

Electrochemical Behaviour of a Gold Film- Glassy Carbon Electrode for Determination of Chromium (VI)

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Abstract

A gold nanostructured film modified glassy carbon electrode (Au_{film}/GCE) was developed for the determination of chromium (VI) in water sample. GCE was immersed into $HAuCl_4$ solution ($10^{-3}M$) and electrodeposition of thin gold layer was conducted at $-0.4 V$ (vs $Ag/AgCl$) for 10 min. The strong affinity between Au and Cr species resulted with increasing of Cr (VI) signal, compared with the bare glassy carbon electrode. The electrodeposition time, type of supporting electrolyte, pH, the scan rate, modulation amplitude, and modulation time were optimized using differential pulse anodic stripping voltammetry (DP-ASV). The calibration graph using accumulation time of 120 s was linear from 10 to $120 \mu gL^{-1}$ with a sensitivity $1.3 \times 10^{-2} \mu A/\mu gL^{-1}$. Under optimum experimental conditions, a good correlation coefficient $R^2=0.9971$, and a low detection limit $5.5 \mu g/L$ Cr (VI) was obtained. The signal was reproducible with a relative standard deviation $\pm 4.5 \%$. The developed Au_{film}/GCE sensor was applied for the Cr (VI) determination of in sewage water samples.

Keywords: Chromium (VI); thin gold film; glassy carbon electrode and differential pulse anodic stripping voltammetry

Introduction

Chromium is a metallic element usually found in aquatic systems in two different oxidation states, Cr(III) and Cr(VI) with completely different natures. Chromium (III) in trace amounts is an essential supplement in the body and combines with various enzymes to transform proteins, sugar and fat, while chromium(VI) which, depending on the pH, is available as CrO_4^{2-} , HCrO_4^- , H_2CrO_4 or $\text{Cr}_2\text{O}_7^{2-}$ is toxic, mutagenic and carcinogenic. The oxidation state of chromium has a remarkable effect on its toxicity and also its bioavailability (Kachosang and Compton 2013). Therefore, as Thacker et al 2012 reported, determination of chromium (VI) is much more important than chromium (III), and the design of an analytical method which is capable of selective measurement of chromium (VI) is of great importance. According to El-Shahawi et al. 2005 and 2008, the chemical speciation of chromium in environmental samples is necessary for accurate assessments of the pollution source and levels. Chromium(VI) is usually determined by UV-VIS spectrophotometry by means of diphenylcarbazide in acidic solutions (Rudel and Terytze 1999).

Electrochemical techniques are considered to be powerful methods. Voltammetric methods are advantageous in speciation of chromium because they offer a low detection limit and the determinations can be carried out without any additional separation step. In particular, adsorptive stripping voltammetry (AdSV) is of interest due to its high sensitivity and selectivity according to Liu et al. 2007. Svancara et al. 2004 and Biswas et al. 2017 developed some of electrochemical methods and techniques for Cr(VI) detection. Also Welch et al. 2005 studied the reduction mechanism of Cr(VI) at solid electrodes in acidic media and its analytical application. Dai et al. 2006 reported that metal nanoparticles have shown superior or advantageous properties for a wide range of technological applications and they provide three important functions for electroanalysis: improved mass transport, high effective surface area, and catalytic properties. Many methods were reported to synthesize metal nanoparticles including reduction with different reagents as Wang et al. 2006 studied, UV light and electron-beam irradiation as Bertino et al. 2004 reported, and electrochemical methods studied by Liu et al. 2008. In this work, a gold thin film modified glassy carbon

electrode $\text{Au}_{\text{film}}/\text{GCE}$ was prepared by electrochemical method, in order to improve analytical performance of Glassy Carbon Electrode (GCE) for quantitative determination of Cr (VI) in water. The influence of several physicochemical (pH, type of supporting electrolyte) and instrumental (deposition time, scan rate, modulation amplitude) parameters on the DP-ASV response has been evaluated. From the estimated results this sensor could be an alternative method for a sensitive detection of Cr(VI) in water sample with DP anodic stripping voltammetry.

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Experimental

Material and Methods:

Differential pulse Anodic stripping voltammetric mode (DP-ASV) were conducted using Electrochemical Analyzer (MEC-12B). The glassy carbon electrode modified with Au- nano film was used as working electrode. Ag/AgCl electrode (saturated KCl) was used as reference electrode and a platinum wire as auxiliary electrode. The Au-nano film onto the surface of the working GCE was prepared by electrodeposition before each electrochemical measurement (see Procedure below). Standard solutions of Cr (VI) (100 mg/L^{-1}), hydrogen chloride HCl 0.1 M, HNO_3 0.1 M, H_2SO_4 0.1M and all other compounds were purchased from Sigma Group Chemical Reagents Co. Ltd, and used without any further purification. A solution of HAuCl_4 (0.108 g Au in 100 ml HAuCl_4) in 0.1 M HCl was used in electrochemical cell to deposit Au- nano film at the GCE surface. All reagents used were analytical grade and solutions were prepared with distilled water.

Preparation of the Au_{film} /GCE

The Au_{film} /GCE sensor was prepared by electrodeposition. Initially the glassy carbon electrode was rinsed with water to remove any residual polishing material. Then the surface of the electrode is polished gently with the Al_2O_3 powder with particle sizes 0.01; 0.5; 1.0 μm , purified with distilled water and ethanol (98 %). The procedure for the electrodeposition of *Au-nanofilm* at GCE was adapted from published reports *Liu et al. 2007*. The GCE was immersed into solution containing 15 mL HCl 0.1 M and 140 μL of HAuCl_4 (0.108 g of Au in 100 ml of HAuCl_4 solution) and deposition was

conducted at the potential of -0.4 V (vs Ag/AgCl) for 10 min. Thereafter the stripping step was performed till +0.6 V in stirring condition for 25 s.

Electrochemical Measurements

The electrochemical measurements were performed using modified Au_{film}/GCE and unmodified GCE electrode applying differential pulse anodic stripping voltammetry (DP-ASV) technique. In the electrochemical cell containing 15 ml HCl 0.1M (pH=1) as a supporting electrolyte anodic stripping voltammograms were recorded between -0.2 to +0.8 V, by applying differential pulse mode with the deposition time 120 s, scan rate 100 m V/s, step potential 4 mV, amplitude 20 mV, and modulation time 5 ms. During the deposition step the potential was kept at -0.2 V for 120 sec. After recording background voltammogram successive standard solution of chromium (VI) was added into electrochemical cell and the voltammogram were recorded after each addition. The same electrochemical conditions were used to determine Cr(VI) in the sewage water samples.

Sewage Water Analysis and Recovery

Sewage water samples were collected near an industrial factory of leather processing and cleaning. Firstly, the water sample was purified by a vacuum filtration process as the sample contained many solid suspensions. 2 mL of filtered sewage water were introduced into electrochemical cell containing 15 ml HCl 0.1M. Recovery experiments were performed by spiking standard Cr (VI) stock solution to the water sample following by the determination of analyte using DP-ASV experiments.

Results and Discussion

Electrochemical response of Cr(VI) on Au_{film}/GCE sensor

The effect of the gold film in the electrochemical detection of chromium (VI) was studied using the differential pulse anodic stripping voltammetry in a solution 0.1M HCl (pH=1) containing Cr (VI). The successive voltammograms were recorded between -0.2 to +0.8 V using a scan rate 100 mV/s, step potential 4 mV, amplitude 20 mV and modulation time 5 ms. Although the anodic peaks of Cr (VI) using modified and bare electrode in the electrochemical cell contained 100 $\mu\text{g L}^{-1}$ of Cr (VI) appeared at potential +0.3 V the highest peak was obtained with modified electrode. This can be attributed to the strong affinity between Au and Cr.

Optimization of experimental parameters

The optimization of DP-ASV instrumental parameters influencing in the current response of analyte it is very important step in the development of electroanalytical methodology. The effect of different parameters such as pH, type of supporting electrolyte, and accumulation time was investigated in order to optimize analytical performance of Au_{film}/GCE sensor for determination Cr(VI) in water solution. All experiments are performed in 50 $\mu\text{g L}^{-1}$ Cr(VI) and step potential of 4 mV.

The response obtained using modified sensor, Au_{film}/GCE in Cr(VI) solution applying different accumulation time (30s; 60s; 120s; 180s), is shown in the Figure 1. It can be seen that the response increases linearly up to 120 s accumulation time, and thereafter

decreases, reflecting the electrode surface saturation. Therefore, an accumulation time of 120 s was used for all further measurements.

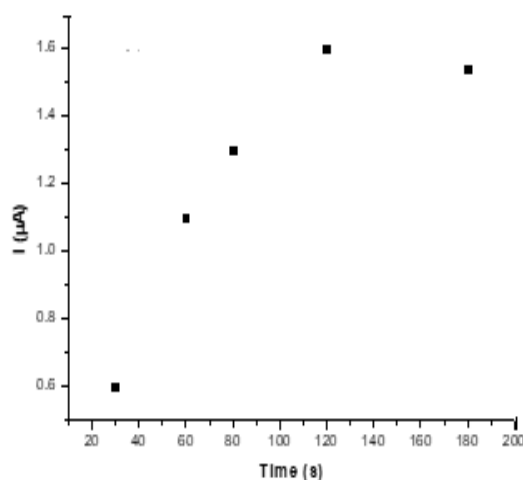


Figure. 1 Effect of the accumulation time (30s; 60s;120s; 180s) at Au_{film}/GCE, in 0.1 M HCl for concentration 50 µg L⁻¹ Cr(VI)

Selection of suitable supporting electrolyte is important on sensor response because has effect on kinetics of the charge transfer processes. Various inorganic acids were used including hydrochloric, nitric and sulfuric 0.1M in order to investigate their impact on the electroanalytical signal of 50 µg L⁻¹ Cr(VI) solution. The best (position shift to negative potential, height and width) anodic peak for Cr (VI) using Au_{film}/GCE was obtained when hydrochloric acid is used as the supporting electrolyte (figure 2a). The difference between the sensitivity of Cr(VI) in HNO₃, HCl and H₂SO₄ according to *Roohollah and Richard 2013* is probably due to the difference in the diffusion rate of species to the electrode surface. Also it may reflect adsorption on the electrode and the variation between acids

suggests that the adsorption of anions plays a significant role in the reduction mechanism as *Roohollah and Richard 2013* mention in their study. In this prospect this electrolyte was used for subsequent experiments.

The effect of pH on peak current using modified sensor was demonstrated in the diagram fig 2b, concentration of HCl vary from 0.001 to 0.1M, which correspond pH 3 to 1, respectively.

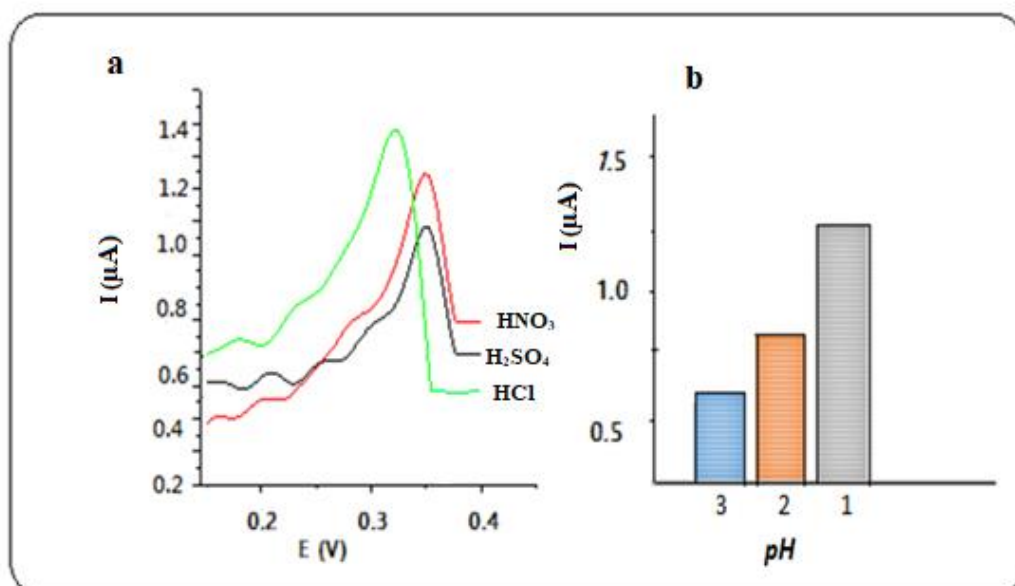


Figure. 2 a) Anodic stripping voltammograms of 50 µg L⁻¹ Cr(VI) at various electrolyte.

b) Effect of pH on the peak current for the determination of Cr(VI) on Au_{film}-GCE

It is obviously shown from diagram that the highest signal in solution of Cr(VI) 50 µg L⁻¹ using Au_{film}/GCE sensor was obtained at concentration 0.1 M HCl (pH=1). Lower signal of anodic peak current explained by toindicate proton-dependent process as it is

reported elsewhere by *Yamadaa et al 2008*. For this reason, lower analytical signal was obtained in the case of lower concentration of indifferent electrolyte (0.001 M HCl), possibly because of the low concentration of protons. Therefore, 0.1 M hydrochloric acid solution was used as the optimum concentration of supporting electrolyte for the rest of this study.

Some experimental condition parameters such as scan rate and modulation magnitude were optimizing in order to obtained the best signal with high sensitivity toward analyte Cr VI. With increasing of modulation amplitude is observed that the peak current increases gradually up to 50 mV, and then it remained constant but the form of the peak becomes wider. It was choosing 20 mV as the most suitable amplitude to give the highest and sharper peak. Also by increasing the scan rate from 50 to 150 mV/s, peak current increased proportionally up to 100 mV/s. With increasing the scan rate more than 100 mV/s no effect to the peak was observed. To obtain the highest signal of Cr VI scan rate 100mV/s was chosen in further experiments. According to the results presented above in all subsequent experiments regarding evaluation of analytical parameters and real sample analysis were used optimal conditions listed in table below. In table 1 are summarizes the operating conditions optimized for the DP-ASV analysis of Cr(VI) using a Au_{film}-GCE.

Table. 1 The operating conditions optimized for Cr(VI) determination with DP-ASV using a Au_{film}-GCE sensor

Experimental conditions: (DP-ASV)	Optimized Value
Supporting electrolyte	HCl 0.1 M
pH	1.0
Deposition time	120 s
Deposition potential	-0.2 V
Detection potential ^a	+0.3 V
Scan rate	100 mV/s
Potential scan	-0.2 to 0.8 V
Modulation amplitude	20 mV
Modulation time	5 ms

^a vs. Ag/AgCl, saturated KCl

Analytical Parameters

The analytical performance of modified sensor Au_{film}/GCE for the determination of Cr(VI) were estimated by DP-ASV technique under optimal conditions. The differential pulse anodic stripping voltammograms for different concentrations of Chromium (VI) were illustrated in figure 3 a. The calibration plot is linear over the range from 10 to 120 $\mu\text{g L}^{-1}$. Limits of detection calculated based on three times the standard deviation of the baseline resulted 5.5 $\mu\text{g L}^{-1}$. Respectively, the calibration curves and correlation coefficients are $y = 0.07593 + 0.01396x$ and $R^2 = 0.9971$ corresponding the accumulation time of 120 s (fig 3b). The relative standard deviation for Cr(VI) determination at a concentration 120 $\mu\text{g L}^{-1}$, was 4.7% (n = 4).

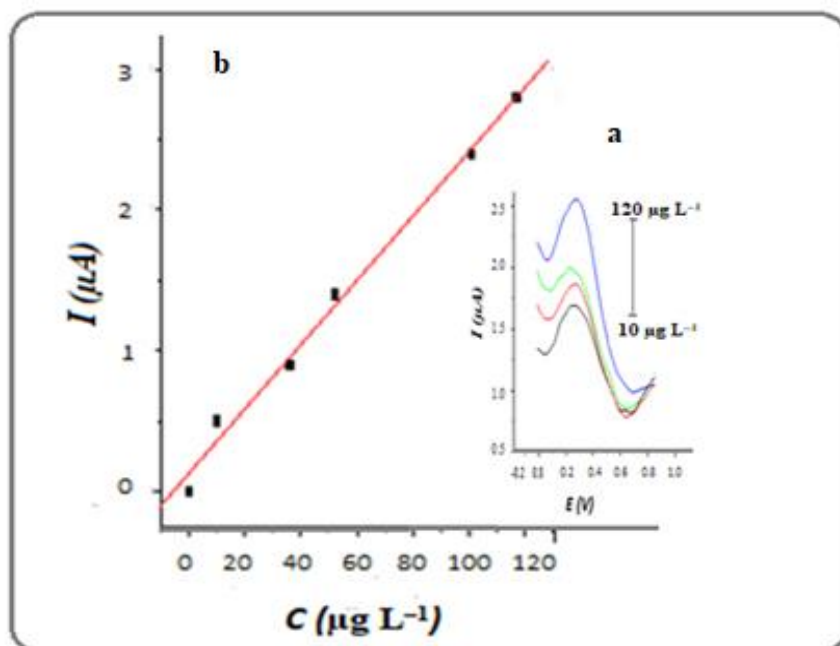


Figure. 3 a) DP-AS voltammograms registered with $\text{Au}_{\text{film}}/\text{GCE}$ electrode in HCl 0.1

M , $t_{\text{dep}}=120$ s, potential from -0.2 to 0.8 V in different concentration of Cr (VI) .**b)**

Calibration curve of various Cr (VI) concentration

The results obtained in this work demonstrate the improvement of the reproducibility and sensitivity for determination of Cr (VI) using $\text{Au}_{\text{film}}/\text{GCE}$ sensor and DP-ASV.

Table. 2 Analytical performance of various modified electrodes for Cr(VI) determination.

Modified electrode	Method	LOD ($\mu\text{g/L}^{-1}$)	LDR ($\mu\text{g/L}^{-1}$)	Reference
				<i>Richtera et al</i>
Electrochemically activated GCE	DPV	6.25	20.8–13000	2016
				<i>Metters et al</i>
Gold screen printed macro electrode	LSV	228	520-84240	2012
				<i>Tsai and Chen</i>
	CV ^c	104	260–5200	2008
AuNP-ITO electrode ^d				
	Amperometry	5.2	26–2600	
				<i>Domínguez-Re</i>
				<i>nedo et al</i>
Ag NPs ^a - carbon SPE ^e	DPV	44.2	26–1976	2008
Au NPs - carbon SPE	DPV	20.8	20.8–1664	
				<i>Stojanović</i>
Ag _{plated} .GCE	DP-ASV	5.2	18.2-2080	<i>et al 2018</i>
				<i>Hallam et al</i>
Graphite screen printed electrode	LSV	18.7	99.8-998.4	2010
			10–120	This
Au _{film} .GCE	DP-ASV	5.5	work	

^aNPs – nanoparticles, ^bLSV – Linear sweep voltammetry, ^cCV – Cyclic voltammetry, ^dAuNP-ITO electrode – Gold nanoparticle- electrodeposited indium-tin oxide electrode, ^e SPE – screen printed electrode

For comparative purposes in table 2 are listed various publications which report the analytical performance of the modified electrodes for Cr (VI) analysis. By the data reported the sensitivity of the method studied in this work shows advantages relating with sensitivity and low detection limit compared with reported electroanalytical methods referred. Regarding other analytical application procedures such as reproducibility, linearity, simplicity of the modification procedures is comparable with other methods.

Analysis of a real sample

The modified glassy carbon electrode ($\text{Au}_{\text{film}}/\text{GCE}$) was applied to Cr(VI) determination in sewage water sample. A solution of the sample was acidified with nitric acid and a portion of 2 mL diluted in 15 mL HCl 0.1 M was used for analysis. The content of Chromium was determine using standard addition methods and the recoveries of the added Cr(VI) were studied. The recoveries results are used as quality control of the analytical determination of Cr in real samples taken near an industrial factory of leather processing and cleaning. The signal of the sample solution before spiking Cr(VI) was firstly recorded (Fig. 4) and then additions of Cr(VI) were done to the solution and the voltammograms are recorded.

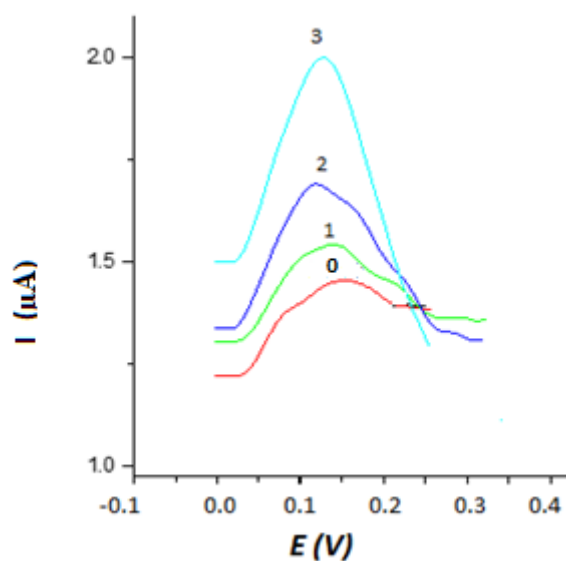


Figure. 4 DP-AS Voltammograms for standard additions of Cr(VI) in a sewage water sample, (0) sample signal before spiking and in concentrations (1)30, (2) 60, (3) 88 $\mu\text{g/L}^{-1}$

Cr(VI)

Voltammetric signal related to additions of Cr(VI), from 30 to 88 $\mu\text{g L}^{-1}$ are shown in Fig. 4. The increase in the anodic signals is obtained with increasing the concentration of Cr(VI). The recovery results of analyses are given in Table 3, together with the total contents of chromium found by $\text{Au}_{\text{film}}/\text{GCE}$ in sewage solution.

Table. 3 Recovery test with sewage water samples

Sample (sewage water) (μgL^{-1})	Cr(VI) Added (μgL^{-1})	Cr (VI) Found (μgL^{-1})	Spike Recovery (%)
Chromium Concentration	88	86.1 ± 0.8	97.8
	150 ± 0.6	176.5 ± 0.5	100.3

The concentration of Cr in analyzed samples taken near an industrial factory of leather processing and cleaning resulted $150 \pm 0.6 \mu\text{gL}^{-1}$ much higher than the allowance level of Cr in surface water according to *U.S. EPA, 1998*). The obtained recoveries of Cr(VI) added in concentrations of 88 and $176 \mu\text{gL}^{-1}$ were 97.3 % and 100.3% with RSD from 4.8% to 5.4 %, respectively. The results suggest that this method allows for Cr(VI) determinations in the presence of excess of Cr(III) and also can be easily adopted for routine analysis of chromium(VI).

Conclusions

A gold thin film- glassy carbon electrode ($\text{Au}_{\text{film}}/\text{GCE}$) is studied using DP-ASV for determination of chromium (VI) in liquid discharges of the leather processing industry. This method has advantages regarding the low cost for the fabrication of modified sensor, simple preparation, wide linear calibration zone, sensitivity and lowest limit of detection. It has been shown that, after proper optimization of the experimental conditions, the electrode prepared was suitable for the determination of Cr(VI) with high sensitivity and good reproducibility. The method developed was applied to real samples which gave satisfactory results and recovery of 97.8% obtained for a concentration of $88 \mu\text{gL}^{-1}$. We can recommend that the proposed sensor can be easily applied for analysis of chromium (VI) in industrial and environmental polluted water.

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