

Article

Pencil Lead Electrode Modified with Gold Thin Layer for Voltammetric Detection of Chromium(VI)

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Abstract. Cr(VI) is a toxic, mutagenic, and carcinogenic metal. This heavy metal have effect harmful on organism and the environment. In this study, an electroanalytic approach was improved for detection of the Cr(VI) using a pencil lead electrode modified with gold thin layer by cyclic voltammetry. Gold thin layer was electrodeposited on the pencil lead electrode surface with potential-sweeping technique at scan of potential from 1.2 V to 0 V. Since the Cr(VI) species depends on the pH, effect of supporting electrolytes matrix at various pH were investigated. It was found that Cr(VI) gave a reduction peak with a peak potential of 0.35 V vs Ag/AgCl in cyclic voltammogram with 0.1M HClO₄ as supporting electrolyte. The calibration curve for Cr(VI) at gold thin layer modified pencil lead electrode shows linearity in range of 5 μM to 100 μM with a detection limit of 2.3 μM achieved

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1. Introduction

Chromium (III) and Chromium(VI) are in a thermodynamically stable form in nature. Cr(VI) is known more toxic than Cr(III) and they have the opposite effect, in which, Cr(III) is considered as an element that play an important role in metabolism processes, whereas, Cr(VI) is reported as

carcinogenic and mutagenic metal [1]. In Industry, Cr(VI) is found as waste of tanning, electroplating, cement, mining, dyeing, production of steel, spray painting, wood preserving, etc [2]. Therefore, a rapid and sensitive analytic method for determination of Cr(VI) needs to be developed. There are several analytical techniques used widely for Cr(VI) detection using atomic absorption spectroscopy [3], [4], UV-Vis spectroscopy [5], [6] and ICP-MS [7], [8]. These methods are accurate and reliable, but they need sophisticated technique, expensive, and time-consuming in analysis process.

Electrochemical methods are very promising for analytical approach because they offer a simple, sensitive, reliable method and require less expensive equipment. Many researches have been done to detection of Cr(VI) using the gold modified electrode. The electrocatalytic effect of gold on the electrode surface have increased the reduction peak current of Cr(VI) [1], [9]–[16], such as carbon composite electrode modified with gold film [10], gold modified glassy carbon electrode [1], [11], gold modified carbon screen-printed electrode [14], gold modified indium tin oxide electrode [16].

In this study, the voltammetric detection of Cr(VI) for the first time was investigated at gold thin layer electrodeposited pencil lead electrode using without pre-concentration process. Pencil lead electrode has many advantages, such as high electrochemical reactivity, low cost, low technology and low background current [9], [17]–[24]. On the other hand, pencil lead electrode exhibits poor electrocatalytic sensitivity. Therefore, Gold thin layer electrodeposited at pencil lead electrode is considered to be very interest technique for Cr(VI) detection. This method offers a simple, sensitive and low cost and fast method.

2. Method

Pencil lead electrode (PLE) used was the neox graphite, pilot (0.9 mm, 2B). $\text{H.AuCl}_4 \cdot 4\text{H}_2\text{O}$ is from Wako Pure Chemical Industries in Osaka, Japan. Perchlorid acid (HClO_4) and Cr(VI) is from Nacalai Tesque in Kyoto, Japan. The Instrument used was the Model 900 electrochemical workstation (CHI- USA) with an Au-PLE working electrode, Pt counter electrode, and Ag/AgCl reference electrode (BAS, Japan).

2.1 Preparation of the Au-PLE

Pencil lead electrode modified with gold thin layer using the potential-sweeping electrodeposition in $50 \mu\text{M HAuCl}_4 \cdot 4\text{H}_2\text{O}$ and 0.1 M KCl for one cycle. The potential at the electrode was applied from 1.2 V to 0 V with a sweep rate of 100 mV/s. The cyclic voltammogram of this procedure was shown in Fig. 3. Pencil lead electrode was fabricated by inserting the pencil lead to teflon tube. The electrode is denoted as Au-PLE. Prior to experiment, the pencil lead electrode was polished by an alumina powder with in particle size of 0.05 mm.



Figure 1. neox graphite pencil (0.9 mm, 2B) made by Pilot

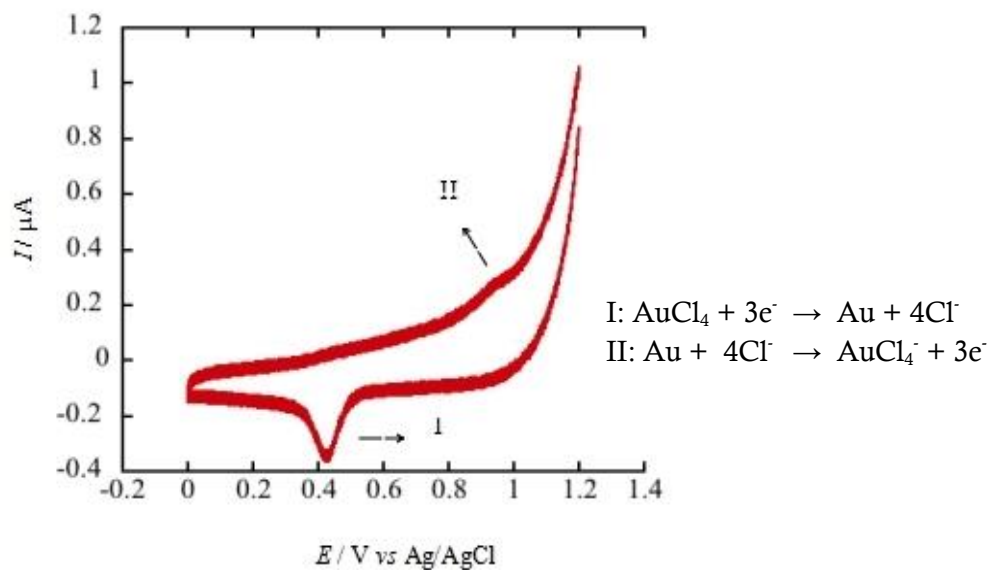


Figure 2. Cyclic voltammogram at a PLE immersed in 50 μM $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ and 0.1 M KCl, Scan rate of 100 mV/s.

2.2 Cyclic Voltammetry Procedure for Cr(VI) Detection

Cyclic voltammetry was carried out in 0.1 M HClO_4 supporting electrolyte. The measurement of Cr(VI) was performed by potential scan in range of 0.6 to -0.2 V vs Ag/AgCl with scan rate of 100 mV/s (without stirring).

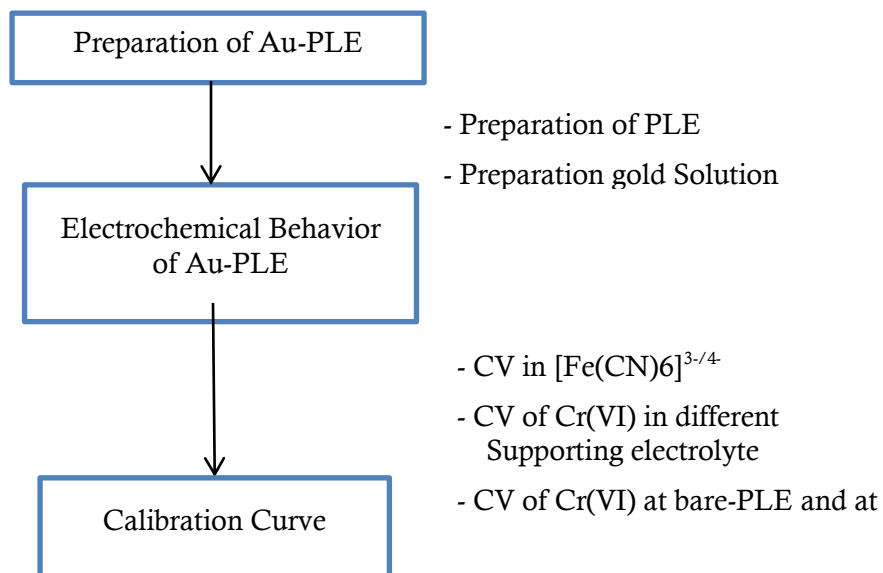


Figure 3. Flow Chart of the Research

3. Results and Discussion

3.1 Electrochemical behavior at different electrodes in [Fe(CN)₆]^{3-/4-}

The effective surface area of Au-PLE compared with bare PLE and Au electrode were studied with cyclic voltammetry in [Fe(CN)₆]^{3-/4-} and 1.0 M KNO₃ (in Fig. 4). The well-defined reduction and oxidation peaks were performed at 0.18 V and 0.25 V. Similar to that at Au electrode, the quasi-reversible electrochemical behavior for [Fe(CN)₆]^{3-/4-} redox couple with ca 70 mV of peak potential separation is shown by Au-PLE. The Au-PLE showed the high electroactive area based on the Randles-Sevcik equation (1):

$$I_p = 2.69 \times 10^5 AD^{1/2} n^{3/2} v^{1/2} C \quad (1)$$

Where A is the electrode area (cm²), v is rate (V/s), and n is number of electrons transfer. This work shows the heterogenous one-electron transfer (n=1), Concentration (C) is 2 mM, and the diffusion coefficient (D) is 6.057 x 10⁻⁶ cm²/s. The electrode area values of bare PLE, Au electrode, and Au-PLE obtained are 0.8 cm², 1.3 cm², 1.3 cm², respectively. The peak current of Au-PLE is higher than bare-PLE due to highly improved electrode kinetics at Au-PLE [2].

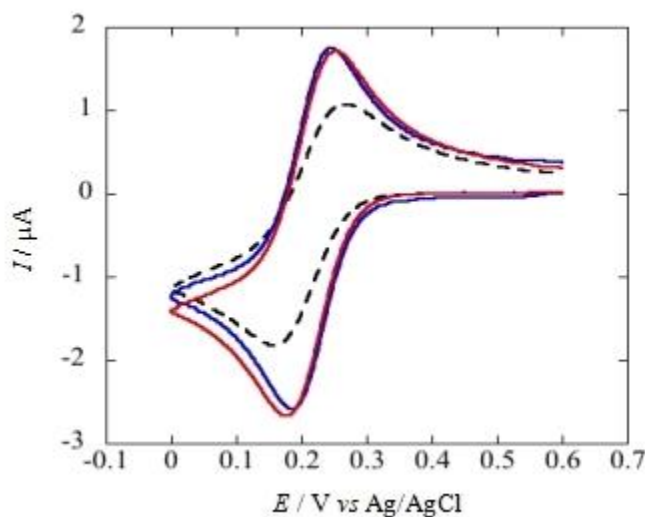


Figure 4. Cyclic voltammogram of Bare PLE(--), Au electrode (blue-line), and Au-PLE (red-line) in 2 mM [Fe(CN)₆]^{3-/4-} and 1 M KNO₃ at 50 mV/s

3.2 Electrochemical behavior of Cr(VI) at Au-PLE in different supporting electrolyte

The speciation of Cr(VI) depends on the solution pH and concentration. Cr(VI) exists in form of H₂CrO₄, HCrO₄⁻, and CrO₄²⁻ salts depending on the pH. At the pH less than 1.0, H₂CrO₄ is predominates, while at pH range of 1 and 6, HCrO₄⁻ is predominates and CrO₄²⁻ at will be predominates at pH above about 6. The dichromate ion (Cr₂O₇²⁻) which is a dimer of HCrO₄⁻ will occur to concentration of chromium exceeds approximately 1 g/L. In this work, The dominant form of Cr(VI) is HCrO₄⁻. [10], [25]

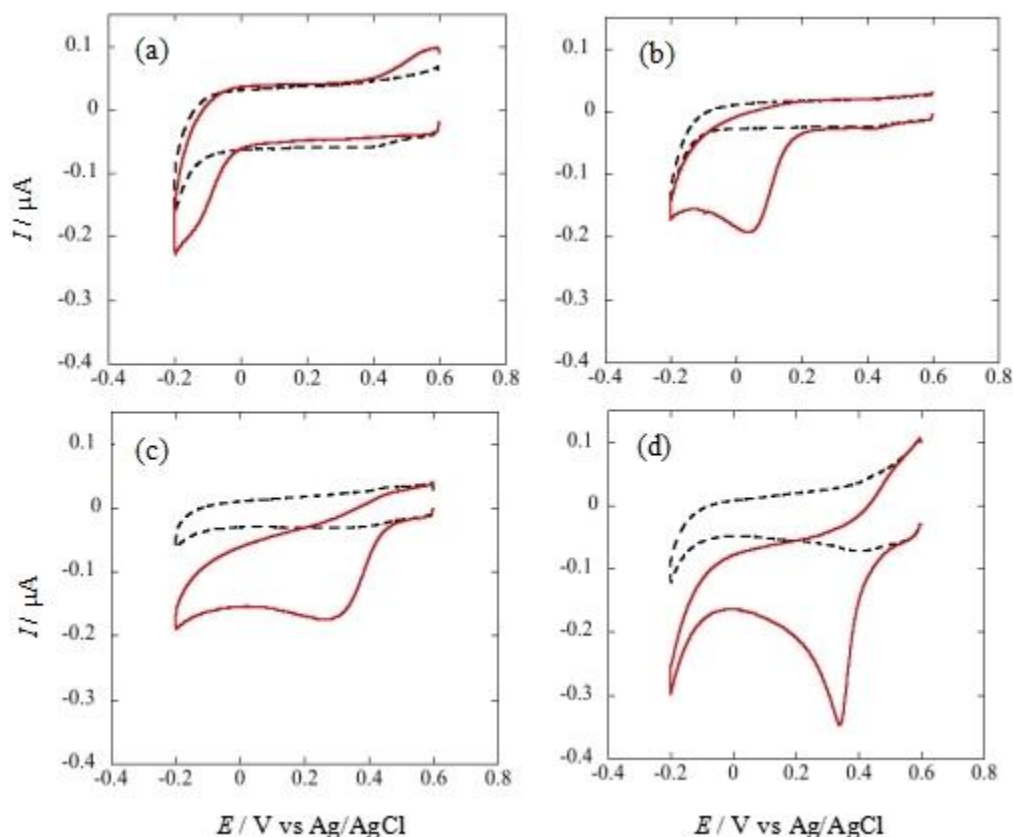


Figure 5. Cyclic voltammogram of Cr(VI) 50 μM at Au-PLE in PBS, pH 7 (a), ABS, pH 4 (b), 0.1 M H_2SO_4 (c), 0.1 M HClO_4 (d), Scan rate of 100 mV/s.

The effect of the supporting electrolyte was investigated using phosphate buffer, PBS (pH 7), acetate buffer, ABS (pH 4), 0.1 M H_2SO_4 , 0.1 M HClO_4 . Figure 5 shows cyclic voltammograms of 50 μM at Au-PLE with various supporting electrolyte and pH. As shown in Fig. 5(a), the peak of Cr(VI) reduction do not appear by addition of PBS (pH 7) supporting electrolyte, which assumed that the Cr(VI) reduction is difficult to occur in the pH netral and higher (alkaline solution) at Au-PLE. It has also been studied using alkaline solution but it is not shown here. A defined peak is obtained when the ABS (pH 4), 0.1 M H_2SO_4 , and 0.1 M HClO_4 is used (Fig. 5b-d). However, the results reveals the highest sensitivity and a sharp and well-defined peak for the reduction of Cr(VI) at 0.1 M HClO_4 . Therefore, in this study, 0.1 HClO_4 was used as the optimum supporting electrolyte. The sensitivity difference of Cr(VI) signal in H_2SO_4 and HClO_4 is indicated probably because of the diffusion rate difference of species at the electrode surface. Moreover, the adsorption of anions in the reduction mechanism of Cr(VI) play an important role [10].

3.3 Electrochemical response of Cr(VI)

The CVs of 50 μM Cr(VI) were recorded at bare-PLE and Au-PLE in 0.1 M HClO_4 with scan rate of 100 mV/s. The figure 6 displays the higher current densities at Au-PLE (0.08 μA) compared to bare-

PLE (0.02 μA). Moreover, the reduction peak of Cr(VI) shift toward more positive potential where the bare-PLE was observed at 0.05 V and the Au-PLE was observed at 0.35 V. The reduction potential shift was indicated due to higher electrocatalytic of gold thin layer electrodeposited on the pencil lead surface [2], [16]. The Cr(VI) presents as HCrO_4^- in acidic solution. The reaction of Cr(VI) reduction at electrode surface can be written in this equation (2),

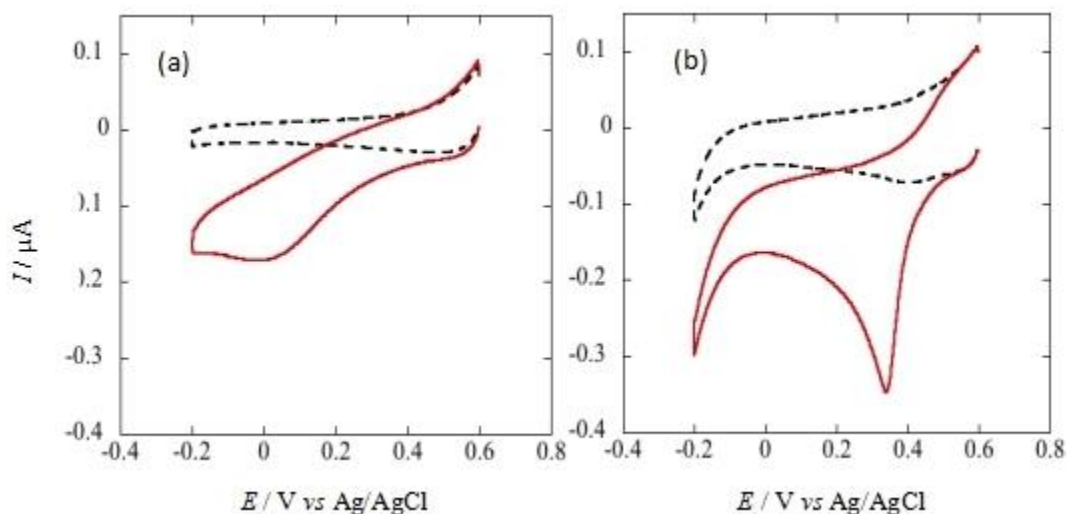
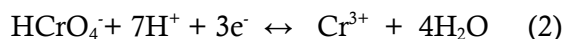


Figure 6. Cyclic Voltammogram of 50 μM Cr(VI) in 0.1 M HClO_4 at bare PLE (a) and Au-PLE (b). Scan rate: 100 mV/s.

3.4 Calibration graph

The figure 7 reveals the CVs at an Au-PLE for increasing the Cr(VI) concentration in 0.1 M HClO_4 . The reduction currents show linearity with concentration of Cr(VI) in range 0 to 100 μM with a correlation coefficient (R^2) of 0.9926. The detection limit of 2.3 μM was estimated as being 3-times ($S/N \geq 3$). The Au-PLE offers the advantages of low cost, fast response without pre-concentration process and well-defined peak current, simple electrode fabrication, and very promising for practical application.

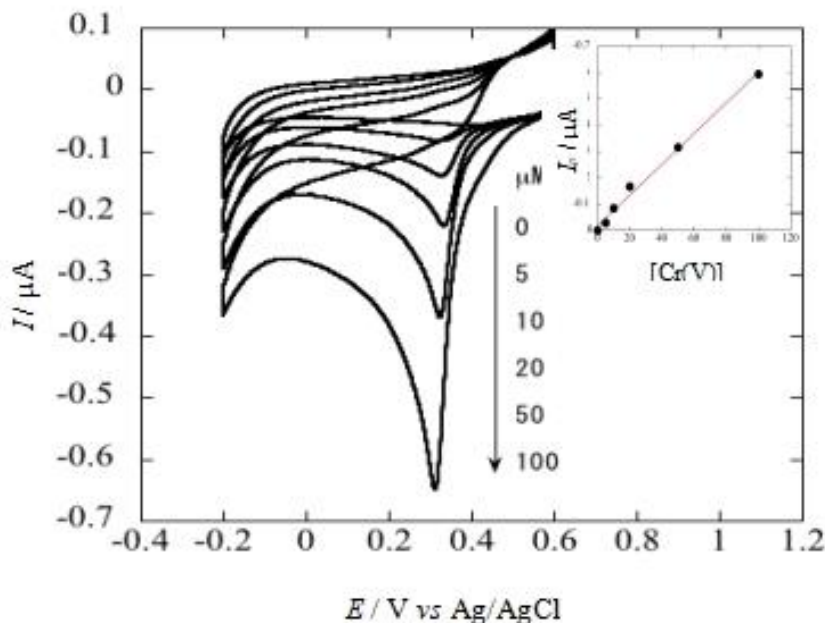


Figure 7. Cyclic Voltammograms on Au-PLE in 0.1 M HClO₄ with varying Cr(VI) concentration. Inset is calibration curve. Other condition same as in Fig 6.

4. Conclusion

The disposable pencil lead electrode modified gold thin layer was investigated for the voltammetric detection of Cr(VI) without pre-concentration process. The Au-PLE showed the greater performance compared to bare-PLE for Cr(VI) detection. The reduction potential shift was suggested to be due to electrochemically catalytic property of gold thin layer electrodeposited on the pencil lead surface. The calibration curve for Cr(VI) at gold thin layer modified pencil lead electrode exhibits linearity from 5 μM to 100 μM with a detection limit of 2.3 μM achieved. This method offer a simplicity, high sensitivity, fast response and low cost of analysis.

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