Development of Gold Nanoparticles Modified Electrodes for the Detection of Heavy Metal Ions

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Abstract. Following the trend of developing mercury-free electrodes for environmental monitoring. Gold-based electrodes are proving to be excellent alternatives, due to their high sensitivity and selectivity especially in the monitoring of heavy metals. In this study, gold nanoparticles (AuNPs) modified screen printed carbon electrodes (SPCE) have been developed for the purpose of simultaneous detection of mercury and lead ions in water. AuNPs were synthesized using the seeding-growth method. Cyclic voltammetry (CV) was performed to investigate the electrochemical properties of the developed SPEs. AuNPs of average size of 50 nm showed optimal electroactivity. Square-wave Anodic stripping voltammetry (ASV) was used for the detection of the target heavy metals. Analysis were conducted with acetate buffer as the supporting electrolyte. Optimal concentration of acetate buffer was found at 0.2 M. The limit of detection (LOD) of Hg was 1.18 µg/L, while the LOD of Pb was 4.62 µg/L.

1. Introduction
Heavy metals are regarded among the most serious pollutants due to their non-biodegradability in the environment and high toxicity to human health. For example, Pb is known to interfere with calcium, therefore, hindering the release of neurotransmitters which can lead to major neurological or neurobehavioral complications especially in infants and young children. Hg and its respective compounds are known to have major effects on the central nervous system leading to various neurological complications [1, 2]. Moreover, these heavy metals tend to be persistent in the environment and bio-accumulate in human body through food consumption. Nevertheless, with the rapid increase of industrial activities and inappropriate disposal of wastewaters, heavy metal concentrations are bound to increase above their specific threshold set by regulatory organizations such as World Health Organization (WHO). Taking into consideration the hazardous effects of these heavy metals, their detection is therefore considered of huge importance and necessity.

Currently, spectroscopic techniques such as Inductive Coupled Plasma Mass Spectroscopy (ICP-MS) and Flame Atomic Absorption Spectroscopy (FAAS) are the commonly adopted approaches for the purpose of trace level heavy metals detection. However, the main drawbacks of these established methods come from their expensive instrumentation, their incapability for in-field analysis and some fall short for multi elemental analysis [3]. In contrast, electrochemical analysis is receiving extensive attention as substitutes for spectroscopic techniques. The techniques employed for the analysis are
known to be suitable for the selective detection of metal species, therefore they are widely used also for in-situ applications. In addition, they require no or minimum sample alteration, thus dramatically reducing chances of contaminations by reagents or losses by adsorption on containers [4].

Many types of materials have been implemented for fabrication and developments of working electrodes in electrochemical sensing applications, such as mercury, bismuth, gold and carbon glassy. Additionally, with the progressive trend towards miniaturization of devices, screen-printed electrodes (SPEs) arose as alternatives to the conventional electrodes which make them well-suited for in-field analysis. SPEs are devices fabricated by printing layers of electroconductive and insulative inks on planar plastic or ceramic substrates. One of the main advantages of SPEs is that they are manufactured by mass production technology while maintaining high cost efficiency. In addition, they provide high reliability for electrochemical analysis with few usages, giving them their huge range of applications [5].

On the other hand, nanostructured materials have been investigated extensively for applications in electrochemistry. This is attributed to their large effective surface area and fast mass transport [6]. Several studies have investigated the effect of nanoparticles on enhancing the electrochemical performance of electrodes. For example, AuNPs were successfully utilized in the modification of ultramicroelectrode array for the detection of copper ions [7]. A comparison with the non-modified electrodes showed a 4 time increase of the output current after AuNPs modification. Additionally, a sensitive method for the simultaneous detection of Pb and Cu was investigated by developing AuNPs modified screen-printed gold electrode (SPGE). The limit of detection (LOD) was found to be at 2.2 ppb and 1.6 ppb for Pb and Cu, respectively.

In this study, a disposable AuNPs modified SPCE was developed for the simultaneous detection of mercury and lead. AuNPs were produced using the seeded-growth method. Cyclic voltammetry (CV) and square wave anodic stripping voltammetry (SWASV) were used in the electrochemical analysis. Systematic experiments were carried out for the concentration of supporting electrolyte and determination of LOD.

2. Experimental Method

AuNPs were synthesized using the seeding-growth method. This method consists of two stages: the seeding stage and the growth stage. At the seeding stage, trisodium citrate and gold chloride (HAuCl₃·3H₂O) was used to synthesize the AuNPs seeds. At the growth stage, reduction of gold chloride was achieved by adding hydroxylamine hydrochloride (NH₂OH·HCl) as the reducing agent. Colloidal AuNPs with different particle sizes were produced in this stage. This was achieved by adding 7 ml, 4 ml, and 2 ml of the seed solution to 50 ml of Milipore water. Then 1 mL of hydroxylamine amine (NH₂OH·HCl) was added into each solution. After the synthesis was completed, 0.02% of sodium azide was then added to the suspension. This was essential to prevent the colloid from coagulation. The characterization of the AuNPs was performed by using XRD and Zeta-sizer. The electrochemical performance of the AuNPs were tested using cyclic voltammetry (CV). The electrochemical properties of bare SPE was compared to the electrochemical properties of the AuNPs modified SPE. The CV analysis were performed in 0.1 mol/L of KCl solution (pH 7.0) containing 2.0×10⁻³ mol/L of potassium ferrocyanide, [Fe(CN)₆]³⁻. Additionally, the scanning range of the CV analysis was performed from -0.3 V to 0.6 V, starting at 0 V with the scan rate of 0.01 V/s and potential step of 0.01 V. ASV was conducted for the detection of Hg and Pb. The tests were conducted in solutions containing concentrations of Hg and Pb ranging from 5 µg/L – 25 µg/L. The AuNPs modified SPE were immersed, and the solution was stirred at 300 rpm.

3. Results and Discussion

3.1. Characterization

XRD patterns of AuNPs produced with varying volumes of seeds solution are shown in Figure 1. Five peaks were clearly observed at 32°, 38°, 64.5°, 78°, and 81.6° that can be assigned to the (111), (200),
(220), (311) and (222) planes that matched with the ICDD No. 089-3697. Thus, the XRD patterns show that AuNPs have FCC crystal structure and crystalline in nature.

Figure 1. XRD patterns of AuNPs synthesized by tuning volumes of AuNPs seeds. (a) 2 ml, (b) 4 ml, (c) 7 ml, (d) seed.

After the completion of the seeding and growth stages, the average sizes of the produced particles were determined. Figure 2 (a-d) show the average sizes of the particles in the seed solution and the three different solutions when the volume of AuNPs seeds was varied. It is expected that average particle size would increase compared to the average size of the seed particles size if growth alone occur on the seed surface. The results were obtained from Zeta-sizer characterization of the produced solutions. The seed solution of AuNPs were effectively enlarged to AuNPs with average sizes of 28.39 nm, 46.47 nm, and 53.85 nm by varying volume of AuNPs seeds: 7 ml, 4 ml, and 2 ml respectively.

Figure 2. Size distribution of AuNPs obtained using Zeta-sizer analysis after seeding-growth process a) seed solution b) 7 ml of seed, c) 4 ml of seed d) 2 ml of seed.
3.2. Cyclic Voltammetry

The electrochemical behaviour of the bare SPE and AuNPs modified SPE was investigated using CV. SPEs were modified with AuNPs obtained from the above solutions. The CV analysis of AuNPs modified SPEs were performed in 0.1 mol/L of KCl solution (pH 7.0) containing 2.0×10⁻³ M of potassium ferrocyanide [Fe(CN)₆]³⁻. Additionally, the scanning range of the CV analysis was performed from -0.3 V to 0.6 V, starting at 0 V with the scan rate of 0.01 V/s and potential step of 0.01 V. These CV curves are shown in Figure 3. The peak current obtained for the bare SPE was 22.93 µA. As can be seen from Figure 3, the peak currents increased as the average size of the AuNPs increased. The increase in the peak currents for the AuNPs modified SPEs could be explained in terms of the enhanced electrocatalytic activity and larger active surface area of AuNPs, as it improves the mass-transport rate of electrons between the SPE and [Fe(CN)₆]³⁻ ions, therefore inducing faster electron transfer kinetics. In addition, the larger electrochemical surface-active area is not only beneficial for enhancing the sensor sensitivity, but also advantageous for lowering the detection limit.

![Cyclic Voltammograms of bare SPE and modified SPEs with different average sizes of AuNPs](image)

**Figure 3.** Cyclic Voltaammograms of bare SPE and modified SPEs with different average sizes of AuNPs, b) Effect of average particle size of AuNPs on the electrochemical behavior of modified SPCE
3.3. Anodic Stripping Voltammetry

The characteristic stripping potentials of Hg and Pb were around 0.74V and 0.03 V respectively. Plot of the resulting stripping voltammograms versus scan potential is displayed in Figure 4a with varied concentration ranging from 5 µg/L – 25 µg/L. The obtained voltammograms showed an increase of the stripping currents of both Hg and Pb upon increasing the concentration of Hg and Pb. The stripping peak currents of Hg and Pb were extracted and a calibration curve of peak currents versus concentration is shown in Figure 4b. In the range of 5 ppb to 25 ppb, peak currents of Hg and Pb presented very good linearity with the increasing concentration. The calibration equation of Hg is $I_{Hg} = 0.2534C + 8.705$ with correlation coefficient of 0.9981 and sensitivity of 0.2534 µA/ppb. Whereas the calibration equation of Pb is $I_{Pb} = 0.376C - 0.54$ with correlation coefficient of 0.9851 and sensitivity of 0.376 µA/ppb. Consequently, the LOD of the developed analytical method was evaluated. The LOD values were found at 1.18 and 4.62 ppb for Hg and Pb, respectively.

![Figure 4](image-url)

**Figure 4.** a) Stripping voltammograms of AuNPs modified SPCE with different concentration of Hg and Pb, b) Calibration plot for increasing concentration of Pb and Hg with their corresponding calibration equation

4. Conclusion

Gold nanoparticles were synthesized via seeding-growth method. The average particle sizes ranged from 20 nm to 50 nm. Characterization were conducted using XRD and Zeta-sizer analysis. SPCEs were
modified by the produced AuNPs of different particle sizes. Cyclic voltammetry was performed to examine the electrochemical behavior of the modified SPCE. The produced AuNPs solution with 50 nm average size was found to have the best electrochemical performance. A volume of 5 µL of 50nm AuNPs was found to be optimal in modification of SPCE, due to its larger surface area. For the detection of the target heavy metals, Hg and Pb, ASV analysis were performed. The LOD of Hg was measured to be at 1.18 µg/L, while the LOD of Pb was measured to be at 4.62 µg/L.

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