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Fabrication of an α -Fe₂O₃ NP-modified ZnO NRs/ Ni-foam nanocomposite electrode for electrochemical detection of arsenic in drinking water

Sreymean Ngok,^{*a} Rem Yann,^{ad} Chan Oeurn Chey,^c Xianjie Liu,^b Magnus Willander^a and Omer Nur ^a

Arsenic is a toxic contaminant that can be found in drinking water. In this study, the development of an efficient electrode as an electrochemical sensor to detect arsenic(v) in drinking water is presented. The surface of ZnO nanorods (NRs) synthesized on a Ni-foam substrate was modified by depositing α -Fe₂O₃ nanoparticles (NPs) to fabricate an electrode for the detection of arsenic(v) contamination in drinking water. This electrode was synthesized through two separate growth steps: a hydrothermal (ZnO NRs) step followed by the dip-coating method (α -Fe₂O₃ NPs). The dip-coating method was repeated multiple times, 2 times (ZNF-2), 3 times (ZNF-3) and 4 times (ZNF-4), in order to achieve a uniform coverage of the ZnO NR surface. The electrodes were characterized using XRD, XPS, SEM and UV-vis spectroscopy. The best efficiency among the α -Fe₂O₃NP-modified nanorod samples was observed for the 3-time dip-coated ZNF-3 sample, which presented a uniform and homogeneous morphology, as observed from the SEM images, accompanied with the highest oxidation current. The electrochemical performance of the sensor electrodes was tested for a wide range of arsenic(v) concentrations from 0 to 50 ppb and was monitored using cyclic voltammetry. The results demonstrated a calibration plot that was linear over a concentration range of 0–50 ppb of arsenic(v), and the regression equation extracted from the calibration curve was found to be $y = 0.003x - 0.6271$ (with $R^2 = 0.991$). The limit of detection (LOD) and limit of quantification (LOQ) were found to be 4.12 ppb and 13.74 ppb, respectively, which are lower than the maximum allowed value recommended by the World Health Organization (WHO) for arsenic in drinking water. This reasonable performance of the ZnO NRs/Ni-foam/ α -Fe₂O₃NP nanocomposite electrode can be further enhanced, and the electrode can be utilized for efficient arsenic(v) detection in drinking water.

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1 Introduction

Arsenic is known as a naturally occurring toxic element and is considered one of the world's environment hazardous agents.¹ Arsenic is generally found in two forms, arsenite (As(III)) and arsenate (As(V)), which are among the inorganic forms of arsenic and the predominant toxic species found in natural drinking water.² The World Health Organization has fixed the maximum contaminant level of arsenic in drinking water at 50–

10 ppb.^{3–5} Therefore, the detection of the trace amount of arsenic has received considerable attention.

Metal oxide nanomaterials have more sensing ability than single-crystalline bulk semiconductor metal oxide.⁶ Furthermore, they exhibit many attractive features such as high chemical and thermal stability, high surface area to volume ratio, tunable electronic states, quantum confinement, high electron mobility, and excellent catalytic properties.⁷ Various types of metal oxide nanomaterials have been explored for sensing applications, *e.g.* tin oxide (SnO₂), indium oxide (In₂O₃), zinc oxide (ZnO), tungsten trioxide (WO₃), cuprous oxide (Cu₂O), cobalt oxide (Co₃O₄) and hematite (α -Fe₂O₃).^{8,9} ZnO and α -Fe₂O₃ are interesting oxides that are abundant, can be achieved using low cost synthesis methods and are considered less toxic materials.^{10,11} Further, different nanocomposites of these oxides with promising synergistic advantageous properties have been reported. Among these nanocomposite materials, ZnO nanostructures modified with α -Fe₂O₃ nanostructures have been effective.^{12–16} The composition of

^aDepartment of Science and Technology, Physics Electronics and Mathematics, Linköping University, SE-60174 Norrköping, Sweden. E-mail: sreymean.ngok@liu.se; Tel: +46 11 36 32 19

^bLaboratory of Organic Electronics, ITN, Linköping University, Norrköping, SE-60174, Sweden

^cGraduate School of Science, Royal University of Phnom Penh, Phnom Penh, Cambodia

^dDepartment of Physics, Faculty of Science, Royal University of Phnom Penh, Phnom Penh, Cambodia



α -Fe₂O₃ and ZnO nanostructures results in their synergistic effect, which can enhance the performance of the composite nanomaterial.^{7,17–20} These nanocomposites have gained interest in the field of sensor development due to their small dimensions, simplicity of the synthesis procedure, and the possibility of fast sensor response.^{21–24} However, these nanomaterials can have some disadvantages, such as low sensitivity, poor selectivity and high operating temperatures, which discourage their utilization in different fields.^{24,25} Thus, many researchers have made efforts to improve the sensitivity and selectivity of these metal oxides by compositing them with other metal oxide semiconductors.^{9,26–31} In this regard, we have fabricated α -Fe₂O₃ nanoparticles on the surface of ZnO NRs grown on a nickel foam substrate in this work for the detection of arsenic(v) in drinking water. The nickel foam substrate has loose porosity, good stability and uniform heat transfer.³² In addition, nickel foam is a commercial material with a 3D porous structure and can be utilized as an efficient electrode/substrate material as it provides excellent electrical conductivity and a large enough surface area, enabling good access for ions and electrons to reach the active surface of the hybrid composite electrode.^{33,34} Moreover, Nickel foam substrates can be used not only to enhance the conductivity performance and promote the penetration of electrolytes in practical applications, but nickel foam has also been used as a current collector in various electrochemical systems, including energy storage devices, chemical sensors and wastewater treatment systems.^{35–37}

Herein, we fabricated α -Fe₂O₃NPs on ZnO NRs/Ni-foam substrate for efficient arsenic(v) detection in drinking water. The ZnO NRs/Ni-foam/ α -Fe₂O₃NPs nanocomposite electrode was grown *via* two separate growth steps: hydrothermal reaction followed by a dip-coating process. The dip-coating step was optimized by carrying the dipping cycles. The structural and optical properties of the fabricated electrode were then characterized using different techniques, such as XRD, XPS, SEM and UV-vis spectroscopy. The electrochemical performance of the sensor electrode in arsenic(v) detection was investigated by cyclic voltammetry in various electrolytes to achieve efficient detection of arsenic(v). The performance of the ZnO NRs/Ni-foam/ α -Fe₂O₃NP nanocomposite electrode in the detection of arsenic(v) in drinking water is promising, verifying it as an excellent candidate that can further be developed to enhance detection efficiency.

2 Experimental methods

2.1 Materials

Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O), hexamethylenetetramine (HMT), iron(III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O) and arsenic standard solutions were purchased from Sigma Aldrich. Nickel foams (10 mm × 15 mm × 1.5 mm) were purchased from Redox.me (Sweden). All chemicals were of analytical grade and used without further purification.

2.2 Fabrication of ZnO NRs/Ni-foam and the ZnO NRs/Ni-foam/ α -Fe₂O₃NPs nanocomposite

The electrode was fabricated in two steps. During the first step, ZnO NRs were grown *via* the hydrothermal method. Briefly, the

nickel foam substrate was cut into small pieces (10 mm × 15 mm × 1.5 mm), cleaned sequentially with deionized water, acetone, and isopropanol in an ultrasonic bath for 10 minutes each and then dried under a nitrogen flow at room temperature. The cleaned substrates were dip-coated using a seed layer of ZnO nanoparticles for 5 minutes. The seed layer-coated substrates were annealed at 120 °C for 20 min. The seed solution was prepared by dissolving zinc acetate dihydrate (0.01 M) in methanol (125 mL) under vigorous stirring at a temperature of about 60 °C. Subsequently, a 0.03 M solution of KOH (65 mL) in methanol was added dropwise at 60 °C. The mixture was stirred for 2 h at 60 °C and then at room temperature for 12 h to obtain the desired rod-shaped particles.³⁸ The precursor solution used to synthesize the ZnO NRs was an equal molar (0.05 M) solution of Zn(NO₃)₂·6H₂O and HMT in 100 mL deionized water. Finally, the annealed nickel foam substrates were fixed to a sample holder with the ZnO-seeded sides pointing downwards and dipped into the ZnO precursor solution. After that, the beaker containing the precursor solution and the seeded samples was closed using aluminum foil and baked in an electronic oven at a temperature of 95 °C for 5 h. After the completion of the growth period, the samples were taken out from the oven, washed with deionized water, and then dried using a nitrogen flow. In the second step, α -Fe₂O₃ NPs were synthesized by the dip-coating method. The modification of ZnONRs/Ni-foam substrate with α -Fe₂O₃ NPs was achieved by dipping the as-grown ZnONRs/Ni-foam into a precursor solution of 0.06 g Fe(NO₃)₃·9H₂O dissolved in 20 mL of deionized water. The products were dipped for 2 minutes per cycle; the dipping process was repeated two, three or four times, and the samples were denoted as (ZNF-2), (ZNF-3) and (ZNF-4), respectively. This was followed by drying under flowing nitrogen at room temperature. The final products were annealed at 400 °C for 2 h in an air environment to convert the hydroxyl-containing phase of Fe₂O₃ to pure α -phase (Fig. 1).

2.3 General characterization techniques

The morphology of the electrodes was characterized by field-emission scanning electron microscopy (FESEM, Sigma 500 Gemini) with the field-emission gun operated at 10 kV. The structure and phase of the grown nanocomposite were

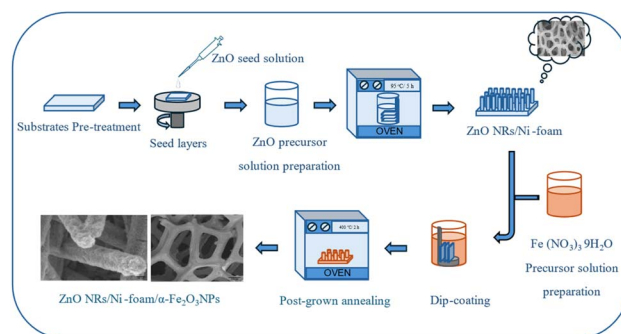


Fig. 1 Schematic showing the process for synthesis of the ZnO NRs/Ni-foam/ α -Fe₂O₃NPs nanocomposite electrode.



investigated by powder X-ray diffraction (XRD) using a Philips powder diffractometer equipped with Cu K α radiation at a voltage of 45 kV and a current of 40 mA. The optical properties were analyzed using a UV-vis spectrophotometer (PerkinElmer Lambda 900). The oxidation states and chemical composition were analyzed by X-ray photoelectron spectroscopy (XPS).

2.4 Electrochemical characterizations

The electrochemical measurements were carried out using an Autolab potentiostat (Metrohm). The electrochemical properties were measured in a three-electrode configuration composed of Ag/AgCl (3 M KCl) as the reference electrode, platinum wire as the counter electrode and ZnO NRs/ α -Fe₂O₃ nanoparticles as the working electrode. The geometric area of the working electrode was estimated to be 0.3 cm². The supporting electrolyte was a 1 M KOH solution with arsenic. All measurements were made in a fume hood at room temperature.

3 Results and discussion

3.1 Morphological analysis

The surface morphology of the ZnO NRs/Ni-foam/ α -Fe₂O₃NPs nanocomposite was examined by FESEM. Fig. 2a and b show the FESEM images of the bare Ni-foam substrate, while (Fig. 2c–f) show the morphology after the growth of the nanorods. Fig. 2f shows a high-magnification FESEM image of the ZnO NRs grown on the nickel foam substrate, demonstrating the expected hexagonal shape. The ZnO NRs were dense highly uniform, and relatively vertically aligned. Fig. 2g–l demonstrate that the α -Fe₂O₃ NPs were deposited on the ZnO NRs. The surfaces of the ZnO NRs modified with α -Fe₂O₃ NPs using different cycles (2, 3 and 4) of dip coating are shown in Fig. 2(g, h), (i, j) and (k, l), respectively. The ZnO NRs surface immersed 2 times in the α -Fe₂O₃ NPs precursor solution for 2 minutes indicated partial covering of the ZnONRs surface with α -Fe₂O₃ nanoparticles (Fig. 2g and h). However, the ZnO NR surface immersed 3 times in the α -Fe₂O₃ NPs precursor solution for 2 minutes each showed full coverage, with gaps between the ZnO NRs (Fig. 2i and j). Furthermore, the gaps between the ZnO NRs were filled with α -Fe₂O₃ NPs after immersing the NRs 4 times in the precursor solution for 2 minutes each (Fig. 2k and l).

3.2 Optical properties

The optical characterization of the sample was carried out by UV-visible spectroscopy. In Fig. 3a and b, the absorption *versus* wavelength plots of the α -Fe₂O₃NP-coated samples obtained by varying the number of dip-coating cycles are displayed. The sample synthesized with 2, 3 and 4 dip-coating cycles of pure ZnO NRs/Ni-foam showed different reflectance values in the visible-light region. ZNF-2, ZNF-3 and ZNF-4 were found to have bandgap energies of approximately 2.05 eV, 1.59 eV and 1.85 eV, respectively, as shown in Fig. 3b. The sample dip-coated 3 times showed the highest absorption in the visible-light region. In Fig. 3c, bare ZnO NRs/Ni-foam shows strong absorption in the ultraviolet range, but there is also fluctuation in light absorption in the 200–400 nm region, with broadening of the optical

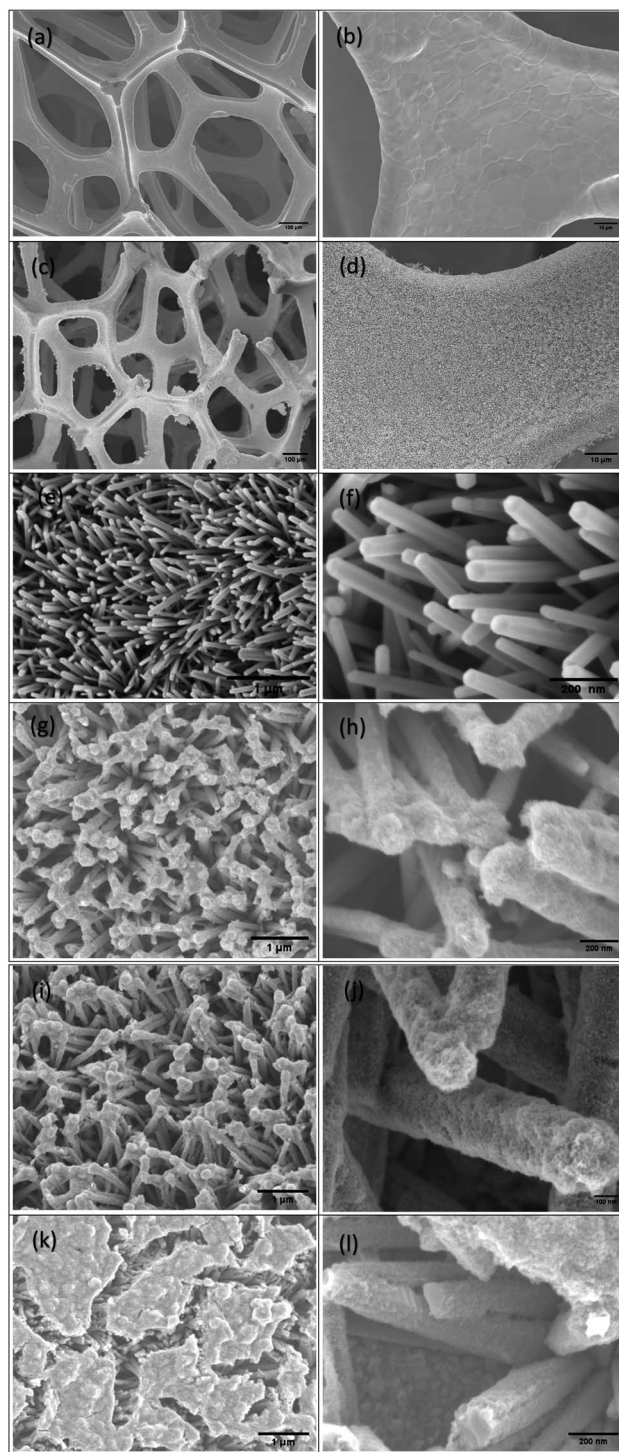


Fig. 2 The SEM images of (a and b) the nickel foam substrate, (c–f) ZnO NRs/Ni-foam and ZnONRs/Ni-foam/ α -Fe₂O₃NPs (ZNF-2) (g and h), (ZNF-3) (i and j) and (ZNF-4) (k and l).

band. However, the spectrum of ZnONRs/Ni-foam/ α -Fe₂O₃NPs shows a characteristic absorption edge at 317 nm and a broader absorption range extending to the visible light region. With an increase in the α -Fe₂O₃ NPs layer thickness, there was an increase in the optical absorption coefficient of the ZnO NRs/Ni-

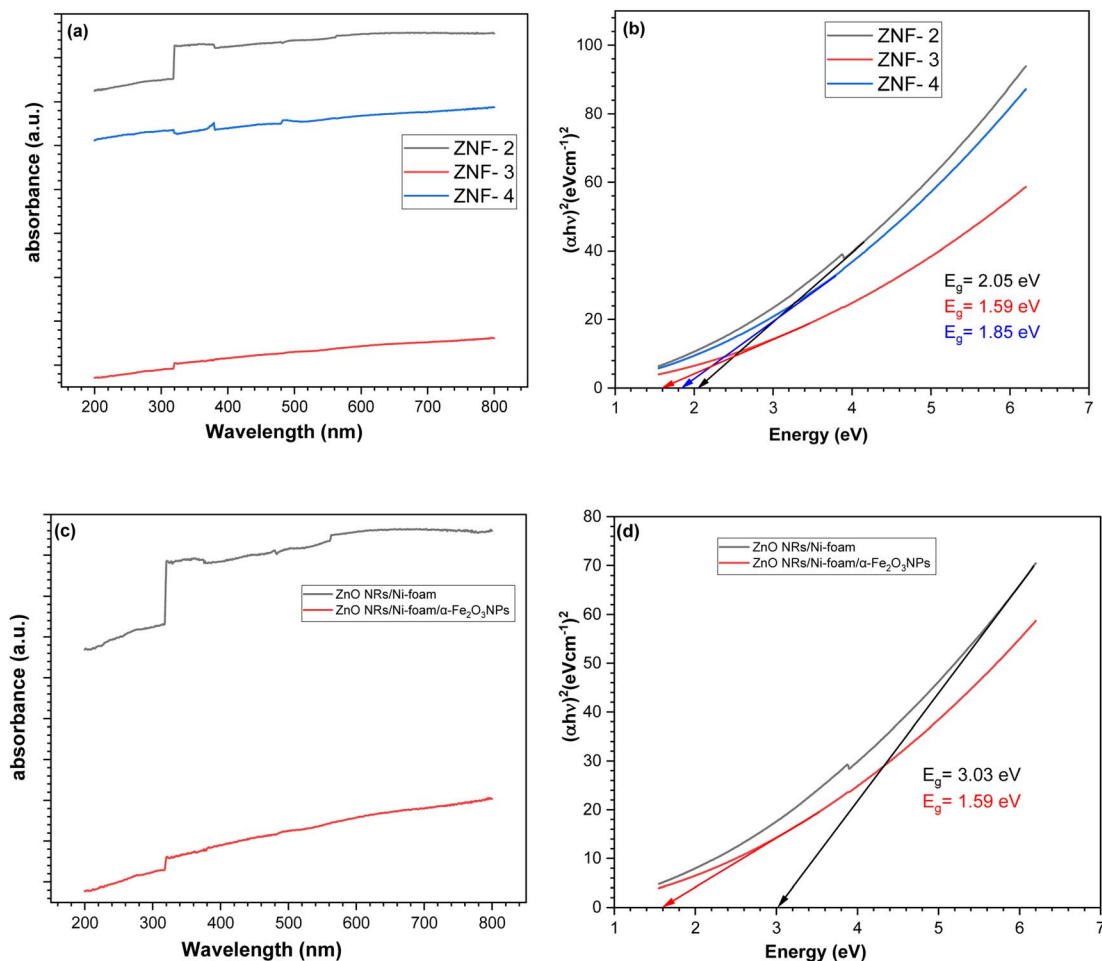


Fig. 3 UV-vis absorption spectra of (a) the ZnO NRs/Ni-foam/ α -Fe₂O₃NPs nanocomposite with different dip coatings. (b) Evaluation of bandgap energies of (ZNF-2), (ZNF-3) and (ZNF-4). (c and d) UV-vis absorption spectra and evaluation of bandgap energies of the bare ZnO NRs/Ni-foam and ZnO NRs/Ni-foam/ α -Fe₂O₃NPs nanocomposite.

foam/ α -Fe₂O₃NPs samples at longer wavelengths compared to ZnO NRs/Ni-foam. ZnO NRs/Ni-foam and the ZnO NRs/Ni-foam/ α -Fe₂O₃NPs nanocomposite revealed bandgap energies of approximately 3.03 eV and 1.59 eV, respectively, as shown in Fig. 3d.

3.3 XRD analysis

The crystallinity and phase purity of ZnONRs/Ni-foam and ZnONRs/Ni-foam/ α -Fe₂O₃NPs were characterized by X-ray diffraction (XRD), as shown in Fig. 4a. The XRD pattern of the bare Ni-foam was recorded from 20° to 90°. The diffraction

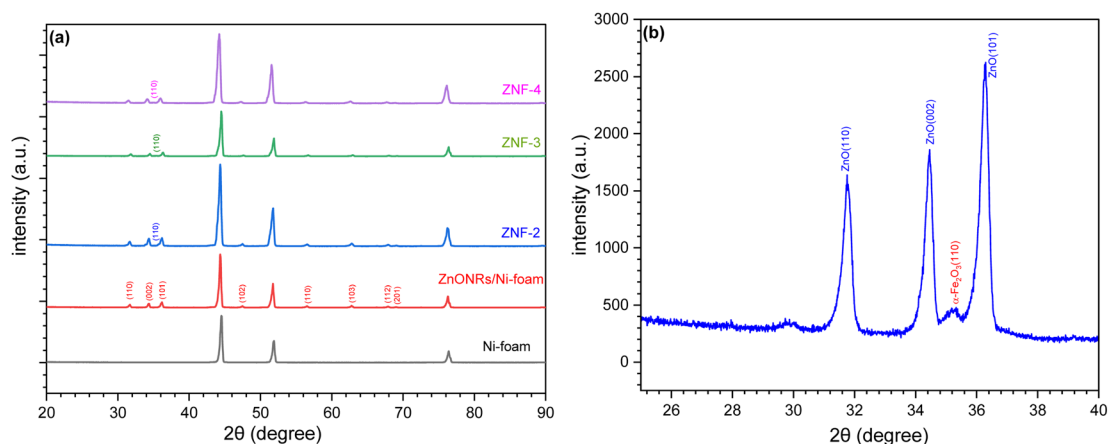


Fig. 4 (a) XRD patterns of Ni-foam, ZnO NRs/Ni-foam, (ZNF-2), (ZNF-3) and (ZNF-4). (b) High-resolution XRD pattern of ZNF-3.



peaks of bare Ni-foam at 44.50° , 51.89° and 76.41° match well with the standard JCPDS card (JCPDS no.: 003-1051). The diffraction peaks of ZnONRs/Ni-foam at 2θ positions 31.66° ,

34.40° , 36.15° , 47.50° , 56.58° , 62.78° , 67.93° and 69.02° attributed to the (110), (002), (101), (102), (110), (103), (112) and (201) planes, respectively, were due to the hexagonal

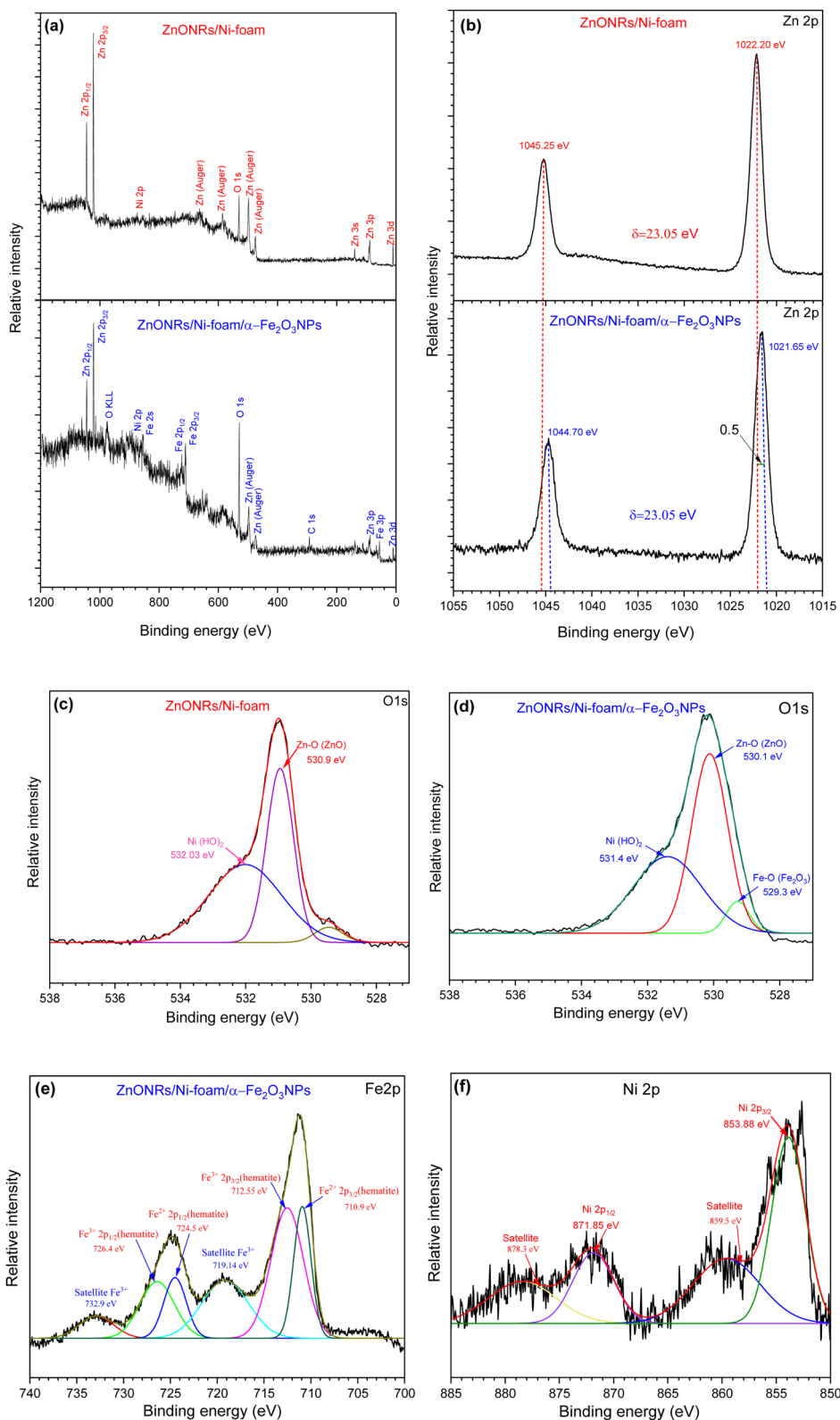


Fig. 5 XPS analysis of the ZnO NRs/Ni-foam and ZnO NRs/Ni-foam/ α -Fe₂O₃ NPs nanocomposite: (a) survey spectra; high-resolution (b) Zn 2p, (c and d) O 1s, and (e) Fe 2p spectra; (f) Ni 2p spectrum of the nickel foam substrate.

wurtzite structure of the ZnO NRs grown on the nickel foam surface and matched JCPDS no. 00-005-0664 in the diffraction database. The additional diffraction peaks of the ZnO NRs/Ni-foam/ α -Fe₂O₃NPs nanocomposite samples obtained 2 (ZNF-2), 3 (ZNF-3) and 4 cycles (ZNF-4) of dip coating were at 35.27°, corresponding to the (110) reflection planes of the rhombohedral structure of the α -Fe₂O₃ NPs, and matched the JCPDS: 00-033-0664 file from the diffraction database, as shown in Fig. 4b.

3.4 XPS analysis

X-ray photoelectron spectroscopy (XPS) measurements were carried out to investigate the chemical bonding states and elemental composition of ZnO NRs/Ni-foam and the ZnO NRs/Ni-foam/ α -Fe₂O₃ NPs nanocomposite samples; the results were fitted by a Gaussian fitting method and are shown in Fig. 5. In Fig. 5a, the survey spectrum of bare ZnO NRs/Ni-foam is shown. It confirms the presence of Zn 3d, 3p, 3s, 2p, auger, O 1s and Ni 2p. After the modification of the ZnONRs/Ni-foam surface by depositing α -Fe₂O₃ NPs, the survey spectrum included peaks of Fe 3p, 2p, 2s, 0 KLL, and C 1s.^{39–42} The high-resolution Zn 2p spectra of the samples are shown in Fig. 5b; doublet peaks are observed at binding energies of 1022.20 eV and 1045.25 eV corresponding to pure ZnONRs/Ni-foam. This is consistent with the oxidation states of Zn 2p_{3/2} and Zn 2p_{1/2}, respectively. However, these oxidation states were shifted to binding energies of 1021.65 eV and 1044.70 eV, respectively, for the ZnO NRs/Ni-foam/ α -Fe₂O₃ NPs nanocomposite sample. Moreover, a spin-orbit energy separation of 23.05 eV demonstrates that ZnO had the wurtzite crystal structure (hexagonal),^{43,44} which is also consistent with the XRD result. The O 1s core-level XPS spectra of pure ZnO NRs/Ni-foam and the ZnO NRs/Ni-foam/ α -Fe₂O₃-NPs nanocomposite samples shown in Fig. 5c and d exhibit peaks at binding energies 530.9 eV and 530.1 eV, corresponding to the bonding of ZnO in the ZnONRs/Ni-foam and ZnO NRs/Ni-foam/ α -Fe₂O₃NPs nanocomposite samples, respectively.^{45,46} The negative shift of the Zn 2p (by −0.5 eV towards the lower binding energy region) and O 1s peaks indicates that a heterojunction was formed by interfacial interaction in the ZnONRs/Ni-foam/ α -Fe₂O₃NP nanocomposite.^{47–52} The other fitted peaks of the high-resolution O 1s spectrum of the ZnO NRs/Ni-foam/ α -Fe₂O₃NPs nanocomposite located at binding energies 529.3 eV and 531.4 eV could be attributed to Fe–O(Fe₂O₃) and Ni(H₂O), as shown in Fig. 5d.⁵³ Meanwhile, the peak at 531.4 eV is characteristic of H₂O, which can be crystal water or water adsorbed on the samples from the air, and it shifted to 532.03 eV in the case of bare ZnO NRs/Ni-foam.³⁶ The core-level Fe 2p spectra showed Fe²⁺ 2p_{3/2}, Fe³⁺ 2p_{3/2}, Fe²⁺ 2p_{1/2} and Fe³⁺ 2p_{1/2} peaks at 710.9 eV, 712.55 eV, 724.5 eV and 726.4 eV, respectively, as displayed in Fig. 5e, indicating the presence of Fe²⁺ and Fe³⁺ species.^{40,54} Additionally, two satellite peaks were observed at 719.14 eV and 732.9 eV.^{55,56} Fig. 5f shows the Ni 2p_{3/2} and Ni 2p_{1/2} XPS peaks at 853.88 eV and 871.85 eV, corresponding to the metallic Ni foam substrate.^{39,40,57,58} Based on the XRD and XPS results, it was concluded that α -Fe₂O₃NPs-modified ZnO NRs were successfully grown on the nickel foam substrate.

3.5 Electrochemical behaviors

3.5.1 Cyclic voltammetry analysis. Cyclic voltammetry (CV) measurements of bare ZnO NRs/Ni-foam and the ZnO NRs/Ni-foam/ α -Fe₂O₃ NPs nanocomposite were performed in 100 mL electrochemical cells to investigate the electrochemical behavior of the electrode material using 70 mL of a 1 M KOH solution and arsenic(v) at different concentrations. The CV curves were recorded in a potential window ranging from −0.4 to 0.6 V vs. Ag/AgCl at a scan rate of 100 mV s^{−1} in the 1 M KOH electrolyte. The oxidation and reduction reactions at the working electrode surface are shown by the CV profiles in Fig. 6a. The CV profiles of bare ZnO NRs/Ni-foam and the ZnO NRs/Ni-foam/ α -Fe₂O₃NPs nanocomposites obtained after different dip-coating cycles showed that the oxidation and reduction peak currents were higher for the nanocomposite. The highest current was observed in ZnO NRs/Ni-foam/ α -Fe₂-O₃NPs nanocomposites, of which ZNF-2 showed a lower current than ZNF-3 and ZNF-4. However, ZNF-3 and ZNF-4 exhibited the same current. In Fig. 6b, the CV curves of the ZNF-3 electrode at different concentrations of arsenic(v) from 0–50 µg per L (ppb) demonstrate that the oxidation and reduction peak current increased with increasing arsenic(v) concentration in the electrolyte. The maximum oxidation and reduction currents 1.3 mA and −0.45 mA were achieved at voltage values of 0.6 V and 0.28 V, respectively, at 50 ppb arsenic(v) concentration. The calibration plot was found to be linear in a wide concentration range of 0–50 ppb of arsenic(v), and the regression equation extracted from the calibration curve was found to be $y = 0.003x - 0.6271$ ($R^2 = 0.991$), as shown in Fig. 6c. These findings show the successful detection of arsenic(v) in an aqueous solution by the as-developed electrode. For further quantitative analysis, the limit of detection (LOD) and the limit of quantification (LOQ) of the sensor developed in this work were evaluated. Further, the LOD and LOQ results reported by others are shown in Table 1. The LOD is the minimum amount of analyte detected by the system, while LOQ is the lowest amount of analyte that can be quantitatively measured. The World Health Organization (WHO) has set 50 to 10 ppb as the maximum allowed arsenic content in drinking water.^{4,5,64} In this work, the LOD and LOQ of the developed ZnO NRs/Ni-foam/ α -Fe₂O₃NPs nanocomposite electrode were calculated using the following equations:

$$\text{LOD} = 3\sigma/S \quad (1)$$

$$\text{LOQ} = 10\sigma/S \quad (2)$$

where σ is the standard deviation, and S is the slope of the calibration curve of current vs. concentration.⁶⁵ From eqn (1) and (2), the calculated LOD and LOQ values of the ZnO NRs/Ni-foam/ α -Fe₂O₃NPs nanocomposite electrodes were found to be 4.12 ppb and 13.74 ppb, respectively. Although these values are quite high compared to other methods, the electrode can only detect arsenic levels lower than the maximum value recommended by WHO. These CV measurements were repeated several times, and the ZnO NRs/Ni-foam/ α -Fe₂O₃NPs nanocomposite sensor electrode was found to be relatively stable.



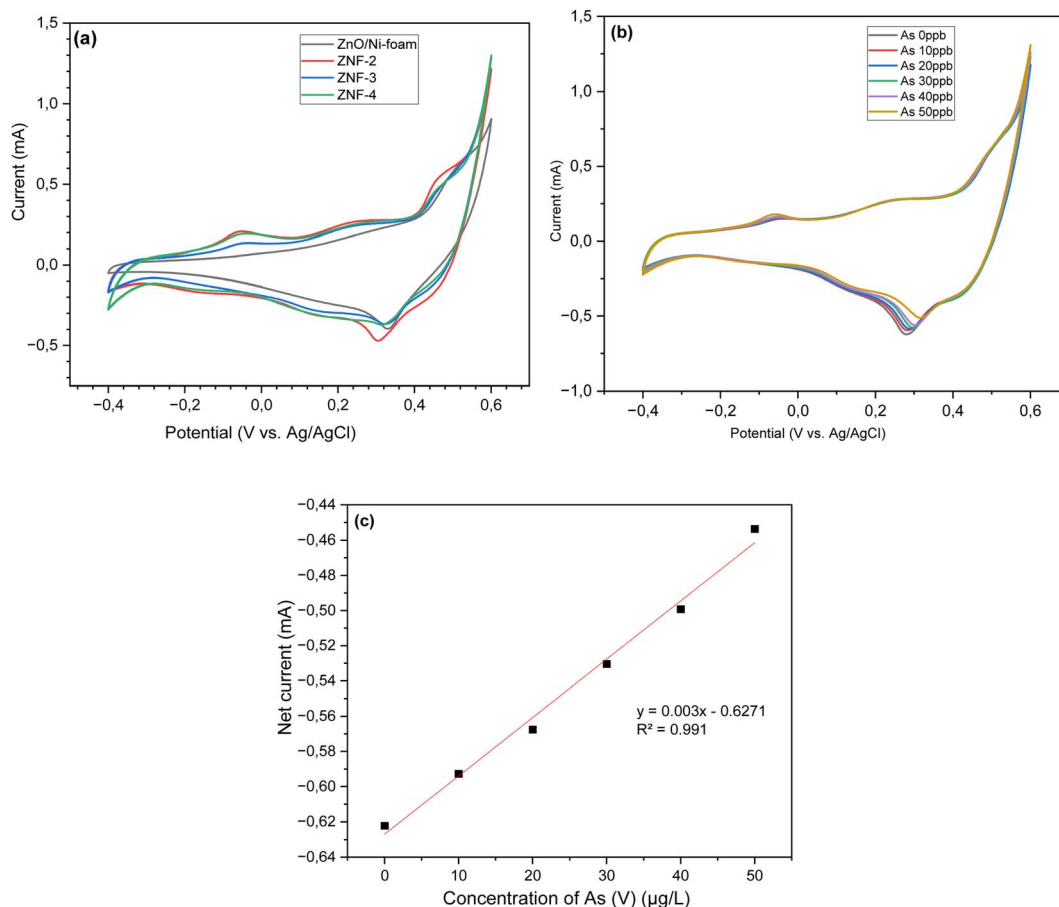


Fig. 6 Cyclic voltammograms of (a) ZnONRs/Ni-foam, (ZNF-2), (ZNF-3) and (ZNF-4) electrodes in a 1 M KOH electrolyte (b). The ZNF-3 electrode at different concentrations of arsenic(v) in the potential range from -0.4 to 0.6 V at a scan rate of 100 mV s^{-1} ; (c) the corresponding linear calibration plot of net current against arsenic(v) concentration.

Table 1 Comparative study of the performance of different electrochemical sensors developed for arsenic detection

Materials	Detection method	Arsenic concentration	LOD	Ref.
Fe_3O_4 nanoparticles/nucleobase	SWV	$1.1\text{--}0.5 \text{ }\mu\text{M}$	0.01 ppm	59
Fe_3O_4 nanocrystals modified GCE	SWASV	$0.08\text{--}1.54 \text{ }\mu\text{M}$	0.01 ppm	60
Fe_3O_4 NPs		$0\text{--}100 \text{ ppb}$	30 ppb	61
ZnO quantum dots		$10\text{--}100 \text{ ppb}$	28 ppb	62
ZnO-NRs@Ni-foam	CV	$0.1\text{--}1.0 \text{ }\mu\text{M}$	0.046 ppm	63
ZnO NRs/Ni-foam/ $\alpha\text{-Fe}_2\text{O}_3$ NPs nanocomposite	CV	$10\text{--}50 \text{ ppb}$	4.12 ppb	This work

3.5.2 Interference effect. The selectivity of a sensor is an important parameter for real aqueous sample applications. The selectivity of the electrode was investigated in the presence of possible interfering metal ions. The effects of different metallic ions, including Ag^+ , K^+ , Cd^{2+} , Zn^{2+} and Fe^{3+} , were tested for the possible interference with arsenic detection by the ZnO NRs/Ni-foam/ $\alpha\text{-Fe}_2\text{O}_3$ NPs nanocomposite electrodes under similar experimental conditions. To study the influence of metal ions, metal salts like KCl, AgNO_3 , $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were employed. The concentration of the metal salts was maintained at 50 ppb in the 1 M KOH electrolyte

solution. There was no strong interaction between arsenic(v) and the interfering species, as shown in Fig. 7. Therefore, these species do not interfere obviously with the electrochemical detection of arsenic(v). The results show that the fabricated sensor has good selectivity towards arsenic(v) ions.

3.6 Sensing mechanism of ZnO NRs/Ni-foam/ $\alpha\text{-Fe}_2\text{O}_3$ NPs nanocomposite electrode

The mechanism of electrochemical detection of arsenic(v) by the ZnO NRs/Ni-foam/ $\alpha\text{-Fe}_2\text{O}_3$ NPs nanocomposite electrode is presented in Fig. 8a. The nickel foam substrate facilitates the



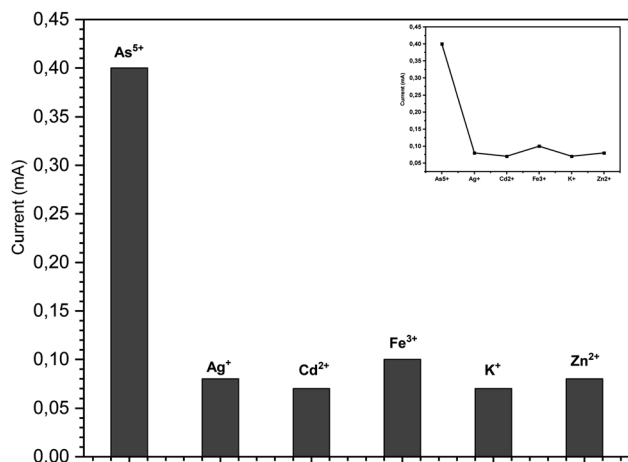
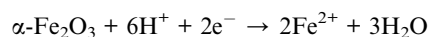


Fig. 7 Interference effect of different metal ions under similar experiment conditions used for the detection of arsenic(v) by the ZnO NRs/Ni-foam/ α -Fe₂O₃NP nanocomposite (50 ppb).

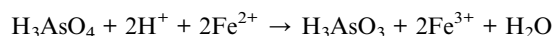
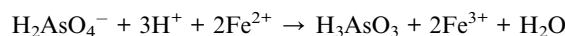
formation of ZnO NRs/ α -Fe₂O₃NPs. The structure resembling a flower provides a large surface area and abundant active areas. This facilitates the fast flow of ions and electrons between the electrode and electrolyte. The enhanced performance of the ZnO NRs/Ni-foam/ α -Fe₂O₃NPs nanocomposite electrochemical sensor compared with bare ZnO NRs/Ni-foam can be attributed to the distinctive electron transport and high absorption properties of the α -Fe₂O₃NPs in the nanocomposite towards arsenic(v) detection; arsenic(v) ions are adsorbed on the surface of the

working electrode and interact with α -Fe₂O₃NPs during the electrochemical measurement, generating Fe²⁺ ions on the electrode surface due to electrochemical reduction.⁶⁷ The arsenic(v) detection mechanism on the electrode surface begins with the adsorption of the H₂AsO₄⁻ and H₃AsO₄ species at the Fe²⁺ sites present on the electrode surface. Afterward, the arsenic(v) species are chemically reduced to H₃AsO₃ by the Fe²⁺ ions generated during the electrochemical measurement of the electrode. These reactions can be coupled with another electrochemical step, in which H₃AsO₃ is reduced to zero-valent arsenic on the electrode surface. Zero-valent arsenic is stripped during the anodic and cathodic scans. The reaction process is demonstrated below.⁶⁶

(1) Reduction of Fe³⁺ to Fe²⁺ on the electrode surface



(2) Chemical reduction of As(v) to As(III) on the electrode surface:



(3) Electrochemical reduction of As(III) to As (0) on the electrode surface:

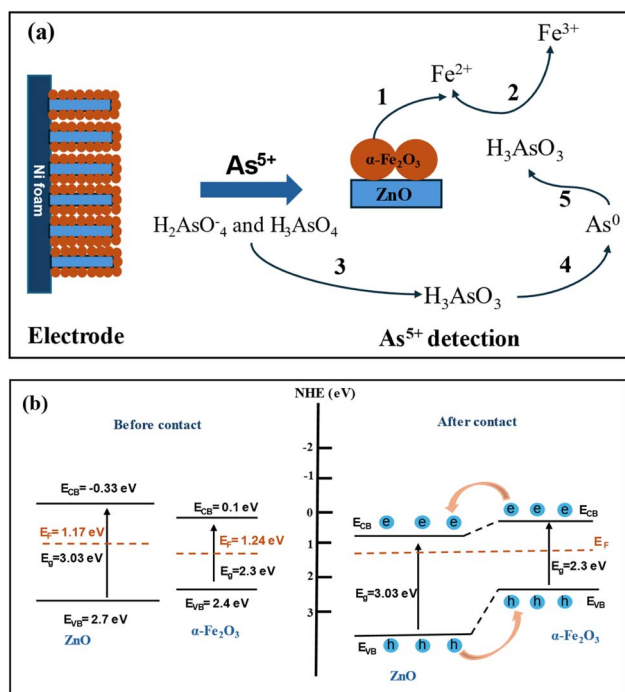
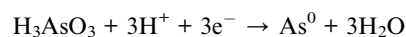


Fig. 8 (a) Schematic of the sensing mechanism (concept based on ref. 66) and (b) equilibrium energy band structure diagram of the ZnO NRs/Ni-foam/ α -Fe₂O₃NPs nanocomposite before and after contact between the ZnO NRs and α -Fe₂O₃NPs.

The mechanism of charge separation and transportation in the ZnO NRs/Ni-foam/ α -Fe₂O₃NPs nanocomposite can be further explained by the generation of an n-n heterojunction between n-type ZnO and n-type α -Fe₂O₃ semiconductors, as shown in Fig. 8b. As the conduction band and valence band of α -Fe₂O₃ (0.1 eV and 2.4 eV) are more negative than those of ZnO (−0.33 eV and 2.7 eV), the electrons are transferred from the conduction band of α -Fe₂O₃ to ZnO. Meanwhile, the holes in the valence band of ZnO migrate to the valence band of α -Fe₂O₃. This migration and separation of electrons and holes are achieved at the heterojunction interface. When the n-n heterojunction of ZnO NRs/ α -Fe₂O₃ is in contact with the electrolyte, electrons at the Fermi level align to attain equilibrium. The Fermi level in α -Fe₂O₃ is located in between its CB and VB at around 1.24 eV. The Fermi level of n-typical semiconductors generally lies at the bottom of the CB at around 0.1–0.2 eV.⁶⁸ As a typical n-type semiconductor, the Fermi level of ZnO is at 1.17 eV. When the semiconductors ZnO and α -Fe₂O₃ are joined together, their Fermi levels overlap at 1.24 eV.

4 Conclusion

The fabrication of an α -Fe₂O₃NPs-modified ZnONRs/Ni-foam nanocomposite was successfully achieved *via* two separate growth steps using hydrothermal and dip-coating methods. The number of dip-coating cycles was varied to optimize electrode



performance. The ZnO NRs/Ni-foam/ α -Fe₂O₃NPs nanocomposite showed the best results when immersed 3 times in the precursor solution, demonstrating the highest oxidation current toward arsenic(v) detection compared with the samples prepared by immersing 2 and 4 times. The electrochemical performance of the optimal electrode in arsenic(v) detection was investigated in a wide range of arsenic concentrations from 0 to 50 $\mu\text{g L}^{-1}$ by cyclic voltammetry. The results demonstrated LOD and LOQ values of 4.12 ppb and 13.74 ppb, respectively; the LOD is lower than the maximum permitted arsenic content recommended by the World Health Organization (WHO) in drinking water. Therefore, the ZnO NRs/Ni-foam/ α -Fe₂O₃ NPs nanocomposite can be utilized as an electrode to develop efficient arsenic sensor systems for monitoring drinking water.

Abbreviations

XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
FESEM	Field-emission scanning electron microscopy
ZnO	Zinc oxide
α -Fe ₂ O ₃	Hematite
DI	Deionized
UV	Ultraviolet
NRs	Nanorods
NPs	Nanoparticles
CV	Cyclic voltammetry
LOD	Limit of detection
LOQ	Limit of quantification

Data availability

All data relevant for the reproduction of the results presented in this work are included within the article.

Author contributions

All authors have contributed to achieve this result, and they are aware and accept the submission.

Conflicts of interest

The authors declare no conflict of interest.

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