Effect of Hydrothermal Reaction Temperature on Properties of Bismuth Nanoparticles and Its Properties as Modified Electrode for Pb Sensors

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Abstract. Heavy metal pollution is a common environmental problem. Therefore a versatile method that can be used to detect heavy metal ions on field is sought after. Electrochemical sensor is a promising method for heavy metal detection, however, electrodes modification is of interest to enhance sensitivity and specificity of sensors. In this work bismuth nanoparticles (BiNPs) was produced using hydrothermal method with varying hydrothermal reaction temperature. X-ray diffraction analysis showed pure-phase bismuth with a Rhombohedral structure was successfully produced. BiNPs/ITO had good CV properties in which BiNPs produced at 170˚C has the highest respond current. However, BiNPs synthesized at 160˚C showed the highest DPASV stripping current response due to high surface area and less agglomeration of particles. The BiNPs modified ITO was successfully fabricated as electrochemical Pb sensor. The modified BiNPs/ITO has LOD of 2.5 μg/L Pb with good specificity.

1. Introduction

Heavy metal elements such as lead (Pb), cadmium (Cd), Mercury (Hg) and Arsenic (As) are typical hazardous pollution due to industrial and agricultural activities. Pb\textsuperscript{2+} is the most serious environmental pollutant that is highly toxic to human immune, nervous, reproductive and gastrointestinal systems [1]. Besides, Pb non-degradable and could be accumulated in ecological system in a long term, which leads to severe pollutions for people’s health [2]. Therefore, it is necessary to develop highly sensitive, rapid and simple methods for detection of these kinds of heavy metal pollutants.

Bi has been chosen as viable replacement of mercury based electrodes for electrochemical sensors. Nanoparticles modified electrode surface is also known to enhance the electroanalytical properties of
the electrode, primarily due to increases surface area to volume ratio and couple with the enhance mass transfer effect [3,4,5]. As a result, BiNPs modified electrodes exhibits high sensitivity and selectivity towards trace heavy metal ions in the analyte solution, which is comparable or even superior to that of Bi film coated electrodes [6]. Recently, several approaches that involves additional processing steps have been reported to synthesize BiNPs due to the high surface area of BiNPs, thereby resulting in enhanced performance of sensing electrodes in heavy metal detection. BiNPs can be synthesized using gas condensation method, chemical synthesis method, thermal plasma method, aerosol quenching, electron beam irradiation and laser ablation techniques [7,8]. However, these methods are inappropriate and impractical for mass production of nanoparticles towards the electrochemical approaches.

In this work BiNPs was synthesized using hydrothermal method with varying hydrothermal reaction temperature. Hydrothermal method is simple, cost effective, low growth temperature and energy-efficient technique to synthesis nanoparticles. The produced BiNPs was immobilized on substrates and tested using Cyclic Voltammetry (CV) and Differential Pulse Anodic Stripping Voltammetry (DPASV). Sensitivity, selectivity and limit of detection (LOD) of the analytical signal for the heavy metal ions interaction were systematically studied.

2. Experimental study

In this work, BiNPs was synthesized using hydrothermal method with varying hydrothermal reaction temperature: 150, 160, 170 and 180°C. Firstly, 2.94 g of polysodium 4-styrene-sulfonate (PSS), Mw = 70000, Aldrich and 2.5 g of hydrazine hydrate (80% water solution) were dissolved in 50 ml distilled water. Next, 3.6 g of bismuth nitrate (Bi(NO3)3) was added and stirred for 30 minutes to obtain a white suspension. The suspension was then transferred into a Teflon-lined stainless steel autoclave with capacity of 80 ml. Hydrothermal reaction was carried out in a preheated oven with varying temperature for 6 hours. After cooled to room temperature, black powder produced were centrifuged at 10000 rpm and rinsed several times with ethanol.

The produced BiNPs were then drop-casted on the pre-cleaned ITO electrodes, and dried overnight at room temperature. The modified electrodes were used for electrochemical analysis. An electrochemical analyzer was used to perform electrochemical measurement of cyclic voltammetry (CV) and differential pulse anodic stripping voltammetry (DPASV) by using BiNPs/ITO modified electrode as a working electrode, a saturated calomel electrode (SCE) as the reference electrode (3 M of KCl), and a platinum wire as the counter electrode. CV analysis of BiNPs/ITO modified electrodes was 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–. Differential Pulse Anodic Stripping Voltammetry (DPASV) measurement of BiNPs/ITO electrodes was performed using Pb(II) standard solution. All measurements were carried out at room temperature in 2.0×10–3 mol/L of acetic acid–sodium acetate (NaAc-HAc) buffer solution at pH 4.5 as supporting electrolyte. In this work, pH value of acetate buffer solution was changed using acetic acid (CH3CO2H) and sodium acetate (CH3COONa). The concentration of Pb(II) standard solution was diluted accordingly in acetate buffer analyte solution in order to obtain limit of detection (LOD) of heavy metal ions for the corresponding sensor electrode. The interference study was performed by using ICP multi-element standard solution. 20 μg/L of 2.0×10–3 mol/L potassium ferrocyanide, [Fe(CN)6]3– was added into the solution in order to act as masking agents. Then, 2.0×10–3 mol/L of acetic acid–sodium acetate (NaAc-HAc) buffer solution at pH 4.5 was mixed with 100 μg/L of the multi-element standard solution.

3. Results and discussion

Phase composition of the synthesized samples were determined using X-ray diffraction (XRD). Figure 1 shows the XRD patterns of the BiNPs synthesized with varying hydrothermal reaction temperature. The increase in hydrothermal reaction temperature increased the intensity of the peaks indicates the increase of crystalline structure with increasing amount of crystalline BiNPs. All XRD patterns can be indexed to a pure-phase bismuth with a Rhombohedral structure belonging to the R-3m
space group, (ICSD Reference Code: 98-002-1658). This is because no unidentified peaks in the diffractogram are noticed within the detection limit of the XRD method, suggesting that the pureness of the final product of BiNPs and also free from impurities. When the hydrothermal temperature is above 160°C, there are continuous sharpening and intensifying of the diffraction peaks for BiNPs with increasing hydrothermal temperature, thereby indicated that the crystallite size of BiNPs increases with the increasing temperature. This observation revealed that particle size increased with increasing reaction temperature. It is known that high reaction temperature contributed to faster growth rate due to faster diffusion of ions on nuclei of BiNPs [7].

**Figure 1:** XRD patterns of BiNPs synthesized using hydrothermal method at 6 hours and 2.5 ml of hydrazine hydrate with varying hydrothermal reaction temperature: (a) 150°C, (b) 160°C, (c) 170°C, and (d) 180°C

Figure 2 shows the changes of reaction temperature contributed to successful hydrothermal reaction to form BiNPs with spherical shapes. However, Figure 2 clearly reveals the detail morphologies of the BiNPs, indicating that the agglomeration of BiNPs synthesized with varying reaction temperature which could later decrease its surface area for electrochemical measurement towards heavy metal ions. As reaction temperature increases, the obtained BiNPs shows only the approximate spherical particles with increasing particle size and with more agglomeration.

**Figure 2:** SEM images of BiNPs synthesized using hydrothermal method for 6 hours and 2.5 ml of hydrazine hydrate with varying hydrothermal reaction temperature (a) 150°C, (b) 160°C, (c) 170°C, and (d) 180°C

During hydrothermal reaction, the reaction temperature is crucial for the morphology and particle size of the synthesized BiNPs. The results revealed that the reaction temperature influenced the particle size, whereby particle size of the BiNPs increased gradually with the increasing reaction temperature. More specifically, the roughness of the particles increased, yielding less spherical particles. Therefore, in response to an increase in reaction temperature, size distribution increased. Nucleation rate of the Bi₂O₃ precursor is slower than the growth rate under the condition of the higher reaction temperature; thereby the formation of precursor Bi₂O₃ tends to grow into larger particle sizes [8]. Table 1 shows the temperature changes produce various sizes of BiNPs which also vary their surface areas later towards sensitivity of heavy metal ions.
Table 1: Average particle size of BiNPs synthesized using hydrothermal method for 6 hours and 2.5 ml of hydrazine hydrate with varying hydrothermal reaction temperature: 150°C, 160°C, 170°C, and 180°C

| Hydrothermal reaction temperature (°C) | Average particle size of BiNPs (nm) |
|---------------------------------------|------------------------------------|
| 150                                   | 127.00                             |
| 160                                   | 91.79                              |
| 170                                   | 110.73                             |
| 180                                   | 124.57                             |

The Cyclic Voltammetry (CV) curves of bare ITO electrode and BiNPs/ITO electrodes synthesized using hydrothermal method with varying reaction temperature analyzed in 0.002 mol/L of K$_3$Fe(CN)$_6$ electrolyte are shown in Figure 3. The result of the anodic peak current with BiNPs clearly shows that BiNPs/ITO electrodes had higher current respond activity for the electrochemical behavior of [Fe(CN)$_6$]$^{3−}$ ions. This is because BiNPs increase the surface area of BiNPs/ITO electrodes, thus there are larger surface area for electrochemical detection of [Fe(CN)$_6$]$^{3−}$ ions. High electron transfer capability of BiNPs/ITO electrodes promotes faster electron transfer through BiNPs. This result prove that BiNPs/ITO electrodes have better sensitivity than bare ITO electrode. Figure 3 also shows the peak current responses of BiNPs/ITO electrodes increase from 150°C > 170°C > 180°C > 160°C. Sample synthesized at 160°C shows the smallest particle size (average size ≈ 91 nm), thereby faster electron transfer kinetic energy between ITO electrodes and [Fe(CN)$_6$]$^{3−}$ ions. The decrease of the peak current responses at CV properties could be due to agglomeration or larger particle size of BiNPs that blocked the connection between [Fe(CN)$_6$]$^{3−}$ and ITO glass substrate which then obstructs the electrons transfer between [Fe(CN)$_6$]$^{3−}$ ions.

Figure 3: CV curves of modified ITO electrodes with BiNPs synthesized using hydrothermal method for 6 hours and 2.5 ml of hydrazine hydrate with varying hydrothermal reaction temperature: 150°C, 160°C, 170°C, and 180°C in 0.002 mol/L of K$_3$Fe(CN)$_6$

Figure 4 shows the stripping current responses of the DPASV measurements recorded for the determination of Pb(II) after a 300 seconds deposition time at −1.2 V in 0.002 mol/L of acetate buffer solution at pH 4.5. High current response of the electrode in this work indicates that drop casting of BiNPs on ITO electrodes has great potential to be used as heavy metal sensors. This is because the large surface areas between spherical BiNPs and ITO electrodes favor the reduction action of heavy metal ions thereby increases the sensitivity of heavy metal ions sensor. Large area of direct surface contact between BiNPs and ITO ease the electron transfer to be detected by the DPASV measurement. Moreover, Figure 4 shows the stripping signal of Pb(II) on the BiNPs/ITO modified electrodes are weaken due to the aggregation of the larger nanoparticle sizes of BiNPs materials which hinder the electron transfer for deposition of target heavy metal cations on ITO electrodes. Hence, BiNPs/ITO electrodes with larger particle size is insufficient to fully functions; thereby the electroanalytical activity produced is poor. Theoretically, small size of nanoparticles has larger surface area. However, in this case, BiNPs synthesized at 170°C did not obey this rule and it did not perform the higher peak current.
than 180°C. This is could be due to the agglomeration of BiNPs synthesized at 170°C has decreased its surface area.

Figure 4: The DPASV stripping current response measured with the BiNPs/ITO electrodes synthesized using hydrothermal method for 6 hours and 2.5 ml of hydrazine hydrate with varying hydrothermal reaction temperature: 150°C, 160°C, 170°C, and 180°C in electrolyte containing 100 μg/L of Pb²⁺ standard solution with acetate buffer solution.

The sensitivity response of the electrode upon changes in heavy metal ions concentration was studied. As shown in Figure 5, for the detection of Pb(II), the exponentially decreasing relationships between BiNPs signal changes and ion concentrations are achieved in a range from 2.5 to 100 μg/L. Throughout this study, the resulting BiNPs/ITO modified electrodes performed adequately in heavy metal ions detection. Herein, based on Figure 5, the limit of detection (LOD) for Pb(II) is 2.5 μg/L.

Figure 5: Graph of current (μA) against concentrations of Pb²⁺ standard solutions (μg/L) measured with the BiNPs/ITO electrodes synthesized using hydrothermal method for 6 hours and 2.5 ml of hydrazine hydrate with varying hydrothermal reaction temperature: 150°C, 160°C, 170°C, and 180°C.

Figures 6 shows the stripping current responses of the DPASV measurements recorded for simultaneous determination of Pb(II) in 100 μg/L of multi-element standard solution added with 0.002 mol/L of potassium ferrocyanide K₃Fe(CN)₆. K₃Fe(CN)₆ was added to alleviate the interference of deposition competition among Cu(II), Pb(II) and Cd(II) on the electrode surface. This is because [Fe(CN)₆]³⁻ is able to form relatively stable compounds with Cu²⁺ ions and therefore aid in alleviate the interference effect on the analyses of Pb(II) [9]. As shown in Figure 6, the recorded peak currents were observed, but the detection currents appeared to be well below than the 100 μg/L of Pb(II) standard solution. This suppression effect was probably due to the electrodeposition competition between the analytes, Pb(II) for the active sites on the BiNPs/ITO electrodes, as well as the formation of intermetallic compound between Cu(II) with Pb(II). Besides, from the electrochemical point of view, other heavy metals ions could also simultaneously accumulated on the BiNPs/ITO electrode surfaces and the corresponding stripping signals were recorded at potentials lower than those of Pb(II). The results from...
this research shows that BiNPs modified electrode has promising properties for electrochemical Pb sensor.

Figure 6: The DPASV stripping current response measured for interference study in electrolyte containing 100 μg/L of multi-element standard solution by using BiNPs synthesized using hydrothermal method for 6 hours and 2.5 ml of hydrazine hydrate with varying hydrothermal reaction temperature: 150°C, 160°C, 170°C, and 180°C.

4. Conclusion

In this study pure-phase bismuth powders with a Rhombohedral structure were successfully produced using hydrothermal method with varying hydrothermal reaction temperature. BiNPs/ITO had good CV properties in which BiNPs produced at 170°C has the highest current response. However, BiNPs synthesized at 160°C showed the highest DPASV stripping current response due to high surface area and less agglomeration of particles. The BiNPs modified ITO was successfully fabricated as electrochemical Pb sensor. The modified BiNPs/ITO has LOD of 2.5 μg/L Pb with good specificity towards Pb.

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