

Arsenic Detection Using Surface Plasmon Resonance Sensor With Hydrous Ferric Oxide Layer

Yasmin MUSTAPHA KAMIL¹, Sura Hmoud AL-REKABI²,
Muhammad Hafiz ABU BAKAR³, Yap Wing FEN^{4,5},
Husam Abduldaem MOHAMMED⁶, Nor Hafizah MOHAMED HALIP³,
Mohammed Thamer ALRESHEEDI⁷, and Mohd Adzir MAHDI^{3*}

¹*inLAZER Dynamics Sdn Bhd, InnoHub Unit, Putra Science Park, Universiti Putra Malaysia, Serdang 43400, Malaysia*

²*Electrical Engineering Department, Al Suwayrah Technical Institute, Middle Technical University, Baghdad 10074, Iraq*

³*Wireless and Photonic Networks Research Centre, Faculty of Engineering, Universiti Putra Malaysia, Serdang 43400, Malaysia*

⁴*Institute of Advanced Technology, Universiti Putra Malaysia, Serdang 43400, Malaysia*

⁵*Department of Physics, Faculty of Science, Universiti Putra Malaysia, Serdang 43400, Malaysia*

⁶*Electronic and Communication Engineering Department, College of Engineering, University of Baghdad, Baghdad 10071, Iraq*

⁷*Department of Electrical Engineering, College of Engineering, King Saud University, Riyadh 11421, Kingdom of Saudi Arabia*

*Corresponding author: Mohd Adzir MAHDI E-mail: mam@upm.edu.my

Abstract: The lethality of inorganic arsenic (As) and the threat it poses have made the development of efficient As detection systems a vital necessity. This research work demonstrates a sensing layer made of hydrous ferric oxide ($\text{Fe}_2\text{H}_2\text{O}_4$) to detect As(III) and As(V) ions in a surface plasmon resonance system. The sensor conceptualizes on the strength of $\text{Fe}_2\text{H}_2\text{O}_4$ to absorb As ions and the interaction of plasmon resonance towards the changes occurring on the sensing layer. Detection sensitivity values for As(III) and As(V) were $1.083^\circ \cdot \text{ppb}^{-1}$ and $0.922^\circ \cdot \text{ppb}^{-1}$, respectively, while the limit of detection for both ions was 0.6 ppb. These findings support the feasibility and potential of the sensor configuration towards paving future advancement in As detection systems.

Keywords: Surface plasmon resonance; di-iron trioxide hydrate; arsenic; heavy metals ion; optical sensor

Citation: "Arsenic Detection Using Surface Plasmon Resonance Sensor With Hydrous Ferric Oxide Layer," *Photonic Sensors*, 2022, 12(3): 220306.

1. Introduction

Arsenic (As) contamination in water sources remains a global issue as it continues to affect an estimate of 500 million people around the world [1].

Among the countries that have been gravely affected by As pollution include Bangladesh, Vietnam, Mexico, USA, and China [2]. High exposure to inorganic forms of As like trivalent arsenite [As(III)] and pentavalent arsenate [As(V)] has exhibited

Received: 23 April 2021 / Revised: 25 August 2021

© The Author(s) 2022. This article is published with open access at Springerlink.com

DOI: 10.1007/s13320-021-0643-4

Article type: Regular

disruptive effects on protein metabolism in general which will eventually lead to carcinogenic diseases [3]. Acknowledging the tenacity and volatility of As, the World Health Organization (WHO) has set 10 ppb as the maximum permissible limit in potable water [4].

Monitoring and detection of As within the maximum permissible limit range can be rather challenging. Ideal analytical methods not only require exceptional sensitivity, they should be able to distinguish As species in highly concentrated silicate, phosphate, and bicarbonate water matrices as well [5]. Among the go-to techniques for As detection include hydride generation atomic absorption spectrometry [6] and inductively coupled plasma [7], both noted with 0.002 ppb limit of detection. Nevertheless, these methods require bulky and expensive facilities which may not be suitable for field-testing nor accessible for under-developed countries that are battling the crisis.

Surface plasmon resonance (SPR) was reported to have successfully detected As in aqueous samples [8–16]. The phenomenon is induced by directing light towards a metal film through a prism which creates an oscillation of electrons on the metal-dielectric interface. At a particular incident angle, these electrons will resonate with light causing a light absorption that dynamically responds towards any changes within the external surrounding. The absorption can be quantified by analyzing the reflectivity curve of the SPR, and sample changes whether if it is due to the presence of a different compound or the occurrence of molecular binding are represented by an angle shift in the reflectivity curve. The sensing performance of SPR has shown to be enhanced by functionalizing nanomaterials.

In this study, the integration of hydrous ferric oxide, $\text{Fe}_2\text{H}_2\text{O}_4$, as a sensing layer and its sensing performance towards As(III) and As(V) are discussed in a prism-based SPR sensor system. $\text{Fe}_2\text{H}_2\text{O}_4$ is highly regarded as a good adsorbent for As especially in As ion removal. Results incorporating $\text{Fe}_2\text{H}_2\text{O}_4$ /magnetite/reduced-graphene

oxide [15] and $\text{Fe}_2\text{H}_2\text{O}_4$ /multi-walled carbon nanotube [16] composites were previously published, however, $\text{Fe}_2\text{H}_2\text{O}_4$ as a stand-alone sensing layer has yet to be reported. Both studies exhibited good sensitivity and selectivity of $\text{Fe}_2\text{H}_2\text{O}_4$ composites towards As ions which suggest $\text{Fe}_2\text{H}_2\text{O}_4$ alone could yield a similar sensing performance.

2. Methodology

The experimental setup used throughout this work is depicted in Fig. 1. A prism-based SPR following the Kretschmann configuration was employed by using a He-Ne laser beam at 632.8 nm operational wavelength with 1.5 mW output power as the light source. The beam was directed to an optical chopper (New Focus 3501) and a polarizer. The chopper was used to modulate the intensity of the laser output and the polarizer was employed to maximize the transverse-magnetic mode. After the polarizer, the beam was directed to a pin hole which focused the beam into a prism with refractive index of 1.7786. The prism was stationed on a rotational platform in order to give us control of the incident angle as the laser entered the prism. The opposite surface of where the beam was internally reflected in the prism was coupled with a glass cover slide (Copens Scientific, Glaser: 22 mm × 22 mm) where a layer of gold (Au) and a layer of $\text{Fe}_2\text{H}_2\text{O}_4$ were deposited onto. The deposited surface was exposed to a sample chamber where samples could be regulated and interact with the Au- $\text{Fe}_2\text{H}_2\text{O}_4$ layer. A photodetector (Thorlabs, PDA100A) was aligned to detect the reflected light from the prism. The converted signal was then amplified with a lock-in amplifier (Stanford Research SR530) before the output was retrieved and analyzed.

Au layer with a thickness of 48.3 nm was deposited onto the glass cover slide using a spin coater (Emitech K575X Turbo) [15]. To prepare $\text{Fe}_2\text{H}_2\text{O}_4$ solution, 10 mg/ml of $\text{Fe}_2\text{H}_2\text{O}_4$ (Strem Chemicals, USA) was sonicated in ethanol for 2 h. Then, to deposit $\text{Fe}_2\text{H}_2\text{O}_4$ onto the Au layer homogeneously, the airbrush method was used [17,

18]. The distance between the airbrush tip and the glass slide surface was maintained in order to retain uniformity. Under this condition, the pressure was fixed to 21 PSI and the air output rate was set at 15 L/min. Once airbrushed, the glass slide was put dried in an oven at 80 °C. The thickness of deposited nanomaterials was controlled by the spraying time. Hence, thickness optimization of $\text{Fe}_2\text{H}_2\text{O}_4$ was performed by fabricating multiple $\text{Fe}_2\text{H}_2\text{O}_4$ -SPR sensors with varied $\text{Fe}_2\text{H}_2\text{O}_4$ spraying time (within the range of 10 s to 60 s) and comparing their reflectivity curve when introduced to deionized

water, 10 ppm, 5 ppm, and 1 ppm of As(V). To test, the sample was injected into the customized cell and readings were taken 10 min after the analyte was introduced. This was to ensure that absorption of As ion onto the surface of the sensor has reached a steady state. After recording the resonance signal, the sensing surface and sample chamber were rinsed with deionized water and dried. The deposition thickness and surface roughness were physically analyzed with atomic force microscopy (AFM) analysis and theoretically validated using a multilayer expression [16].

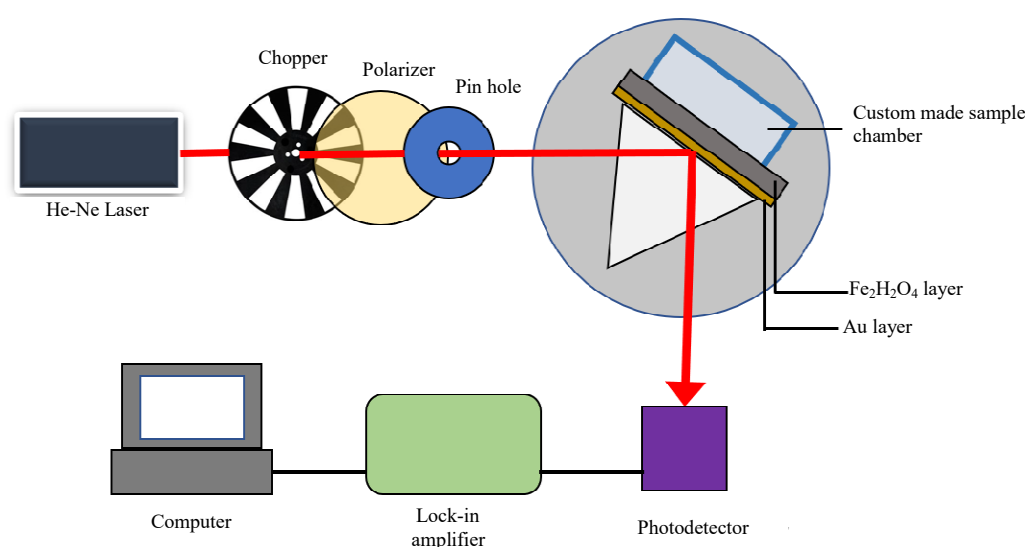


Fig. 1 Experimental setup of Au- $\text{Fe}_2\text{H}_2\text{O}_4$ sensing layer in prism-based Kretschmann configuration for As detection.

Stock solutions of As(III) and As(V) with a concentration of 1 000 mg/mL were prepared. For As(III), 25 ml of 20% (w/v) sodium hydroxide (NaOH) was used to dilute 1.32 g of As_2O_3 . The pH value of the solution was determined using Sartorius's pH-10 pH meter which was calibrated daily using standard solutions [19]. On the other hand, 1.542 g of As_2O_5 was dissolved in 20% (w/v) of NaOH to make 1 000 mg/mL of As(V) as the stock solution. A systematic dilution was used to vary the concentration of the As ions; 1 ppm, 5 ppm, and 10 ppm [20]. These stock solutions were prepared daily and stored in a flask at 5 °C in order

to retain their chemical properties.

3. Results and discussion

3.1 Optimization of sensing layer

The SPR response curves from the fabricated $\text{Fe}_2\text{H}_2\text{O}_4$ -SPR sensors when tested with deionized water are depicted in Fig. 2. It was observed that, higher deposition time led to a larger angle shift and increment of reflectance. When spectra obtained at 10 s and 60 s were compared, an increase in the resonance angle was observed from 54.026 5° to 54.582 6° and the reflectance was shifted from 0.288 to 0.764, respectively.

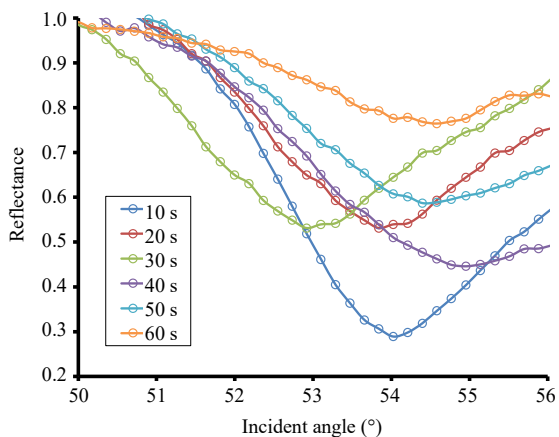


Fig. 2 Measured resonance signals for Fe₂H₂O₄ sensing layer deposited at different times.

The experiment was continued by testing all fabricated Fe₂H₂O₄-SPR sensors with 10 ppm, 5 ppm, and 1 ppm of As(V). In Fig. 3, the fabricated sensor with deposition of 40 s has the largest angle shift when compared to the other Fe₂H₂O₄-SPR sensors. The trend was distinguishable in all three concentrations of As(V) that were tested. To refine the observation, deposition times of 35 s and 45 s were also analyzed, and the angle shift produced with 40 s deposition was still distinctive. Hence, for this experiment, the optimum time for Fe₂H₂O₄ deposition was 40 s.

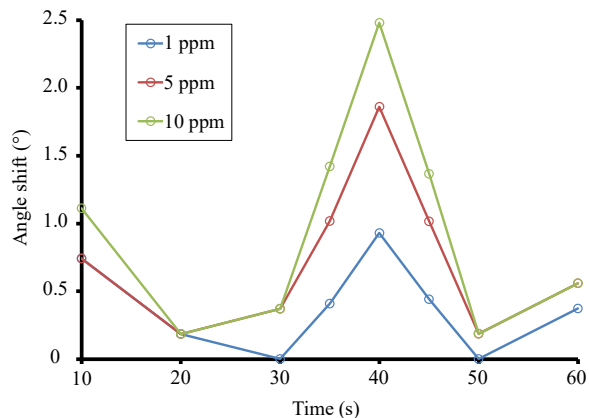


Fig. 3 Response of SPR signals with respect to time at different As(V) concentrations.

Figure 4(a) exhibits the AFM image taken at the boundary between a bare area and an area that was deposited with Au-Fe₂H₂O₄ with spraying time of 40 s. An average thickness of 60 nm was obtained for Au-Fe₂H₂O₄ with Fe₂H₂O₄ making up ~10 nm of the total thickness. The surface roughness was also analyzed [Fig. 4(b)] and a rough surface was observed which confirmed successful deposition of Fe₂H₂O₄ that would lead to the promotion of As absorption onto the sensing layer.

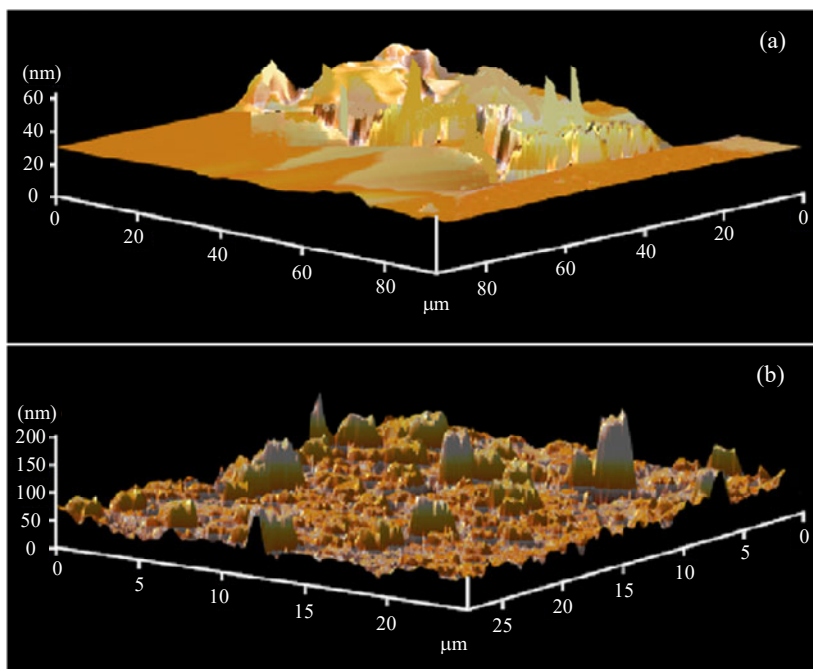


Fig. 4 3D AFM images of (a) region deposited with Au-Fe₂H₂O₄ and a bare region on the same glass slide and (b) surface roughness of the Fe₂H₂O₄ deposited region.

3.2 Performance of Fe₂H₂O₄-SPR sensor

The performance of the fabricated Fe₂H₂O₄-SPR sensor was evaluated by observing the angle shift produced in response to As(III) and As(V) at different concentrations. The SPR curves obtained from As(III) and As(V) within the concentration range of 0 ppb – 10 ppb are depicted in Figs. 5(a) and 5(b), respectively. A consistent increase in angle shift was observed in response to the increment of As ion concentration. This is in accordance to the higher metal uptake as a response to the concentration tested [21]. When results obtained from both ions were compared, it is worth to note that the angle shift produced for As(V) was smaller than that produced for As(III). For example, at 10 ppb of As(V) and As(III), the attained angle shifts were 0.698 6° and 1.635 3°, respectively, showing a difference of almost 3 folds. Moreover, the

correlation between the concentration and angle shift produced when tested with As(V) was not consistent. From these observations, it can be summarized that the SPR sensor was more sensitive towards As(III) than towards As(V).

With the presence of As in the sample, Fe(III) cations from Fe₂H₂O₄ will coordinate with the As ions, forming inner-sphere surface complexes. For As(V), a bidentate binuclear-bridging complex will form. The same occurs with As(III) with the addition of mono-dentate complexes and outer-sphere complexes where the As(III) anions bound to the hydroxyl functional groups instead, via hydrogen bond. Due to the variety of chemical pathways, the adsorption of As(III) is more favorable as compared to As(V) [22].

Figure 6 shows the SPR response when As(III) and As(V) of concentrations below 1 ppb were

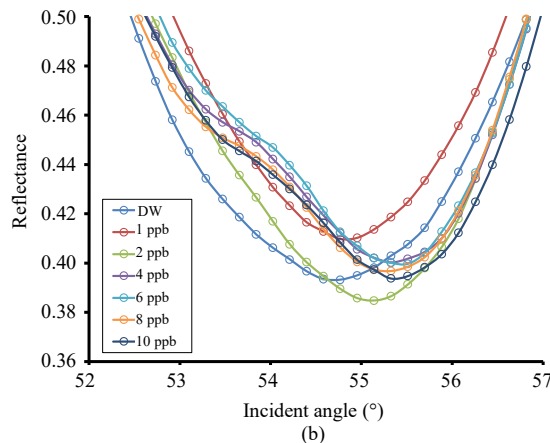
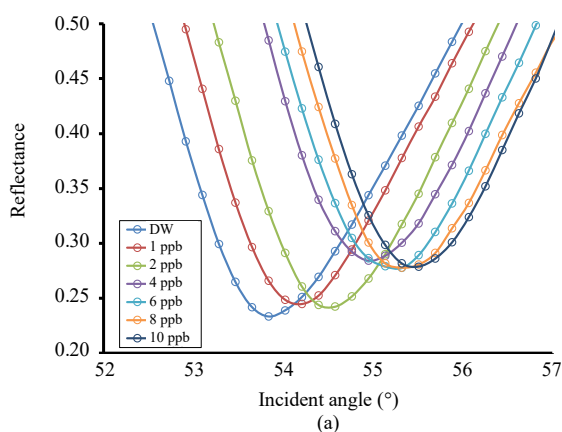


Fig. 5 Response curve of Fe₂H₂O₄-SPR sensor when evaluated with (a) As(III) and (b) As(V) within the concentration range of 1 ppb – 10 ppb. DW: deionized water.

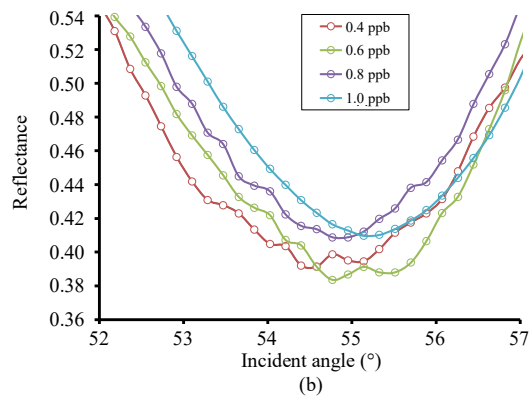
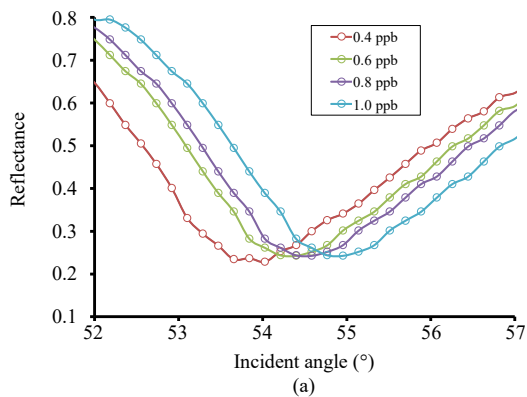


Fig. 6 Response curves of Fe₂H₂O₄-SPR sensor when evaluated with (a) As(III) and (b) As(V) ion solutions within the concentration range of 0.4 ppb–1 ppb.

introduced. The sensitivity values of the $\text{Fe}_2\text{H}_2\text{O}_4$ SPR sensor towards As(III) and As(V) were $1.083^\circ \cdot \text{ppb}^{-1}$ and $0.922^\circ \cdot \text{ppb}^{-1}$, respectively. These values were retrieved from the linear trend fitting shown in Fig. 7 which indicated that the sensing layer of $\text{Fe}_2\text{H}_2\text{O}_4$ was more sensitive towards As(III) as opposed to As(V) .

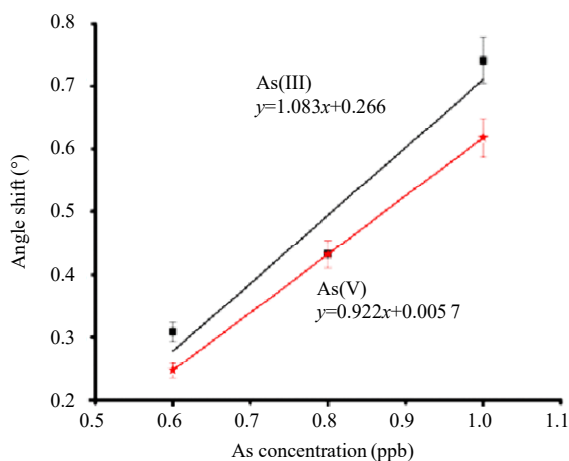


Fig. 7 Sensitivity of $\text{Fe}_2\text{H}_2\text{O}_4$ -SPR sensor towards As(III) and As(V) with a standard deviation of $\pm 0.1^\circ$.

From these findings, the lowest detectable concentrations for both ions were attained at 0.6 ppb, which was lower than given value of the highest allowable As concentration given by the Environmental Protection Agency of the European Union and USA guidelines. For concentrations lower than 0.6 ppb, angular shifts were not obtained as the spectra overlapped with the spectrum obtained for deionized water. The adsorption capacity of As on $\text{Fe}_2\text{H}_2\text{O}_4$ is dependent on the hydroxyl groups (Fe-OH) formed on the sensing layer and adsorption of As on to $\text{Fe}_2\text{H}_2\text{O}_4$ which occurs by the creation of bidentate edge-sharing and bidentate corner-sharing complexes between As and Fe-OH [23, 24]. In terms of sensing performance, the $\text{Fe}_2\text{H}_2\text{O}_4$ -SPR sensor has successfully attained lower detection limit than most of the previously reported studies tabulated in Table 1. This is likely to be caused by the property of $\text{Fe}_2\text{H}_2\text{O}_4$ being highly absorptive of As ions. However, the incorporation of additional elements to $\text{Fe}_2\text{H}_2\text{O}_4$ have shown to yield better detection limit. This was the case for $\alpha\text{-Fe}_2\text{O}_3/\text{SnO}_2$, $\text{Fe}_2\text{H}_2\text{O}_4/\text{magnetite}/\text{reduced-graphene oxide}$ and

$\text{Fe}_2\text{H}_2\text{O}_4/\text{multi-walled carbon nanotube}$ with detection limits of 0.47 ppb, 0.1 ppb, and 0.2 ppb, respectively. It is presumed that the additional elements could either boost catalytic reactions or provide more active sites for the harboring of As ions which in turn heightened the sensing performance [11, 15, 16]. Nonetheless, the fabrication of fiber-based SPR and the addition of other elements to the composite can be tedious which gives the current proposed sensor its own leverage.

Table 1 SPR-based sensors for the detection of As.

Sensing layer	Sensitivity	Determinant	Ref
Glutathione	1 ppb	As(V)	[8]
Carbon nanotubes	0.1 ppb	As(III)	[9]
Polypyrrole-chitosan-cobalt ferrite	1 ppb	As(V)	[10]
$\alpha\text{-Fe}_2\text{O}_3/\text{SnO}_2$	0.47 ppb	As(III)	[11]
DNA	10 ppb	As(III)	[12]
Gold nanorods	10 ppb	As(III)	[13]
$\text{Fe}_2\text{H}_2\text{O}_4 - \text{Fe}_3\text{O}_4\text{-rGOD}$	0.1 ppb	As(III)/As(V)	[15]
$\text{Fe}_2\text{H}_2\text{O}_4 - \text{MWCNT}$	0.2 ppb	As(III)/As(V)	[16]

4. Conclusions

An SPR sensor with integrated nanomaterial for the detection of As(III) and As(V) ions was developed and demonstrated. Optimized thickness for the deposition of $\text{Au}/\text{Fe}_2\text{H}_2\text{O}_4$ sensing layer was 60 nm with sensor sensitivity values of $1.083^\circ \cdot \text{ppb}^{-1}$ and $0.922^\circ \cdot \text{ppb}^{-1}$, for As(III) and As(V) within concentration range of 0.6 ppb – 1 ppb, respectively. The minimum limit of detection for both tested ions was 0.6 ppb. These findings exhibit the sensing capability of the $\text{Fe}_2\text{H}_2\text{O}_4$ -SPR sensor to detect As ions. The sensing performance is at par with standard As sensing techniques and also recent reported research works.

Acknowledgment

This work was funded by Ministry of Higher Education Malaysia; Fundamental Research Grant Scheme (Grant No. FRGS/2/2014/TK03/UPM/01/1) and the King Saud University, Kingdom of Saudi Arabia; Researchers Supporting Project (Grant No. RSP-2021/336).

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

- [1] E. Shaji, M. Santosh, K. V. Sarath, P. Prakash, V. Deepchand, and B. V. Divya, "Arsenic contamination of groundwater: a global synopsis with focus on the Indian Peninsula," *Geoscience Frontiers*, 2021, 12(3): 101079.
- [2] S. Shankar, U. Shanker, and Shikha, "Arsenic contamination of groundwater: A review of sources, prevalence, health risks, and strategies for mitigation," *The Scientific World Journal*, 2014, 2014: 304524.
- [3] L. Zhang, X. R. Chen, S. H. Wen, R. P. Liang, and J. D. Qiu, "Optical sensors for inorganic arsenic detection," *TrAC Trends in Analytical Chemistry*, 2019, 118: 869–879.
- [4] F. Fernández-Luqueño, F. López-Valdez, P. Gamero, S. Luna, E. N. Aguilera-González, A. Martínez, *et al.*, "Heavy metal pollution in drinking water—a global risk for human health: A review," *African Journal of Environmental Science and Technology*, 2013, 7(7): 567–584.
- [5] S. Thakkar, L. F. Dumée, M. Gupta, B. R. Singh, and W. Yang, "Nano-enabled sensors for detection of arsenic in water," *Water Research*, 2021, 188: 116538.
- [6] S. Saha and P. Sarkar, "Differential pulse anodic stripping voltammetry for detection of As(III) by chitosan-Fe(OH)₃ modified glassy carbon electrode: a new approach towards speciation of arsenic," *Talanta*, 2016, 158: 235–245.
- [7] D. E. Mays and A. Hussam, "Voltammetric methods for determination and speciation of inorganic arsenic in the environment—a review," *Analytica Chimica Acta*, 2009, 646(1–2): 6–16.
- [8] E. S. Forzani, K. Foley, P. Westerhoff, and N. Tao, "Detection of arsenic in groundwater using a surface plasmon resonance sensor," *Sensors and Actuators B: Chemical*, 2007, 123(1): 82–88.
- [9] Y. C. Reyes, L. E. Coy, L. Yate, S. Jurga, and E. E. González, "Nanostructured and selective filter to improve detection of arsenic on surface plasmon nanosensors," *ACS Sensors*, 2016, 1(6): 725–731.
- [10] A. R. Sadrolhosseini, M. Naseri, and H. M. Kamari, "Surface plasmon resonance sensor for detecting of arsenic in aqueous solution using polypyrrole-chitosan-cobalt ferrite nanoparticles composite layer," *Optics Communications*, 2017, 383: 132–137.
- [11] Y. Yao, S. Miao, S. Yu, L. P. Ma, H. Sun, and S. Wang, "Fabrication of Fe₃O₄/SiO₂ core/shell nanoparticles attached to graphene oxide and its use as an adsorbent," *Journal of Colloid and Interface Science*, 2012, 379(1): 20–26.
- [12] P. R. Solanki, N. Prabhakar, M. K. Pandey, and B. D. Malhotra, "Surface plasmon resonance-based DNA biosensor for arsenic trioxide detection," *International Journal of Environmental Analytical Chemistry*, 2009, 89(1): 49–57.
- [13] A. Das, S. Mohanty, and B. K. Kuanr, "Label-free gold nanorod-based plasmonic sensing of arsenic(III) in contaminated water," *Analyst*, 2019, 144(15): 4708–4718.
- [14] T. Li and W. Feng, "Fiber-optic surface plasmon resonance sensor for trace cadmium-ion detection based on Ag-PVA/TiO₂ sensing membrane," *IEEE Sensors Journal*, 2021, 21(17): 18650–18655.
- [15] S. H. Al-Rekabi, Y. M. Kamil, M. H. A. Bakar, Y. W. Fen, H. N. Lim, S. Kanagesan, *et al.*, "Hydrrous ferric oxide-magnetite-reduced graphene oxide nanocomposite for optical detection of arsenic using surface plasmon resonance," *Optics & Laser Technology*, 2019, 111: 417–423.
- [16] Y. M. Kamil, S. H. Al-Rekabi, H. A. Mohamed, M. H. A. Bakar, S. Kanagesan, Y. W. Fen, *et al.*, "Di-iron trioxide hydrate-multi-walled carbon nanotube nanocomposite for arsenite detection using surface plasmon resonance technique," *IEEE Photonics Journal*, 2019, 11(4): 1–9.
- [17] Y. Guo, C. Di, H. Liu, J. Zheng, L. Zhang, G. Yu, *et al.*, "General route toward patterning of graphene oxide by a combination of wettability modulation and spin-coating," *ACS Nano*, 2010, 4(10): 5749–5754.
- [18] Y. V. Stebunov, O. A. Aftenieva, A. V. Arsenin, and V. S. Volkov, "Highly sensitive and selective sensor chips with graphene oxide linking layer," *ACS Applied Materials & Interfaces*, 2015, 7(39): 21727–21734.
- [19] A. Varma, "CRC Handbook of Atomic Absorption Analysis," America: CRC Press, 1984.
- [20] A. D. Eaton, H. C. Wang, J. Northington, and A. R. Foundation, "Analytical Chemistry of Arsenic in Drinking Water," America: AWWA Research Foundation and American Water Works Association, 1998.
- [21] D. Borah, S. Satokawa, S. Kato, and T. Kojima, "Surface-modified carbon black for As(V) removal," *Journal of colloid and interface science*, 2008, 319(1): 53–62.
- [22] Y. Yoon, W. K. Park, T. M. Hwang, D. H. Yoon, W. S.

- Yang, and J. W. Kang, "Comparative evaluation of magnetite-graphene oxide and magnetite-reduced graphene oxide composite for As(III) and As(V) removal," *Journal of Hazardous Materials*, 2016, 304: 196–204.
- [23] S. Dixit and J. G. Hering, "Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility," *Environmental Science & Technology*, 2003, 37(18): 4182–4189.
- [24] D. M. Sherman and S. R. Randall, "Surface complexation of arsenic(V) to iron(III) (hydr)oxides: structural mechanism from ab initio molecular geometries and EXAFS spectroscopy," *Geochimica et Cosmochimica Acta*, 2003, 67(22): 4223–4230.