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## Voltammetric determination of Cr(VI) using gold nanoparticles-modified glassy carbon electrode

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### Abstract

Gold nanoparticles-modified glassy carbon electrode was utilized in the present study to determine trace amount of Cr(VI). The steps employed in the present study were fabrication of gold nanoparticles colloids, modification of glassy carbon electrode using the gold nanoparticle colloids, and voltammetric determination of Cr(VI) using the modified electrode. The results of the present study indicate that 290  $\mu\text{L}$  of 0.1 M  $\text{NaBH}_4$  was required to form gold nanoparticles colloids. Self assembly process was found to give better gold nanoparticles binding onto glassy carbon electrode compared to adsorption process as indicated by more gold nanoparticles attached onto the glassy carbon electrode. Modification of the glassy carbon electrode using gold nanoparticles increase sensitivity as indicated by good limit of detection (2.38 ng/L) with an acceptable linearity range within 0.050 – 0.250  $\mu\text{g/L}$ . The correlation coefficient and precision of the method were 0.9948 and 99.14%, respectively.

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### Nomenclature

AuNP	Gold nanoparticles
GCE	Glassy carbon electrode
AuNP-GCE	Gold nanoparticles-modified glassy carbon electrode
UV	Ultraviolet
SEM-EDS	Scanning electron microscope – energy dispersive X-ray spectroscopy
DPV	Differential pulse voltammetry

### 1. Introduction

Naturally occurring chromium has two valencies, Cr(III) and Cr(VI). In term of their toxicity and reactivity, these two chromium species have very distinct properties<sup>1</sup>. Cr(VI) has high toxicity while Cr(III) is less toxic and the later is also known to be one of essential ion for human, which required in particular amount in the diet. Due to their opposite nature in toxicity, it is important to distinguish between Cr(III) and Cr(VI). Therefore, specific and sensitive determination methods to distinguish both of the species are required. Since Cr(III) belongs to essential nutrition ion required for maintaining normal physiological function, thus trace amount determination of Cr(VI) become very important to avoid toxic intake in diet<sup>2</sup>. There has been several sensitive methods used for Cr(VI) determination including atomic absorption spectrophotometry (AAS)<sup>3,4</sup>, plasma-mass spectroscopy<sup>5</sup>, spectrofluorimetry<sup>6</sup>, chemiluminescence<sup>7</sup>, spectrophotometry<sup>8</sup>, and electrochemical methods<sup>9-11</sup>.

Electrochemical methods for Cr(VI) determination are time efficient, has high sensitivity and specificity, and also the instrument is easy to use<sup>12</sup>. Glassy carbon electrode modified by gold nanoparticles (AuNP-GCE) has been applied to detect Cr(VI) by adsorption stripping voltammetry to increase analytical performance and

achieve limit of detection of 0.01  $\mu\text{g/L}$ <sup>13</sup>. Increased sensitivity of the electrode can improve detection ability for low concentration samples. One of the means to increase sensitivity is by modifying working electrode by end hydrogen group substitution (-H) with amine group (-NH<sub>2</sub>), which is known as self assembly process. Gold nanoparticles (AuNP) is one of the preferred modifying agent for the working electrode<sup>14</sup>.

The present study develop AuNP-GCE using self assembly process and applied the modified electrode for determination of trace amount of Cr(VI) using voltammetric method.

## 2. Materials and Methods

### 2.1. Chemical reagents

Ammonium hydroxide, acetic acid, concentrated hydrochloric acid, ethanol, potassium dichromate, sodium citrate, sodium acetate, sodium tetrahydroborate, hydrogen tetrachloroaurate(III) trihydrate were of analytical grade and supplied by Merck.

### 2.2. Preparation of colloidal gold nanoparticles

The gold nanoparticle was prepared by reduction of Au(III) using NaBH<sub>4</sub><sup>15</sup>. To a volume of 15 mL of 0.1 mM HAuCl<sub>4</sub>, 5 mL of double distilled water was added and stirred using magnetic stirrer for 5 minutes. To the mixture, 290  $\mu\text{L}$  of 0.1 M NaBH<sub>4</sub> was added and the pH was adjusted to 6.5<sup>16,17</sup>. The product was characterized using UV-Vis spectrophotometer at 518 nm and TEM to characterize size and shape of the AuNP formed.

### 2.3. Preparation of gold nanoparticles modified glassy carbon electrode

The surface of glassy carbon electrode (GCE) was polished using 8 nm Al<sub>2</sub>O<sub>3</sub> on 1000 mesh sandpaper. Then it was sonicated in methanol and double distilled water for 5 minutes, successively, followed by drying. The first modification was conducted by immersing the activated electrode into AuNP colloid for 24 hours. After the immersion, the AuNP-GCE was characterized by scanning electron microscope (SEM). The second modification was performed by photochemical reaction. The reaction was initiated by immersing the modified GCE into concentrated ammonium hydroxide solution followed by irradiation under UV light at 254 nm for 6 hour. This step is known as self assembly process<sup>15</sup>. The modified electrode is then used as working electrode.

### 2.4. Electrochemical measurement using differential pulse voltammetry

The electrochemical measurement was conducted in a single compartment cell using potentiostat (Metrohm<sup>®</sup>  $\mu\text{Autolabtype III}$ ) 757 VA at room temperature (23°C). An Ag/AgCl electrode was used as reference electrode, while platinum rod was used as auxiliary electrode. Cr(VI) determination was conducted in 0.01 M hydrochloric acid. All potential value reported in this study were with respect to the Ag/AgCl sat. reference electrode (0.2 V vs. SHE).

## 3. Results and Discussion

### 3.1 Fabrication and characterization of gold nanoparticles modified glassy carbon electrode

AuNP was synthesized using citric ion as capping agent. After reduction using NaBH<sub>4</sub> solution, the gold solution colour was changed from yellow to red ruby ( $\lambda_{\text{max}} = 518 \text{ nm}$ ), which indicate that AuNP colloid was formed with average dimension of 2-5 nm<sup>18</sup>. Characterization using TEM indicate that the average diameter of the colloid was  $\sim 2.2 \text{ nm}$  (Fig. 1). This gold nanoparticles was then used to modify the GCE.

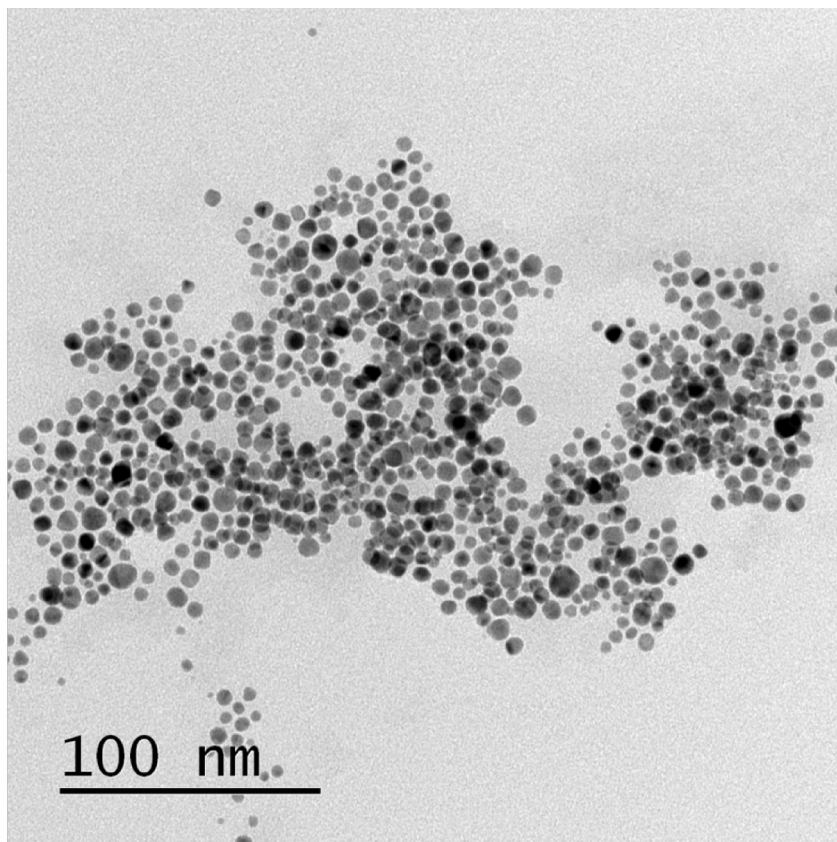


Fig. 1. TEM image of gold nanoparticles.

GCE was modified by attaching AuNP onto the electrode surface. Modification of GCE was initiated by polishing the electrode followed by activation. This step was performed so that the electrode can be covered evenly and maximally by the AuNP, which eventually can increase sensitivity when used to determine the analyte. Photochemical reaction is one of many methods to activate the GCE surface. In the present experiment, the photochemical reaction was performed by immersing the electrode into concentrated ammonium hydroxide and followed by irradiation under UV light for 6 hours at 254 nm. This process is known as self assembly which can substitute hydrogen group ( $-H$ ) with amine group ( $-NH_2$ ) of the electrode. Due to the nature of the amine group, more AuNP can be attached to the electrode and improve binding to the electrode<sup>15</sup>, as indicated by SEM-EDS data. SEM-EDS data demonstrated that the self assembly process was better than adsorption process. Modification of GCE by self assembly process reached 11.55% of AuNP covering the electrode, while adsorption process (direct immersion of the electrode) only reached 2.05% covering according to SEM-EDS data.

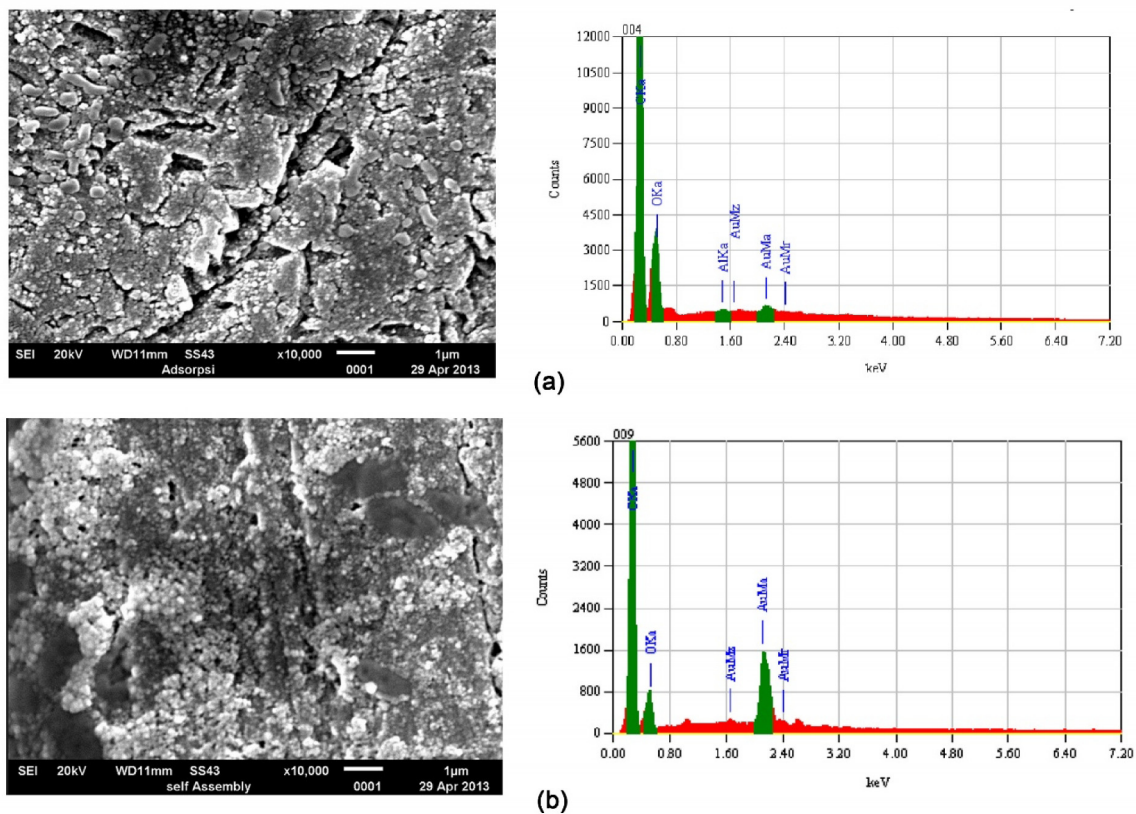


Fig. 2. SEM image of gold nanoparticles modified glassy carbon electrode surface. Modification was conducted using (a) adsorption and (b) self assembly process

### 3.2 Application of the modified glassy carbon electrode for Cr(VI) determination

Optimization of deposition potential and time was performed using differential pulse voltammetry (DPV) technique, with deposition potential variation at +600, +700, +800 and +900 mV against Ag/AgCl as reference electrode with scan rate and amplitude modulation at 50 mV/s and 500 mV, respectively. When higher deposition potential applied, higher current was observed. This occurred because when higher deposition potential applied, the ability to reduce Cr(VI) become higher. The electrical current increase was observed up to 800 mV, while a further increase in potential reduces the current as presented in Fig. 3. This occurred because all the Cr(VI) in the sample were completely reduced at 800 mV.

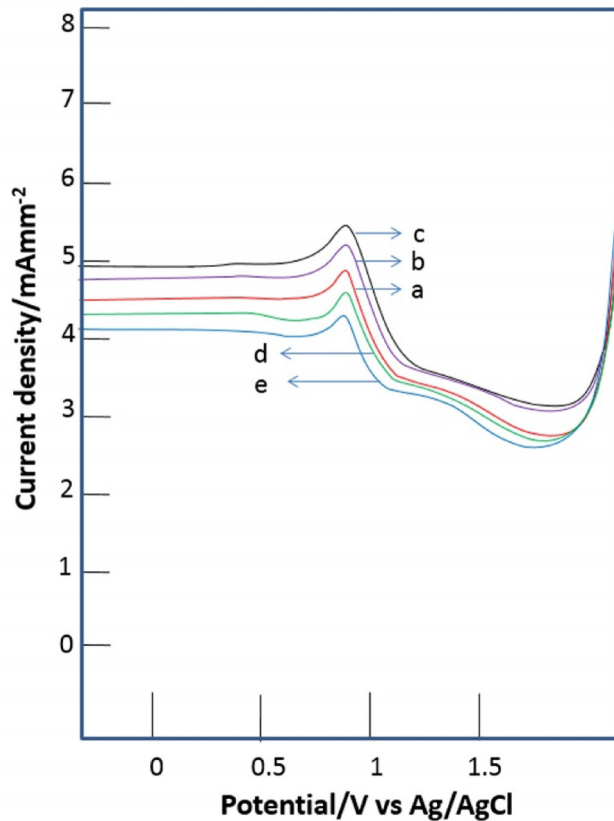


Fig. 3. Voltammogram of variation of deposition potential at (a) 600, (b) 700, (c) 800, (d) 900 and (e) 1000 mV for 0.5  $\mu\text{g/L}$  Cr(VI) solution with deposition time, scan rate and amplitude modulation at 180 s, 50 mV/s and 500 mV, respectively.

In the present study, deposition time was optimized to increase sensitivity of the method and the result is presented on Fig. 4. From Fig. 4, it can be observed that the optimum deposition time is 120 s. Long deposition time causing the working electrode become saturated during the deposition process, and hence can not measure optimally.

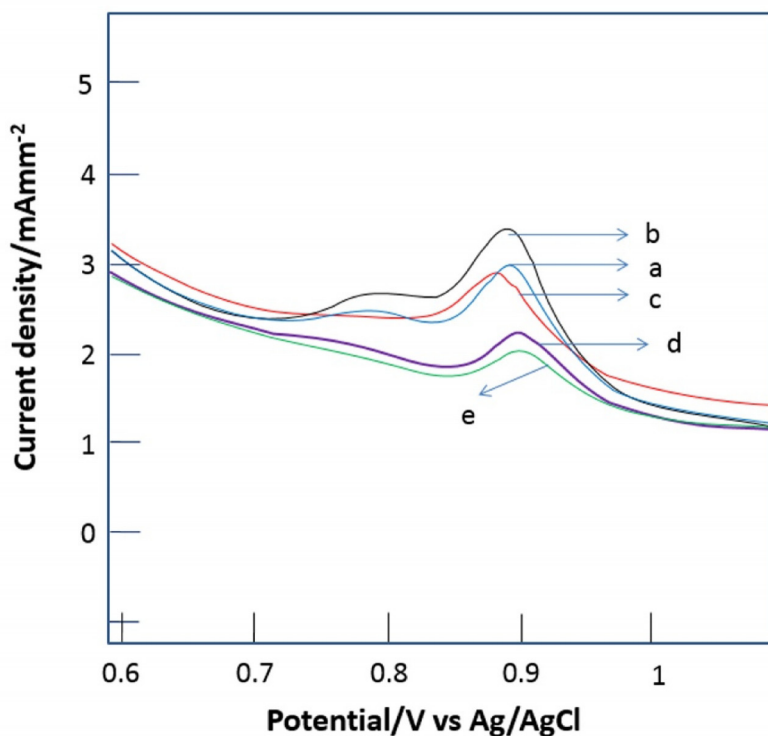


Fig. 4. Voltammogram of variation of deposition time at (a) 90 s, (b) 120 s, (c) 150 s, (d) 180 s and (e) 210 s for 0.5  $\mu\text{g/L}$  Cr(VI) solution with deposition potential, scan rate and amplitude modulation at 800 mV s, 50 mV/s and 500 mV, respectively.

From the present study it was found that optimum deposition potential and deposition time for determination of 0.5  $\mu\text{g/L}$  Cr(VI) in 0.01 M hydrochloric acid as supporting electrolyte solution was 800 mV and 120 s, respectively. The optimum condition was then applied to create calibration curve with concentration ranging from 0 to 25  $\mu\text{g/L}$ , and the current density to potential data of the concentrations is presented in Fig. 5. From the data, a linear calibration curve ( $r^2 = 0.9896$ ) was developed and is presented on Fig. 6 with correlation coefficient and linear regression equation of 0.9948 and  $I = 2.25 \times 10^{-3}C + 5.89 \times 10^{-4}$ , respectively. Through calculation, it was obtained that limit of detection and precision of the method is 2.38 ng/L and 99.14%, respectively.

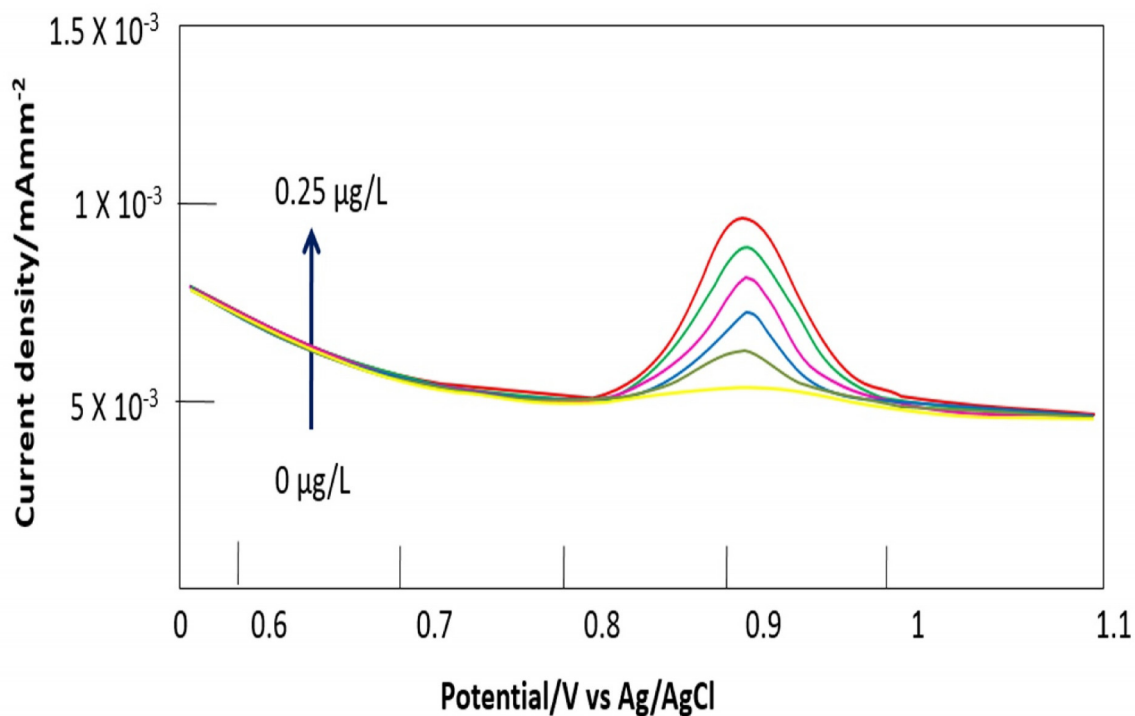


Fig. 5. Voltammogram of various Cr(VI) concentration (0 – 0.25  $\mu\text{g/L}$ ) with deposition potential, deposition time, scan rate and amplitude modulation at 800 mV, 120 s, 50 mV/s and 500 mV, respectively.

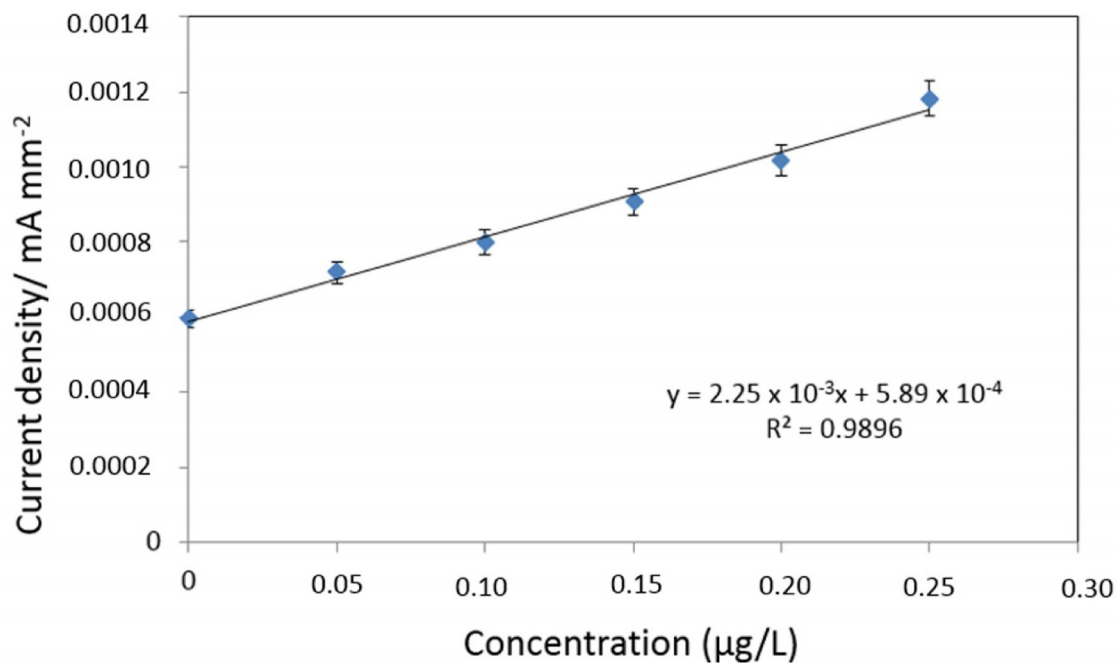


Fig. 6. Calibration curve of various Cr(VI) concentration with deposition potential, deposition time, scan rate and amplitude modulation at 800 mV, 120 s, 50 mV/s and 500 mV, respectively.

Different method may have different sensitivity, and method that is more sensitive considered better for quantitative analysis method since it can detect low amount of analyte. Compared to other published methods, the proposed method in this study has better limit of detection as presented in Table 1. Even with another voltammetry method<sup>13</sup>, the present proposed method has four fold better limit of detection.

Table 1 Comparison of limit of detection of several method for Cr(VI) determination

Method	LOD	Reference
Atomic absorption spectrometry	3.3 ng/g	Virgilio <i>et al.</i> (2012) <sup>19</sup>
Neutron activation	0.45 µg/L	El-Taher (2010) <sup>20</sup>
High performance liquid chromatography	1.0 µg/L	Ying <i>et al.</i> (2011) <sup>21</sup>
Square wave voltammetry	10 ng/L	Liu <i>et al.</i> (2008) <sup>13</sup>
Differential pulse voltammetry	2.38 ng/L	This study

#### 4. Conclusion

From the present study it was found that AuNP colloid with ~2.2 nm size was formed by reducing 6 mg of chloroauric acid (HAuCl<sub>4</sub>) with 1.102 mg sodium borohydrate (in 290 µL water) as reducing agent in 0.1 M sodium citrate. The percentage of gold nanoparticles deposited onto glassy carbon electrode by self assembly process is 11.55% from total surface mass of the glassy carbon (C = 76.38%; O = 12.07%). When the AuNP-GCE was applied for determination of Cr(VI) by differential pulse voltammetry, the limit of detection and precision was found to be 2.38 ng/L and 99.14%, respectively.

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