The Use of Nanocomposite Au/ Fe$_2$H$_2$O$_4$–GO Based on Surface Plasmon Resonance to Detect Toxic Arsenic(V) in Aqueous Solution

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Abstract. In this study, the Au/ Fe$_2$H$_2$O$_4$-GO films are shown to improve the optical sensors based on the plasmon resonance technique, through the modification of the sensor chip with gold film (48.3nm) for the detection of toxic heavy metal Arsenic (V) in solution, the concentrations of ions in the parts per billion range. Mat lab software employing Fresnel formula for a layer system was used in data analysis. The sensor ranged linearly from 1 to 10 ppb. The SPR curves for the Au/Fe$_2$H$_2$O$_4$-GO with different percentages of graphene oxide GO to Fe$_2$H$_2$O$_4$ (1:10 % (v/v)) respectively were attached separately the prism. The results show that when the films with 3% GO which can be observed as the optimum percentage enhancement of sensitivity for detecting ions from 0.0773º ppb$^{-1}$ for Au/Fe$_2$H$_2$O$_4$ to 0.2509º ppb$^{-1}$ for Au/Fe$_2$H$_2$O$_4$-GO. With a limit of detection 0.6 μg/L fulfills the detection requirement below the 10 and 5 μg/L contaminant levels of Arsenic as suggested by World Health Organization (WHO) and Environmental Protection Agency (EPA). The analytical method was verified by linearity, detection limits, precision, accuracy, and recovery experiments, achieved acceptable results in all states.

1. Introduction
Poisoning with heavy metal resulting from contamination of soil, surface water and ground water has been one of the main concerns in various parts of the world. The method that is currently being used in detecting heavy metal ions and other matrices in water is still significantly dependent on sending of a technician to the field who collects samples and brings them back to a laboratory where they are analyzed. Besides being inconvenient and time-consuming, this approach is expensive and liable to errors that may happen during the handling and transportation of sample [1, 2]. The water is becoming polluted and contaminated with various hazardous impurities including heavy metal ions. This contaminated water is then used for drinking and in harvesting, causing significant issues for human beings. Arsenic (As), one of the heavy metals is an element that is toxic for animals and most of the plants; although evidence indicates that, it is a crucial element. Nitrification can be prevented by high concentrations of Arsenic. Moreover, data indicates that arsenate-rich soils can inhibit microorganisms’ growth. Arsenic is the element accountable for the development of kidney, skin, bladder and liver cancer. Moreover, taking small doses of arsenic compounds that are inorganic for long periods of time is one of the factors contributing to various other diseases [3]. The maximum level of contaminant for total arsenic in potable water is established at 0.050 mg/L arsenic by the United States, the European Union, the World Health Organization (WHO) and governments of various other countries. But, due to evidence indicating harmful health impacts at lower degrees of exposure, WHO set 0.010 mg/L arsenic in its new guideline as the acceptable level of contaminant for total arsenic in potable water [4]. Arsenic exists in various oxidation forms such as −3, 0, +3, and + 5. But the Arsenic in natural water is in the form of oxyanions of trivalent Arsenic As (III) or pentavalent Arsenic As (V) [5].
Surface plasmon resonance (SPR) is a strong and powerful method employed in retrieving information from the optical properties of nanomaterials and biomaterials. Basically, SPR is dependent on a metal layer’s optical properties, and uses prism-base on optical excitation of surface plasmons through attenuated total reflection method which was shown by Otto [6] and Kretschmann [7]. The Modern SPR sensing system’s sensitivity is based on Kretschmann configuration and allows the detection of refractive indices that are as high as $5 \times 10^{-7}$ refractive index units, and correspond to a 1 pg/mm$^2$ surface coverage of material [8,9,10].

In this study, we concentrated on Au/Fe$_2$H$_2$O$_4$-GO films with deferent percentage selectivity based on the angular examination of SPR and used it in detecting heavy metal ions Arsenic (V) that can have adverse effects on the environment.

2. Experimental

2.1. Materials and Methods

Graphene oxide 2 mg/ml, dispersion with H$_2$O purchased from (Sigma-Aldrich). Di-iron trioxide-hydrate Fe$_2$H$_2$O$_4$ Nanopowder (Fisher Scientific). The powder suspension sonicated using (Hielscher UP 200S) for four hours to improve the disaggregation of any particles bundles. The solution was then sprayed using airbrush onto the Au film. All glassware and storage bottles were kept in 10% nitric acid for at least 48 h, rinsed three times with ultrapure water, and preserved dry until next usage. All equipment used with nanoparticles were first cleaned with ethanol and then rinsed with ultrapure water.

2.2. Ions Standard Solution

10 M HC1 was diluted with double distillate water (DIW) to prepare 1 M HC1. The prepared 1 M HC1 was utilized in making standard Arsenic solutions [30]. To prepare the reserved and stored solution of 1000 mg mL$^{-1}$ As (v), 1.542 g of As$_2$O$_3$ was dissolved in 25 ml 20% NaOH and modified to 3 with 1M of HCL media concentration. To prepare the reserved and stored solution of 1000 mg mL$^{-1}$ arsenic (V), As$_2$O$_3$ was dissolved in 20% NaOH accompanied by other concentrations (1 ppb -10 ppb) which were made through systematic dilution. These solutions were utilizing in daily preparation.

2.3. The pH Measurement

The entire chemicals have analytical grade and weren’t further purified before utilization. Deionized water with 18.2 $\mu$S.cm$^{-1}$ Conductivity, which attained using a Milli-Q water purification system (Millipore), used in preparing the entire solutions. Acetone used in cleaning and rinsing every part of the spectroscopic tool utilized in extracting and filling the sample cells, properly. Moreover, the entire Arsenic ion solutions, pH value were assessed by pH meter (pB-10 sartorius) with attached combination. The pH electrode was calibrated with three pH buffers (pH 4.0, 7.0, and 10.0) daily.

3. SPR System

Prism with refractive index value of $n = 1.7786$ and the glass cover slips, 22 x 22 mm$^2$, were supplied from Copens Scientific, Glaser. Acetone was used in cleaning the dirt off the glass cover slips and removing the fingerprint marks on the slide surface. Emitech K575x Turbo Sputter Coater was used to deposit the gold layer. The SPR setup depicted in Figure1. An optical stage operating with a stepper motor with 0.001º (Newport MM 3000) resolution, an optical chopper (SR 800) and a polarizer. A sensitive photodiode and a lock-in amplifier (SR 530) were used in detecting the reflected beam and processing it respectively.
A cell with thin films was made in order to maintain the As (V) ion solution and create a connection with the glass cover slip. An open brass cylindrical cavity which has an O-ring seal was linked to the glass cover slip which in turn was connected to the prism through the utilization of index matching liquid. A hollow was created which was filled with the As(V) in order to allow the laser light to reach the solution. In order to control the light’s angle, the cell and the prism were situated on a rotation plate.

4. Results and Discussion
First, the initial SPR experiment for gold film which was in contact with deionized water (single layer), was conducted to identify the gold layer’s optical properties (the thin film’s thickness (d); refractive index’s imaginary part (k); refractive index’s real parts (n) and deionized water’s refractive index. Figure 2 illustrates both the fitted and the experimental data. The gold layer’s optical properties were obtained. Gold layer had a refractive index n (0.2726± 0.005) of and a refractive index k of (3.6975 ± 0.002) and its thickness (d) was at (48.3± 0.1) nm and the refractive index for deionized water is 1.3325.

We also determined the SPR spectra of the different films. The results show that when the refractive index of the arsenic concentration changes producing the displacement of the minimum and thus demonstrated. This method was successfully applied for analyses of as (v) in real water Samples with detection limit 0.6 µg/L not as LOD reported in [11]. nanocomposite GO – Fe₃H₂O₄ enhanced affinity bonding and the sensitivity towards as (v). This is due to the augmentation of nanoscale surface roughness that increases mechanical interlocking with Fe₃H₂O₄ Figure 3, which results in a better adhesion at the surface interface. It was reported by Wang et al., the presence of covalently bonded functional groups (epoxy, hydroxyl and carboxyl) makes the GO becoming atomically rough in the nanostructured thin film formation [12]. According to the properties of GO has a high surface area and
sp2 within a sp3 matrix that can confine π-electrons, GO contain oxygen at their surfaces in the form of epoxy (−O), hydroxyl (−OH), carboxyl (−COOH), and ether functional groups on a carbon framework [13-15].

Figure 3. SPR Curve for Prism/Gold/Di iron Trioxide Hydrate Fe\textsubscript{2}H\textsubscript{2}O\textsubscript{4} Thin Film with Baseline DIW Arsenic(V) Concentration (1-10 ppb)

Figure 4. SPR Curve for Prism/Gold/Di iron Trioxide Hydrate Fe\textsubscript{2}H\textsubscript{2}O\textsubscript{4} - Graphene Oxide GO Thin Film with Baseline DIW Arsenic(V) Concentration (1-10 ppb)

Figure 5. A linear Relationship Shift in SPR Curves of ∆RU Versus Arsenic(V) Ions Concentration and Versus Percentage Ratio for Au/Fe2H2O4-GO Surface
The SPR curves for the Au/Fe$_3$H$_2$O$_4$-GO nanostructured thin films in Figure 5, the sensing layers with different percentages ratio (5%, 4%, 3% and 2%) for GO, were attached separately to the prism. For are presented in Figure 5, the films with 3%, which can be observed as the optimum percentage enhancement of sensitivity for detecting ions with 0.2064. [16]. The sensitivity of Au/Fe$_3$H$_2$O$_4$-GO sensors is high from 1 ppb to 6 ppb but slowly decrease Figure 4. Conversely, of sensors without graphene oxide, may due to a faded coating on the thin film, within this range of concentration [17]. That is, when the surfaces of the thin films are congested with ions, then the SPR angle shift will be reduced further [18]. For were exposed to 2 ppb of as (V), (Ω) increased to 0.1852°. As the Arsenic (V) concentration was increased to 4 ppb, 6 ppb, 8 ppb and 10 ppb, (Ω) increased to 0.7412°, 0.9269°, 2.0432° and 2.0432° respectively. In addition, for this sensor, the relationship between the SPR angle values and the Arsenic(V) concentrations over the tested range was linear. Under the conditions used in this research, responses of the above Au/ di iron trioxide hydrate to different heavy metal ions solution with different concentration. Similarly, when the sensors were exposed to Arsenic(V) analyst solutions with concentration 1 ppb to 10 ppb, the measured (Ω) increased to 0.3703, 0.5557, 0.7412, 0.9269, 1.1127 and 1.2985 for 5% percentage ratio, 0.3709, 0.5561, 0.7418, 0.9276 and 1.1134 for 4%, 0.1854, 0.3709, 0.7414, 1.1142 and 1.3003 respectively. In this research, responses of the above Au/ di iron trioxide hydrate to different heavy metal ions solution with different concentration.

5. Conclusion

The aim of this study was to prepare a sensor area based on Au/ di iron trioxide hydrate Au/ Fe$_3$H$_2$O$_4$-GO composite films for detecting Arsenic(V) ions. This technique it is a positive optical method for distinguishing, recognizing, and detection of metal ions in liquids such as polluted water, which used to detect low concentrations of Arsenic(v) ions in aqueous solutions with Detection of a value of 0.6 μg/L fulfills the detection requirement below the 10 and 5 μg/L poison levels of Arsenic as proposed toxic by WHO and EPA, respectively [19]. The sensitivity of current work was interface demonstrated higher sensitivity 0.2509°PPb 'or Au/ Fe$_3$H$_2$O$_4$-GO respectively.

6. References

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