Disposable bismuth-based electrodes for heavy metal ion detection

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Abstract. This work presents the efficacy of bismuth-based mixed oxide nanosstructures for heavy metal ion detection. Four samples with varying proportions of Na3BiO4, Bi2O3 and Na2O were synthesized using potentiostatic electrodeposition. X-ray diffraction (XRD) indicates the presence of poly-crystalline Na3BiO4 and Na2O in sample 1 while presence of poly-crystalline Na3BiO4 and Bi2O3 were seen in samples 2 and 3. Poly-crystalline Bi2O3 was seen in sample 4. Scanning electron microscopy (SEM) showed the presence of microplates of varying shapes and sizes with an average thickness < 1µm. Linear stripping voltammetry confirms that Sample 2 shows highest sensitivity towards detection of heavy metal ions.

1. Introduction

Heavy metal ion detection is quite significant from the environmental point of view [1]. Dumping of industrial waste into rivers and oceans has led to their contamination with heavy metal ions like lead and mercury [2, 3]. Even trace concentrations of these metals can severely affect the health of living beings [4, 5]. Developing countries suffer most due to this contamination as proper diagnostic tools are not available in remote areas. If cheap, disposable and portable sensors for detection of these heavy metals in water can be developed, than on-site analysis of drinking water samples is possible in the remote areas. Electrochemical sensors provide an ideal way of achieving this [6]. Stripping voltammetry is one of the most promising electrochemical techniques for high sensitivity and remote analysis [7, 8]. However their efficiency and effectiveness is dependent on the material used at the working electrode. Development of new cost-effective and efficient materials for such sensors requires global research efforts.

Bismuth is an unique element and finds application is areas like hydrogen storage [9, 10], detection of heavy metal ions [11], photocatalysis [12, 13], electrocatalysis [14, 15] etc. Bismuth-based electrodes are gaining wide popularity for heavy metal ion sensing because of its low toxicity, partial insensitivity to dissolved oxygen, ability to form a number of alloys [16]. Many potential bismuth-based alloys can be developed for application in heavy metal ion detection [17, 18, 19, 20, 21, 22, 23].
In this work, four samples were prepared using electrodeposition. Sample 1 was prepared by using Na\(^+\) and Bi\(^{3+}\) ions in a molar ratio of 5:1. The molar ratio was changed to 3:1 for sample 2. Sample 3 has a molar ratio of 1:1 while sample 4 was only prepared by using Bi\(^{3+}\) ions. These samples were then tested for their sensitivity towards detection of Pb\(^{2+}\) and Hg\(^{2+}\) using linear stripping voltammetry.

2. Experimental Section

2.1. Materials

Bismuth nitrate pentahydrate (Bi(NO\(_3\))\(_3\).5H\(_2\)O) was purchased from Loba. Nitric acid (HNO\(_3\)) was purchased from Qualigens while sodium nitrate (NaNO\(_3\)) was purchased from Merck. Mercury (II) Chloride (HgCl\(_2\)) and Lead (II) Chloride (PbCl\(_2\)) were purchased from Sigma Aldrich.

2.2. Synthesis

Electrodeposition with three electrode setup was used for synthesis. ITO substrate was used as the working electrode while platinum wire was used as the counter electrode. Ag/AgCl in saturated KCl was used as the reference electrode [24, 25]. Four different electrolytes were prepared. First electrolyte contained NaNO\(_3\), Bi(NO\(_3\))\(_3\).5H\(_2\)O and HNO\(_3\) in molar concentrations of 0.065 M, 0.013 M and 1 M respectively. Second electrolyte had molar concentrations of 0.039 M, 0.013 M and 1 M respectively. Third electrolyte was prepared by adding the respective salts in the molar ratio of 0.013 M, 0.013 M and 1 M respectively. Fourth electrolyte contained only Bi(NO\(_3\))\(_3\).5H\(_2\)O and HNO\(_3\) in the molar concentrations of 0.013 M and 1 M respectively. Deposition was performed at a reduction potential of -0.15 V. Solutions containing 1 ppm each of Hg\(^{2+}\) and Pb\(^{2+}\) ions was prepared by using HgCl\(_2\) and PbCl\(_2\) for heavy metal ion detection.

2.3. Characterization

Structural studies were performed using XRD (Panalytical X’pert Pro). Morphology was studied using SEM (Nova nanoSEM FEI). Detection of heavy metal ions was done using potentiostat purchased from Kanopy Techno Solutions Pvt. Ltd., Indian Institute of Technology, Kanpur, India.

3. Results and discussion

3.1. Morphological studies

Four samples were prepared by varying the concentration of sodium. Scanning electron microscopy was performed to understand the morphology of the synthesized samples (figure 1). Sample 1 showed the presence of microplates with an average thickness of 600 nm. Regular hexagons with an average thickness of 500 nm were seen in sample 2. Sample 3 again shows micro plates with thickness varying from 400 nm to 600 nm. Sample 4 shows much thicker microplates (Average thickness 800 nm).

3.2. Structural studies

Samples were studied for the structural properties using XRD (figure 2). The results indicate the formation of crystalline sodium bismuth oxide (Na\(_3\)BiO\(_4\)), bismuth oxide (Bi\(_2\)O\(_3\)) and sodium oxide (Na\(_2\)O) in different proportions (JCPDS:01-071-1583, 00-041-1449, 01-077-2148 respectively). Table 1 summarizes the composition of all the samples.
Figure 1. Scanning electron microscopy images for Sample 1 (a), Sample 2 (b), Sample 3 (c) and Sample 4 (d)

Figure 2. X-ray diffraction pattern for Sample 1 (a), Sample 2 (b), Sample 3 (c) and Sample 4 (d)
Table 1. Percentage composition of Sample 1, Sample 2, Sample 3 and Sample 4

| Sample | Na$_3$BiO$_4$ (%) | Bi$_2$O$_3$ (%) | Na$_2$O (%) |
|--------|-------------------|----------------|-------------|
| 1.     | 70%               | 0%             | 30%         |
| 2.     | 50%               | 50%            | 0%          |
| 3.     | 20%               | 80%            | 0%          |
| 4.     | 0%                | 100%           | 0%          |

3.3. Heavy metal ion detection

Heavy metal ion detection was performed using linear stripping voltammetry (figure 3). Result shows two separate peaks at -0.25 V and 0.85 V respectively. These peaks correspond to Pb$^{2+}$ and Hg$^{2+}$ ions respectively. Peak corresponding to Hg$^{2+}$ ions has lowest intensity for sample 1. For samples 2 to 4, a gradual decrease in its intensity is observed. SEM results show the presence of microplates with thickness varying from 500 nm to 800 nm. The percentage composition of various oxides is mainly responsible for this phenomenon. As seen in Table 1, a gradual decrease in the percentage of Na$_3$BiO$_4$ is seen from Sample 2 to 4. This observation is in line with the decreasing peak intensity. Thus it can be concluded that higher percentage of Na$_3$BiO$_4$ gives better results towards the detection of Hg$^{2+}$ ions. Sample 1 gives lowest peak intensity. Although it has highest percentage of Na$_3$BiO$_4$, it shows lowest sensitivity. This is probably due to the replacement of Bi$_2$O$_3$ by Na$_2$O. Thus it appears that a mixed oxide comprising of Na$_3$BiO$_4$ and Bi$_2$O$_3$ is ideally suited for heavy metal ion detection. Similar results are seen for Pb$^{2+}$ ions with minor variations probably due to variation of concentration around the working electrode.

![Figure 3. Heavy metal ion detection (Hg$^{2+}$ and Pb$^{2+}$) using Sample 1 to 4](image)

Other bismuth-based electrodes reported for heavy metal ion detection are summarized...
in Table 2. 3D honeycomb-like N-doped carbon nanosheet framework decorated with bismuth nanoparticles [17], Graphene-cysteine composite modified bismuth film electrode [18] and glassy carbon electrode modified with Bi, nafion and 2-mercaptoethanesulfonate (MES)-tethered polyaniline (PANI) [19] shows good sensitivity.

Na$_3$BiO$_4$ and Bi$_2$O$_3$ mixed oxide electrodes offer great potential for application in heavy metal ion detection. These electrodes are disposable and easy to synthesize. The average cost associated with the synthesis of a single electrode is much below the industry average. The toxicity is also very less as compared to the traditionally used mercury based electrodes. Nanostructures further enhance the sensitivity due to the availability of large surface area [26]. Thus by tuning the shape and size of the nanostructures, the sensitivity can be tuned for specific metal ion.

| Electrode                              | Reference |
|----------------------------------------|-----------|
| Bi/N doped Carbon                      | [17]      |
| Bi/Gold/Graphene/Cysteine              | [18]      |
| Bi/Nafion/PANI                         | [19]      |
| Bi/Carbon Paste                        | [20]      |
| Bi/Zeolite/Carbon Paste                | [21]      |
| Bi/Nafion/Medical Stone                | [22]      |
| BiOCl/MWCNT/GCE                        | [23]      |

4. Conclusions
Mixed oxide nanostructures with different proportions of Na$_3$BiO$_4$, Bi$_2$O$_3$ and Na$_2$O were synthesized using potentiostatic electrodeposition. XRD indicated the presence of polycrystalline metal oxides. SEM revealed the presence of microplates with average thickness of 650 nm. Sample 2 showed best performance towards detection of heavy metal ions. A gradual decrease in sensitivity is seen with decreasing proportion of Na$_3$BiO$_4$. Sample 1 with no Bi$_2$O$_3$ showed lowest sensitivity.

Acknowledgments
We thank DST, New Delhi (IFA-13/PH-84), SERB, New Delhi (ECR/2016/1888) and UGC DAE CSR, Indore (CSR-IC/CRS-73/2014-15/581) for providing financial support. We are also thankful to MNIT Jaipur for providing characterization facilities.

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