation of guanine residue in the ss-DNA sample.

Fig. 6.13 shows that the linear dynamic concentration range of this system for DNA is 0-25µgml⁻¹. The peak current of guanine increases linearly with the concentration of ss-DNA (Fig.6.13). Also, the calibration curve for ss-DNA ranging from 0 to 60 µgml⁻¹ at the modified electrode is shown in Fig. 6.13. By using 3sb in the calibration equation, the detection limit concentration was calculated. The detection limit of 900 nM (based on 3sb), was estimated.

![Graph](image)

**Fig. 6.13.** Calibration curve obtained from the DPV voltammograms
6.6 Stability of the modified electrode

The stability of the CoHCF modified aluminium electrode toward various influences was also examined and was found satisfactory. There were no changes in the height and separation of the cyclic voltammograms after 100 cycles of repetitive scanning in 0.25 M phosphate buffer solution.

6.7 Reproducibility

After each measurement, the modified electrode was washed with distilled water and the adsorbed guanine was removed by performing 5-10 cyclic voltammograms in the supporting electrolyte (PBS, pH = 4.0) in the working potential window. The reproducibility of CoHCF/Al was estimated by comparing the oxidation peak current obtained for 10 determinations on a 2 x 10⁻⁶ M guanine solution in PBS, pH = 4. The relative standard deviation (RSD) of 3.4% (n = 10) revealed a good reproducibility of the method.

6.8 Interference study

In the present work, the interference effects of 1 mM ascorbic acid (AA), 0.1 mM uric acid (UA), 10 μM dopamine (DP), 1 mM glucose (Glu) and adenine (ad) were tested on the voltammetric response of 10 μM guanine. In the mixture of all these compounds by using the modified electrode, five well-defined waves with a very good resolution are resulted. Among these interferences, glucose has no response but AA, UA, and DP showed oxidation peaks in the selected potential range. Therefore, in this study it was proved that this method can be successfully applied for determination of guanine in the presence of the other interference compounds in the clinical analysis.
<table>
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<td>Cobalt(II) phthalocyanine-modified carbon paste electrode [36]</td>
<td>DPV</td>
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<td>550</td>
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<tr>
<td>β-Cyclodextrin incorporated carbon nanotube-modified electrode [37]</td>
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<td>0.79</td>
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<td>200</td>
</tr>
<tr>
<td>Carbon screen-printed electrode [38]</td>
<td>DPV</td>
<td>0.9</td>
<td>----</td>
<td>200</td>
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<tr>
<td>Molybdenium(VI) complex-TiO₂ nanoparticle-modified carbon paste electrode [39]</td>
<td>DPV</td>
<td>0.75</td>
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<td>Polythionine/Au-nanoparticles/MWCNT-modified electrode [40]</td>
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<td>CoHCF modified aluminium electrode (present work)</td>
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6.9 Conclusions

Electrochemical sensor technology is still limited in scope, and hence cannot solve all experimental monitoring needs. Yet, a vast array of electrochemical sensors have been applied in recent years for monitoring a wide range of drugs and biological molecules. Electrocatalytic oxidation of guanine using a electrochemical sensor, Cobalt Hexacyanoferrate modified aluminium electrode has been investigated at various thickness of CoHCF, pHs, scan rates.

From the data and figures, the following conclusions were made

1. In this work, the electrocatalytic activity of CoHCF-modified aluminium electrode toward the oxidation of guanine in phosphate buffer medium was demonstrated.

2. The experimental parameters were optimized.

3. The thickness of CoHCF on aluminium was optimized and it was 5 µm based on the peak current.

4. Well-defined oxidation peak potential of CoHCF that appears in phosphate buffer medium can electrocatalyze and improve dramatically the oxidation signal of guanine.

5. The optimized pH was 4 at CoHCF modified aluminium from peak current obtained in cyclic voltammetry.

6. A possible electrocatalytic mechanism for the oxidation of guanine by CoHCF on aluminium electrode has been proposed satisfactory.
7. From the differential pulse voltammetry, the detection limit of guanine was found to be 52 nM

8. From the real sample analysis, i.e. ss-DNA, the detection limit was found to be 900 nM

9. Comparing this sensor, with those reported previously, it can be pointed out that a big advantage of aluminium like electrode materials is the ease of modification in order to obtain higher selectivity, to lower the overpotential, or to achieve lower limits of detection and a wider range of linear response toward the analyte.
References


