

Sensitive and Selective Detection of Chloroform by Current-Voltage Using ZnO Nanorods Modified Electrode

(Pengesanan Sensitif dan Memilih Kloroform oleh Voltan Arus Menggunakan Elektrod Ubah Suai ZnO Nanorod)

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ABSTRACT

The development of *in situ* chloroform detection is crucial due to the high risk of carcinogenic effects associated with chloroform exposure. In this study, an electrochemical-based chloroform sensor was fabricated using undoped ZnO nanorods on indium tin oxide (ZnONRs/ITO) electrode to detect chloroform in aqueous-phase samples. Based on the results, the FESEM imaging showed that the ZnONRs exhibited an evenly distributed circular structure with a diameter of 62-90 nm, while the EDX and XRD findings confirmed the presence of Zn and O elements deposited on the electrode surface. Furthermore, the phosphate buffer solution (PBS) solution significantly affected the performance of the modified electrode with an optimal concentration and pH of 0.1 M and pH 7. The results also highlighted the vital function of the modified ZnONRs/ITO electrode as an efficient electron mediator and its catalytic potential to induce chloroform oxidation. Most importantly, the modified ZnONRs/ITO electrode was able to detect the presence of chloroform in real seawater samples, where the repeatability and reproducibility tests achieved a Relative Standard Deviation (RSD) of 1.41% and 2.61%, respectively, indicating the exceptional performance of the modified electrode. Moreover, the modified ZnONRs/ITO electrode recorded a low limit of detection and high sensitivity of 1.50 μM and 2.11 $\mu\text{A}/\text{cm}^2 \cdot \text{mM}$, respectively, within a 0.010-10 mM linear dynamic range. In conclusion, the current-voltage (I-V) method proved the reliable, satisfactory, and effective fabrication of the modified ZnONRs/ITO electrode for chloroform sensing in aqueous-phase samples, including in real seawater samples.

Keywords: Chloroform detection; I-V method; seawater; undoped ZnO nanorods

ABSTRAK

Pembangunan pengesanan kloroform *in situ* adalah penting kerana risiko tinggi kesan karsinogenik yang berkaitan dengan pendedahan kloroform. Dalam kajian ini, penderia kloroform berasaskan elektrokimia telah direka menggunakan nanorod ZnO yang tidak didop pada elektrod indium tin oksida (ZnONRs/ITO) untuk mengesan kloroform dalam sampel fasa akueus. Berdasarkan keputusan, pengimejan FESEM menunjukkan bahawa ZnONRs menunjukkan struktur bulat yang tersebar sama rata dengan diameter 62-90 nm, manakala penemuan EDX dan XRD mengesahkan kehadiran unsur Zn dan O yang dienapkan pada permukaan elektrod. Tambahan pula, larutan PBS memberi kesan ketara kepada prestasi elektrod diubah suai dengan kepekatan optimum dan pH pada 0.1 M dan pH 7. Hasilnya juga menyerlahkan fungsi penting elektrod ZnONRs/ITO yang diubah suai sebagai pengantara elektron yang cekap dan potensi pemangkinnya untuk mendorong pengoksidaan kloroform. Paling penting, elektrod ZnONRs/ITO yang diubah suai dapat mengesan kehadiran kloroform dalam sampel air laut sebenar dengan ujian keboleholangan dan kebolehasilan mencapai Sisihan Piawai Relatif (RSD) masing-masing 1.41% dan 2.61%, menunjukkan prestasi luar biasa bagi elektrod yang diubah suai. Selain itu, elektrod ZnONRs/ITO yang diubah suai merekodkan had pengesanan

yang rendah dan kepekaan tinggi masing-masing $1.50 \mu\text{M}$ dan $2.11 \mu\text{A}/\text{cm}^2 \cdot \text{mM}$ dalam julat dinamik linear 0.010-10 mM. Kesimpulannya, kaedah I-V membuktikan fabrikasi yang boleh dipercayai, memuaskan dan berkesan bagi elektrod ZnONRs/ITO yang diubah suai untuk penderiaan kloroform dalam sampel fasa akueus, termasuk dalam sampel air laut sebenar.

Kata kunci: Air laut; kaedah I-V; pengesanan kloroform; ZnO yang tidak didop

INTRODUCTION

Over the years, the worrying environmental pollution has been significantly contributed by the swift development of numerous major industries, including automotive, textile, pharmaceutical, and food and agriculture (Mirzaei, Leonardi & Neri 2016). These industries release toxic and detrimental chemicals that not only affect the ecosystem but also pose a serious threat to the well-being of public health. One of the most toxic chemicals from the industries is tri-chloromethane or methyl-tri-chloride, more commonly known as chloroform, which easily evaporates when directly exposed to air. Subsequently, most of the chloroform that enters the atmosphere is degraded into toxic phosgene (Veerapandian et al. 2017). Nevertheless, certain amounts of chloroform would remain in water due to its low water solubility properties (Fong et al. 2015). The uncontrolled amounts of chloroform may persist in water bodies and potentially pollute the environment. Therefore, the detection of low-concentration aqueous-phase chloroform is highly critical to prevent such disastrous calamity associated with chloroform pollution (Hamid et al. 2019).

A number of standard techniques have been developed to detect chloroform, such as aqueous-phase microextraction (Grau et al. 2022), mid-infrared sensing (Zhang et al. 2021), and liquid chromatography (Yaqub et al. 2017). Although these methods provide delicate and adequate detection limits, these approaches are relatively costly, time-consuming, and often require qualified technicians to run the analysis. Moreover, they are non-portable, making them extremely challenging for on-site surveillance applications. Thus, the development of a simple and effective method to detect and quantify chloroform is crucially important and overcome the poor portability and slow environmental monitoring response faced by the available techniques. In view of this, various sensor technologies have been developed to detect chloroform, which includes colorimetric sensor (Sheng et al. 2019), optical sensor

(Mohamad Ahad et al. 2018), fluorescence sensor (Peng et al. 2016), luminescence sensor (Wu et al. 2018), and electrochemical sensor (Hamid et al. 2019). Interestingly, electrochemical sensors are among the various sensing methods that have gained extensive focus due to their simplicity, high sensitivity, low cost, and low detection limit. In addition, electrochemical sensors can analyse chemical reactions in terms of electrical response (Cho et al. 2022), which makes it an attractive detection method.

The main component of an electrochemical sensor is the electrode at which the chemical reaction occurs and is referred to as the redox process. While studies on electrode development have included semiconductor nanoparticles (Hamid et al. 2021) and carbon-based materials (Prasadam et al. 2022), metal-oxide semiconductor materials (Nurhaswani et al. 2020) offer outstanding properties, such as large active surface area, high stability, and easy to fabricate (Banitaba & Ehrmann 2021). Recently, the development of hybrid metal-oxide semiconductor electrodes has shown improved electrode performance in terms of sensitivity, stability, and selectivity for chemical detection, including chloroform. In one study, Rahman (2017) fabricated an ethanol sensor using CdO/ZnO/Yb₂O₃ ternary-doped metal-oxides nanosheets, which acted as an efficient mediator to detect ethanol in an aqueous solution with low detection limit, high sensitivity, and excellent selectivity. However, the fabrication of the ternary-doped metal-oxides was immensely complex and time-consuming. In another study, Nie et al. (2015) fabricated a hybrid zinc oxide/copper oxide/aluminium (ZnO/CuO/Al₂O₃) composite electrode via hydrothermal and co-precipitation method for the detection of chloroform. Based on the X-Ray Diffraction (XRD) result, it was shown that the composites comprised of ZnO and CuO, which had similar morphologies and overlapped each other, while Al₂O₃ was presented as an amorphous state. Further research on hybrid metal-oxide semiconductor electrodes has been conducted to improve their performance (Chaudhary et al. 2018).

Additionally, undoped metal-oxide semiconductors have also been developed to overcome the limitations of hybrid metal-oxide semiconductors electrodes. For instance, Feliciano-Ramos et al. (2016) fabricated palladium (Pd) nanoparticles through the chemical reduction method to detect ethanol in an aqueous solution. The electrical response showed that Pd nanoparticles exhibited greater stability and reproducibility. However, the result indicated poor sensitivity and detection limit, which may be due to the formation of nanoparticle aggregates. The small size and strong van der Waals interactions between the nanoparticles could have increased the tendency towards the formation of aggregates, subsequently rendering unstable particles in the solution. The aggregation process may also generate irregular particles and minimise the overall surface area of the electrode (Gawenda 2021). Previously, Abdullah et al. (2015) utilised undoped gadolinium(III) oxide (Gd_2O_3) nanostructures to modify the surface of a silver electrode (AgE) for the detection of ethanol in an aqueous solution. Despite that the results showed good sensitivity, the limit of detection remained unsatisfactory as Gd_2O_3 nanostructures were found to be aggregated on the surface of the modified electrode. Nevertheless, undoped metal-oxide semiconductors provide many advantages over other materials, including low cost, high surface area, reliability, robustness, and ease of fabrication as well as viable for large-scale production (Khan, Saeed & Khan 2017). Thus, the collective findings from other reports have projected the potential application of undoped metal-oxide semiconductors, such as ZnO (Teimoori et al. 2017) and CuO (Yan et al. 2015)^c, as effective chemical sensors, including the detection of chloroform.

ZnO is one of the metal-oxide semiconductors that exhibits broad bandgap energy of 3.2 eV, large exciton binding energy of 60 meV, high bond strength, chemically and thermally stable, non-toxic, able to be fabricated at fairly low temperatures, and diverse morphological structure (Galdámez-Martínez et al. 2020). Moreover, the morphology of ZnO plays a vital part in detecting chloroform given that different morphologies provide varying advantages that enhance the performance of the electrode, such as sensitivity, stability, the limit of detection, and selectivity (Nguyen et al. 2019). The nanorod morphology is the most preferable option as the upright structure of the nanorod arrays can ease electron transport mobility upon direct contact with a substrate. Furthermore, the nanorods can be developed either through the gas phase synthesis or solution phase

synthesis (Chalanger et al. 2021). In particular, the solution phase synthesis, which includes precipitation, microemulsion, sol-gel, hydrothermal, and chemical bath deposition, offers a low-cost and simple setup under relatively mild conditions of synthesis at low temperatures (Danielson et al. 2019). The hydrothermal method is the most reliable solution-phase synthesis due to its ability to alter the morphology of nanorods across their nucleation sites, allowing for a well-coordinated growth, and providing a large surface area (Mehdi et al. 2021). Realising the demand for an efficient chloroform-sensing technique, this study was performed to investigate the development of ZnO nanorod-modified electrodes for aqueous-phase chloroform detection. The characteristics of the fabricated modified electrode were examined following the hydrothermal modification process. The performance of the modified electrode as a chloroform sensor was then evaluated. In addition, the effect of Phosphate Buffered Saline (PBS) as the electrolyte to transport electrons between the chloroform and the modified electrode, including the concentration, pH level, and scan rate, was explored.

MATERIALS AND METHODS

PREPARATION OF ZNO SEEDS AND FABRICATION OF MODIFIED ELECTRODE VIA HYDROTHERMAL REACTION

This study utilised indium tin oxide (ITO) glass substrates with an approximate size, thickness, and sheet resistance of $2 \times 1 \text{ cm}^2$, 1.1 mm, and $10 \text{ } \Omega/\text{sq}$, respectively. The electrodes were cleaned with a mixture of ammonium hydroxide ($Al(OH)_3$), hydrogen peroxide (H_2O_2), and deionised water at a volume ratio of 1:4:20 mL for 20 min at 60 °C before rinsed with distilled water three times. Next, the ITO glass substrates were soaked in 2-propanol for 3 min before they were left to dry in an oven at room temperature. Meanwhile, referring to a previous report, the sol-gel method was employed to synthesise the ZnO seeds by dissolving 1.65 g of zinc acetate dehydrate ($C_4H_{10}O_6Zn$) in 15 mL of methanol (CH_3OH) and vigorously agitated for 20 min at 60 °C (Hamid et al. 2019). Approximately 15 mL of ethanolamine solution was then added to the mixture before constantly stirred for another 2 h at 60 °C. Once the solution has been left for 24 h at room temperature, the ZnO seed solution was drop-casted onto the ITO glass substrates and underwent an annealing process for 2 h at 500 °C to allow the ZnO Nanorods (ZnONRs) to grow. The hydrothermal reaction

was performed in a preheated oven for 4 h at 80 °C with the ZnO seeds/ITO electrode in the growth solution containing 0.65 g of zinc nitrate tetrahydrate and 0.35 g of hexamethylamine in deionised water. After the electrodes were rinsed with distilled water, they were dried in an oven at room temperature for 30 min and ready for further analysis.

CHARACTERISATION OF THE MODIFIED ZNONRS/ITO ELECTRODE

The modified ZnONRs/ITO electrodes were subjected to several characterisation analyses. The surface morphology of the electrode was first observed under a Zeiss SUPRA 35VP Field-Emission Scanning Electron Microscope (FESEM) fixed with an Energy Dispersive X-Ray (EDX) at 5 kV e-beam. The phase composition and purity of the modified ZnONRs/ITO electrode were then evaluated using a P8Advan-Bruker XRD with a Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) within the 20–65° range and 0.01° step size. The wettability was also determined to essentially explain the surface properties and interaction of solid material when come in contact with a liquid substance. Wettability involves the measurement of the contact angle as the primary data, which indicates the degree of wetting when a solid and liquid interact (Li et al. 2019). A contact angle goniometer (KSV CAM 101) was used to evaluate the wettability of the surface samples by gently depositing a droplet of millipore water on the sample surface. Furthermore, the electrochemical behaviour of the modified ZnONRs/ITO electrodes was analysed via the Cyclic Voltammetry (CV) and Current-Voltage (I-V) technique. As shown in Figure 1, the electrochemical measurements were conducted using the portable three-electrode Bipotentiostat/Galvanostat μ STAT 400 (Dropsens), where the ZnONRs/ITO electrode, Ag/Cl, and Pt were set as the Working Electrode (WE), reference electrode, and auxiliary electrode, respectively. The effect of chloroform concentration as the electrolyte solution on the current response of the modified ZnONRs/ITO electrode was assessed by preparing a series of chloroform concentrations ranging from 0.010 mM to 10 mM.

EFFECTS OF PBS PARAMETERS ON THE PERFORMANCE OF MODIFIED ZNONRS/ITO ELECTRODE

Apart from the characterisation of the fabricated ZnONRs/ITO electrode, this study analysed the effect of concentration, pH, and scan rate of PBS on the performance of the electrode to detect chloroform. This

is due to the fact that chloroform is insoluble in water. Hence, PBS solution was utilised as the supporting electrolyte to optimise the transport of electrons between the ZnONRs/ITO electrode and chloroform molecules, thus, increasing the sensitivity of the chloroform sensor. The performance of the modified ZnONRs/ITO electrode to detect 1 mM chloroform was investigated using various concentrations of PBS solution via the I-V method (0.01, 0.05, 0.10, 0.50, and 1.0 M). In addition, the I-V method was employed to determine the influence of the PBS solution between pH 5 and pH 8 (pH 5, 6, 7, and 8) on the detection efficiency of the modified ZnONRs/ITO electrode against 1 mM chloroform. Meanwhile, the CV analysis was performed to study the influence of scan rate on the performance of the modified ZnONRs/ITO electrode using the optimal PBS concentration mixed with 5 mM ferrocyanide. The scan rate, ν was analysed at 20, 40, 60, 80, 100, 120, 140, 160, 180, and 200 mV/s. Ferrocyanide is a simple and frequently used redox solution to observe even the slightest change in the charge transfer kinetics given its highly sensitive small-surface molecules. The slope ratio of I_{pa}/I_{pc} for the I_{pa} vs ν and I_{pc} vs ν plots was close to 1, and the ΔE_p ($E_{pc} - E_{pa}$) scanned at 100 mV/s was 0.1 V.

APPLICATION OF THE MODIFIED ZnONRs/ITO ELECTRODE ON REAL SEAWATER SAMPLES

Following the characterisation analysis, real seawater samples were used to determine the chloroform sensing performance of the modified ZnONRs/ITO electrode and assess the validity of the I-V method. In addition, the repeatability test was carried out for 10 successive measurements ($n = 10$) using optimised PBS solution conditions with 1 mM chloroform, while the reproducibility of the modified ZnONRs/ITO electrode was determined by comparing the current response toward the presence of 1 mM chloroform using five different electrodes ($n = 5$).

RESULTS AND DISCUSSION

SURFACE MORPHOLOGY AND BEHAVIOURAL ANALYSIS OF THE MODIFIED ZNONRS/ITO ELECTRODE

Figure 2(a) illustrates the surface characteristics of the deposited ZnO seed layer on the ITO glass substrate following the annealing process at 500 °C. As seen from the FESEM imaging in Figure 2(a), the surface of the nanosized ZnO seed layer was coated with evenly-distributed circular particulates with a diameter range of

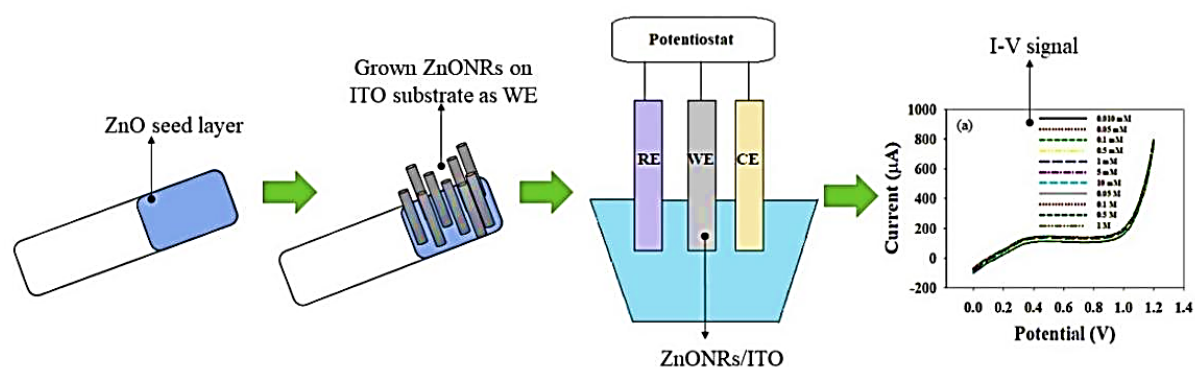


FIGURE 1. The schematic diagram of the fabrication of the ZnONRs/ITO electrode and the subsequent electrochemical analysis via the CV and I-V method

52-90 nm. The small-sized seed is a desirable feature that improves the surface area to volume ratio, which would facilitate the size and density determination of the grown nanorods. Figure 2(b) shows the hexagonal shape of the ZnONRs that grew vertically aligned on the seeded ZnO substrate after 4 h of hydrothermal reaction at 80 °C. The diameter range of the ZnONRs was approximately 62-90 nm. The synthesised nanorods via the hydrothermal method were comparable with the standard growth process of ZnO crystals, which displayed the polar Zn-terminated [0001] and O-terminated [000] on top and bottom surfaces, respectively, and bounded by six non-polar crystallographic planes [0110].

Figure 2(c) and 2(d) depicts the XRD patterns of the ZnO seed and grown ZnONRs, accordingly. The obtained results corresponded with the ICSD card No. 980065190. All the diffraction peaks from the ZnO seeds in Figure 2(c) confirmed to the (100), (002), (101), (102), (110), and (103) planes positioned at 31.79°, 34.42°, 36.28°, 47.57°, 56.65°, and 62.80°, respectively. Specifically, the highest peak intensity at 34.42° compared to other peaks implies that the ZnO seeds were mainly restricted to the (002) plane and grew in the c-axis direction. When the ZnO seed solution was deposited on the bare surface of the ITO glass, the heat treatment process effectively forced the ZnO crystals to self-nucleate and became well-crystallised through the highly favoured (002) orientation. In addition, the heat treatment provided a greater amount of energy for the nucleation growth and diffusion of atoms, which led to the dynamically preferable (002) orientation. Moreover, a preferred orientation that corresponds to the (002) plane was also detected in the XRD pattern of

the ZnONRs sample, as shown in Figure 2(d). The (002) peak indicated a major impact on the nucleation and grain growth, especially during the early growth stage, which determined the subsequent development stage of the ZnO nanostructure. Most importantly, there were no impurities peaks detected, which showed the high purity of the ZnO seed. Thus, the findings demonstrate the crucial role of the ZnO seed layer in the development of high-quality ZnONRs (Abdulrahman et al. 2021).

Figure 3(a) presents the EDX elemental composition of ZnONRs with significant Zn and O peaks without impurities. The EDX analysis was also employed to verify the elemental distribution of ZnONRs. Based on the elemental mapping in Figure 3(b)-3(d), Zn and O were dispersed evenly on the surface of the ITO electrode. It is vital to determine the wettability behaviour of the modified ZnONRs/ITO electrode to achieve the required criteria as a practical aqueous detection sensor. Generally, the Water Contact Angle (WCA) of a solid surface is considered hydrophilic (water-loving) when the WCA < 90° or hydrophobic (water-hating) when the WCA > 90°. Hence, a small contact angle corresponds to a high wettability and vice versa. According to the result in Figure 4, the modified ZnONRs/ITO electrode suggests a hydrophilic characteristic with a static WCA of 66.39°. Given that the modified ZnONRs/ITO electrode was synthesised in an aqueous solution under low-temperature conditions, the hydroxyl (-OH) group became thermally stable across a broad temperature range of 50-400 °C, which contributed to its hydrophilic properties (Lagauche et al. 2017). Additionally, the hydrophilic properties indicated that the -OH group on the surface of the modified ZnONRs/ITO electrode served

as key reactive sites to attract water molecules. The polar water molecule that consists of the H-OH bond interacts with the electrode surface in a specific orientation (a perpendicular OH-O bond), subsequently promoting the formation of hydrogen bonds between the ZnO surface and water molecules (Gomez-Flores et al. 2019).

Therefore, the water droplet would simply spread onto the ZnONRs surface, enhancing the surface wettability and reducing the degree of WCA of the modified ZnONRs/ITO electrode. Under these circumstances, the modified ZnONRs/ITO electrode is conveniently applicable for water-based environmental detection.

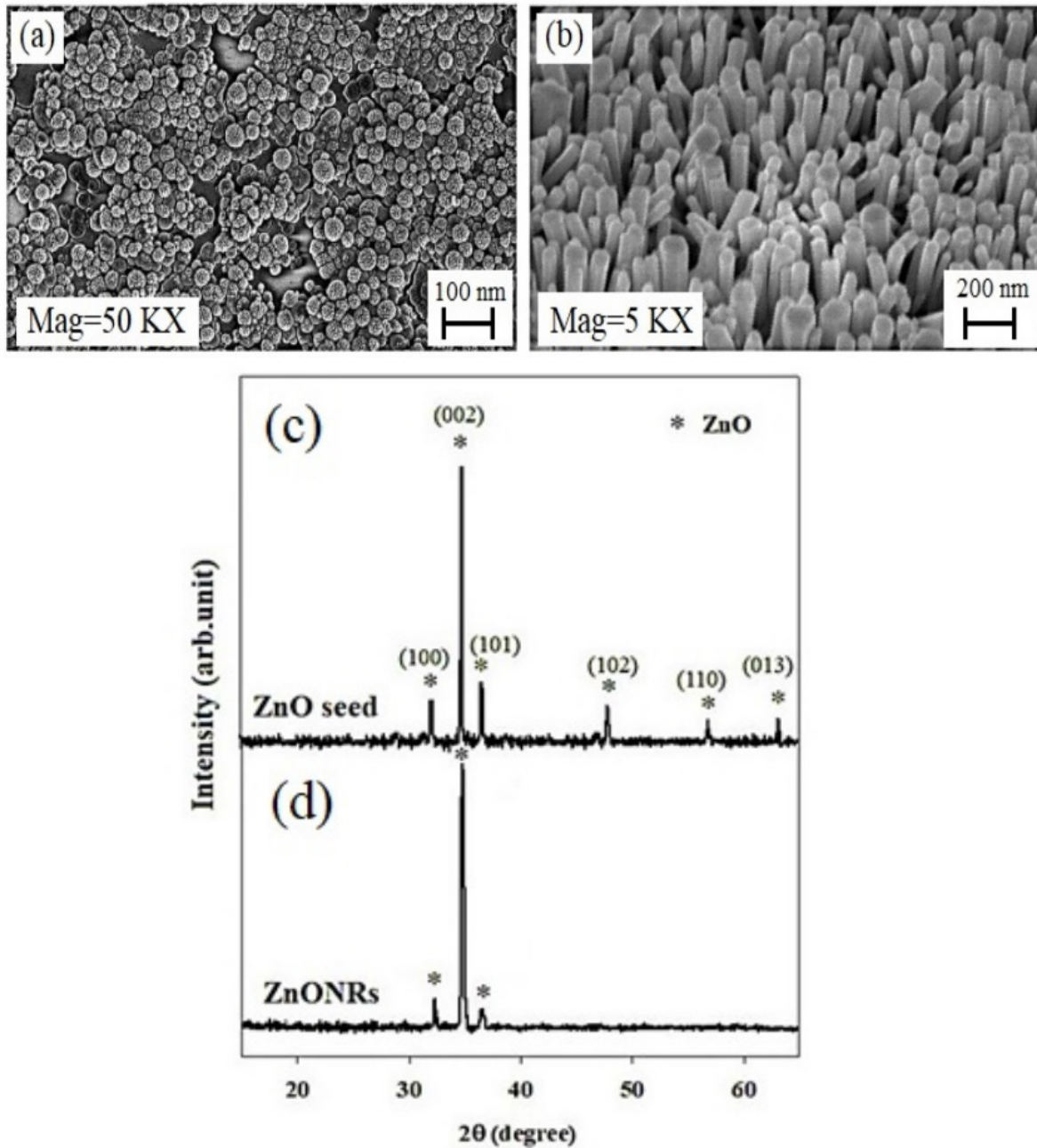


FIGURE 2. FESEM surface imaging of (a) ZnO seed layer after annealed, (b) ZnONRs grown on ITO substrate and XRD analysis of the (c) ZnO seed layer and (d) ZnONRs

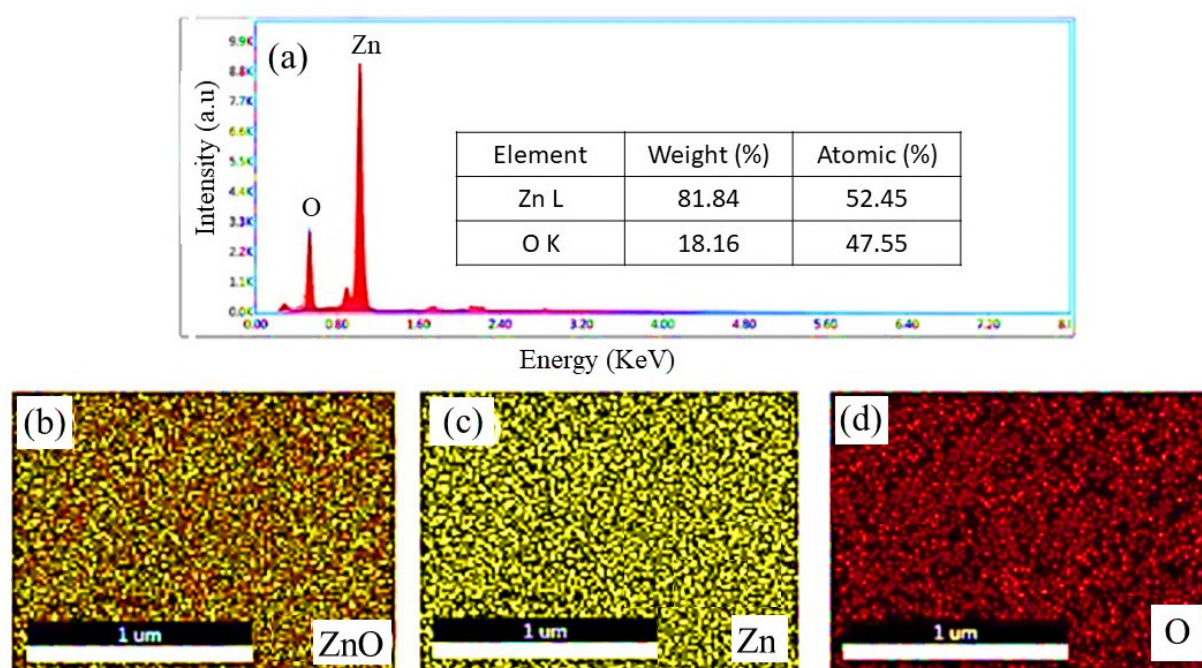


FIGURE 3. EDX analysis displaying the elemental (a) composition of ZnONRs and mapping of (b) ZnONRs (c) Zn atom and (d) O atom

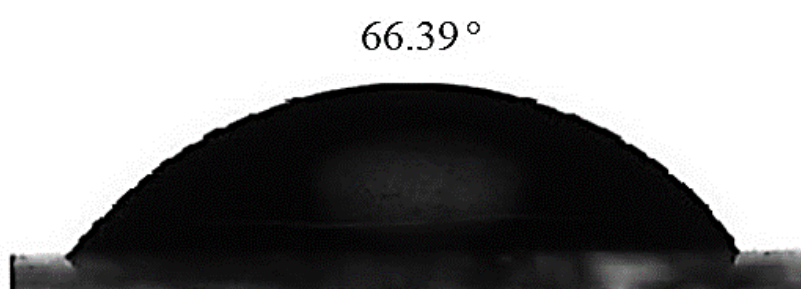


FIGURE 4. The shape of the water droplet and the corresponding WCA value of the modified ZnONRs/ITO electrode

IMPACT OF CONCENTRATION, pH, AND SCAN RATE OF PBS ON CHLOROFORM DETECTION

Basically, PBS is a stable water-based salt solution that contains potassium dihydrogen phosphate (KH_2PO_4), disodium hydrogen phosphate (Na_2HPO_4), sodium chloride (NaCl), and potassium chloride (KCl). The presence of negatively charged ions, such as phosphate ions, and positively charged ions, for example, hydrogen ions (H^+),

results in a zero-net charge in PBS so that electrons can flow continuously without interruption. Thus, the PBS concentration could impact the conductivity properties of the modified electrode during chloroform detection. Based on the obtained data, the ion concentration was relatively limited at a lower PBS concentration of 0.01 M and 0.05 M, which allowed only a minimal quantity of charged electrons to transport between the electrolyte

and electrode. On the contrary, a tolerable level of ions was present at a higher PBS concentration, which allowed more electrons to carry the charges, subsequently increasing the conductivity of the electrode. As shown in Figure 5(a), the higher concentration of the PBS solution improved the current value due to the larger conductivity value of the PBS solution. A high current peak value at 0.10 M PBS in Figure 5(b) implies the adequate presence of ions to transport the charges during the detection of 1 mM chloroform. Nevertheless, further addition of the PBS concentration to 1.00 M caused the peak current to decrease, indicating slower electron transfers due to the excessive presence of phosphate ions that obstruct the reaction. In short, 0.10 M of PBS was identified as the optimum PBS concentration required to achieve an outstanding electrochemical performance of the modified ZnONRs/ITO electrode.

Meanwhile, the influence of pH level on the I-V response of the modified ZnONRs/ITO electrode is shown in Figure 5(c), while Figure 5(d) depicts the linear curve of the I-V response. A change in pH from 5 to 7 increased the current value before it drastically dropped upon reaching pH 8. The low current value was expected under acidic PBS conditions (pH 5-6) due to the high concentration of positive ions (H^+) generated in the PBS solution. However, the H^+ is not involved in the reaction since they exhibit a low affinity towards electrons, causing the overall current value to reduce. In contrast, the highest peak current value was recorded at neutral pH, which was associated with the balanced ion concentration between H^+ and negative ions (OH^-) in the PBS solution. In fact, these ions are always present in pairs and generate equal ion amounts in the reaction. The severe drop in current value under alkaline PBS conditions (pH 8) was also predicted as a result of the overwhelming number of -OH groups in the PBS solution.

The influence of scan rate is also a crucial parameter that requires a thorough understanding of the charge transfer kinetics of the modified ZnONRs/ITO electrode. Figure 6(a) illustrates the CV curves of the modified ZnONRs/ITO electrode at varying scan rates of 20-200 mV/s with 20 mV/s increments. The electrochemical behaviour of the modified ZnONRs/ITO electrode corresponded to that of the quasi-reversible surface control electrochemical system. This observation was based on the proportional electron transfer rate to the mass transport rate as the direct electron transfer was controlled by the surface of the modified ZnONRs/ITO electrode (Kim et al. 2022). Furthermore, the anodic and cathodic peak currents in Figure 6(b) and 6(c),

respectively, increased linearly with the increased scan rate of 20-200 mV/s, while the square root of the scan rate indicates that the redox reaction of the modified ZnONRs/ITO electrode was a surface-controlled process (Zhang et al. 2022). These findings suggest a rapid direct electron transfers kinetics of the ZnONRs/ITO electrode. As the recorded CV response at varying scan rates in Figure 6(b) showed the influence of the modified ZnONRs/ITO to regulate the direct transfer of electrons, the Randles-Sevcik equation can be utilised to measure the electroactive surface area, A_e of the redox species and the diffusion coefficient, and D as follow (González-Meza et al. 2019):

$$i_p = 2.69 \times 10^5 n^{3/2} A_e D^{1/2} C \nu^{1/2}$$

where i_p refers to the maximum current in μA ; n represents the number of electrons; C denotes the concentration of the redox species in mol/cm^3 ; and ν describes the scan rate in mV/s. Based on the calculation, the D value of the modified ZnONRs/ITO electrode was 1.02×10^{-6} cm/s, while the slope from the plot of I_{pa} vs $\nu^{1/2}$ was $1521.39 (mV/s)^{1/2}$. Therefore, the A_e of the modified ZnONRs/ITO electrode was $1.12 cm^2$.

ELECTROCHEMICAL PROPERTIES OF THE MODIFIED ZnONRs/ITO ELECTRODE AND THE MECHANISM FOR CHLOROFORM DETECTION

The electrochemical behaviour of the modified ZnONRs/ITO electrode was further analysed via the I-V method at a scan rate of 100 mV/s in 0.1 M PBS solution at pH 7 and the results were compared to that of the bare ITO electrode under similar parameters. Figure 9 shows the comparison of the electrochemical response between the bare ITO electrode and modified ZnONRs/ITO electrode with and without 1 mM chloroform. The electrocatalytic activity of the bare ITO electrode was insignificant since the analyte was not oxidised in the absence of chloroform. The enlarged inset in Figure 7(a) highlights the minimal current response of the bare ITO electrode across the whole potential range, which was contrary to the measured current response of the modified ZnONRs/ITO electrode that rose sharply when the potential reached 0.4 V with chloroform. Conversely, the current response of the modified ZnONRs/ITO electrode was substantially higher in the presence of 1 mM chloroform compared to that without chloroform, as displayed in Figure 7(b). Hence, the results emphasised the crucial role of the modified ZnONRs/ITO electrode as

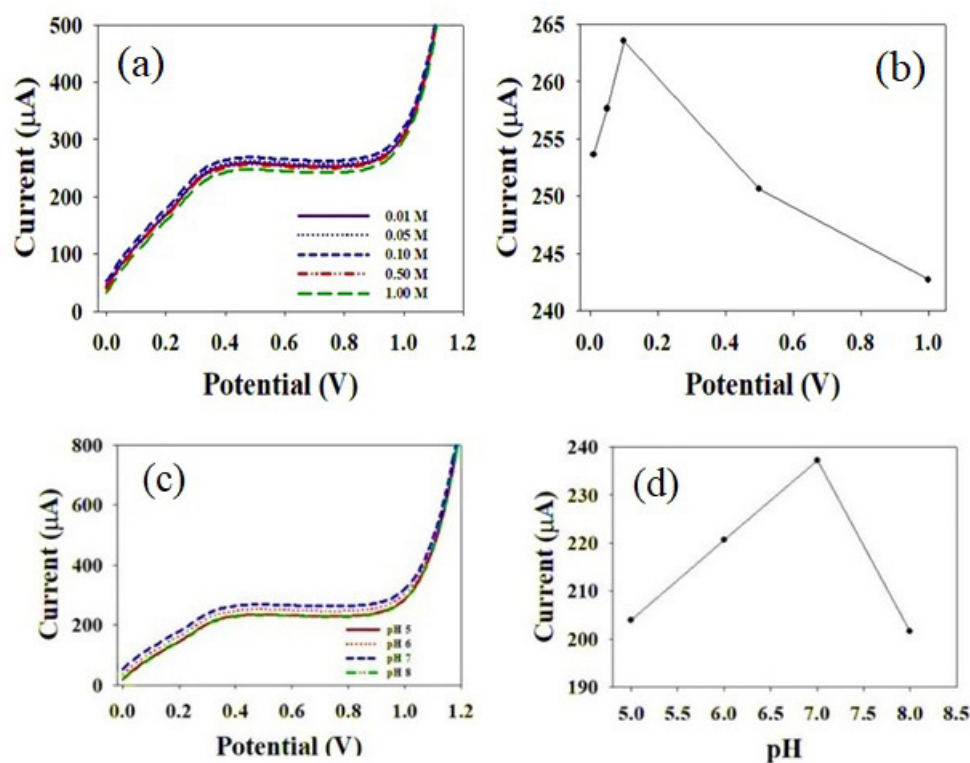


FIGURE 5. (a) Effect of PBS concentration at 0.01, 0.05, 0.1, 0.50, and 1 M on the I-V response of modified ZnONRs/ITO electrode with 1 mM chloroform, (b) linear plot of I-V response and (c) influence of PBS solution at pH 5, 6, 7, and 8 on the I-V response of the modified ZnONRs/ITO electrode with 1 mM chloroform and (d) linear plot of the I-V response

an effective electron mediator and its catalytic potential to induce the oxidation of chloroform.

Additionally, the impact of chloroform addition at regular intervals in 0.1 M of PBS solution at pH 7 on the I-V response of the modified ZnONRs/ITO electrode was examined. As depicted in Figure 8(a), the increment of the chloroform concentration from 10 μM to 1 M resulted in the dramatic increase of the current peak at room temperature conditions. Moreover, the linear current response was detected within the 0.010-10 mM and 0.01-1.0 M chloroform concentration range, where the sensitivity of the modified ZnONRs/ITO electrode was remarkably high at 2.11 μA/cm²·mM and 0.02 μA/cm²·mM, respectively, as expressed by the linear calibration equation in Figure 8(b).

Studies on the sensing performance of undoped metal-oxide to detect chloroform are relatively limited. Thus, the sensing mechanism of the modified ZnONRs/ITO electrode should be interpreted to fully understand

the electrochemical response towards chloroform detection. ZnO and ITO are n-type semiconductors with large bandgaps of 3.2 eV and 4.0 eV, respectively, which indicate that the predominant carriers in the conduction band consist of electrons (Abdulrahman et al. 2021). Figure 9(a) illustrates the energy diagram of the chloroform sensor with respect to the ZnONRs/ITO structure. Since the conduction band of ZnO (4.5 eV) is very near to that of ITO (4.7 eV), the minimal energy difference of 0.2 eV allows the ZnONRs to easily extract and transport the electrons into the ITO conduction band. Eventually, the electrons became prominent in the ITO electrode.

Upon exposure to air or aqueous environment, the surface of the modified ZnONRs/ITO electrode absorbs oxygen molecules and extracts the electrons from the conduction band to generate ionised oxygen species, such as O⁻ and superoxide anion (O₂⁻) (Yi et al. 2019). Subsequently, the concentration of the electron charge

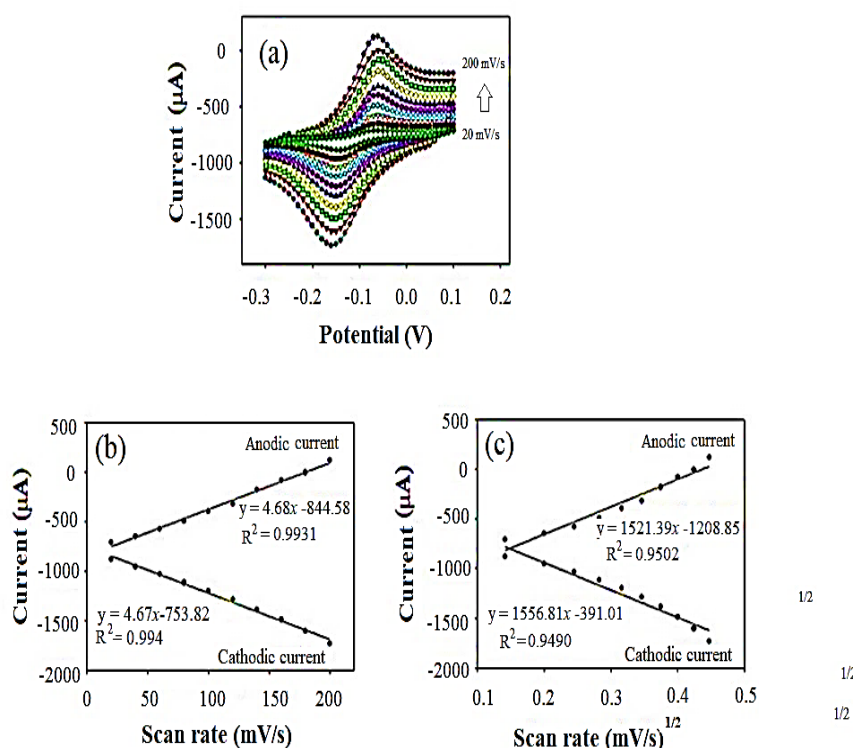


FIGURE 6. (a) CV curve of the modified ZnONRs/ITO electrode at varying scan rates in 0.1 M PBS solution containing 5 mM ferrocyanide, (b) the influence of scan rate on the anodic and cathodic current peaks, and (c) the effect of the square root of the scan rate

carrier becomes reduced and induced the formation of a depletion layer. As a result, the resistance of the ZnONRs/ITO electrode increased. However, the adsorbed oxygen species plays a functioning role in chloroform detection when chloroform was introduced into the system, as shown in Figure 9(b). When the modified ZnONRs/ITO electrode was exposed to chloroform, the adsorbed oxygen species reacts with the electrode before the trapped electrons are released back into the conduction band. Consequently, the concentration of the electron charge carrier increased, which conversely reduced the resistance of the ZnONRs/ITO electrode.

The exceptional sensitivity of the ZnONRs/ITO electrode heterojunctions to chloroform can be attributed to the ZnONRs. The small particle size of the ZnONRs provides a larger surface area for chloroform absorption and additional active sites for catalytic activity. In turn, the enhanced interaction between the adsorbed oxygen ions and the chloroform molecules results in reduced

electrode resistance. Furthermore, the nanorods provide an efficient and direct route for electrons to mobilise throughout the ITO electrode, as evidenced via the I-V analysis. In short, the enlarged surface area of the modified ZnONRs/ITO electrode facilitated impressive chloroform sensing performance.

The selectivity is also a crucial parameter that defines the ability of an aqueous detector to effectively identify a specific target analyte that is present in the aqueous environment and surrounded by multiple foreign analytes. The selectivity of the modified ZnONRs/ITO electrode to detect chloroform was analysed by mixing 1 mM chloroform in a mixture of Volatile Organic Compounds (VOCs) that consists of methanol, ethanol, 1-propanol, acetone, and benzene. Figure 10(a) displays that the modified ZnONRs/ITO electrode demonstrates the highest sensitivity toward chloroform compared to other analytes. Thus, the findings verified the ability of the modified ZnONRs/ITO electrode for chloroform monitoring in real samples.

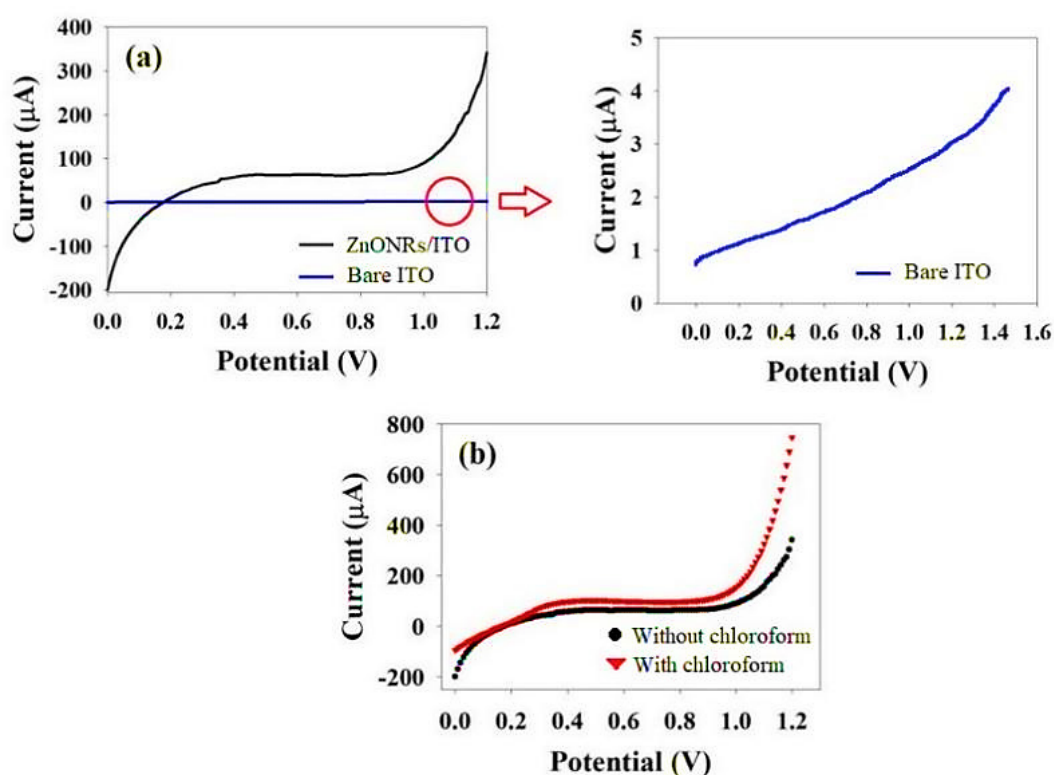


FIGURE 7. Comparison of I-V response curves between (a) the bare ITO and modified ZnONRs/ITO electrodes in 0.1 M PBS solution without chloroform and (b) the measured current using the modified ZnONRs/ITO electrode with and without 1 mM chloroform

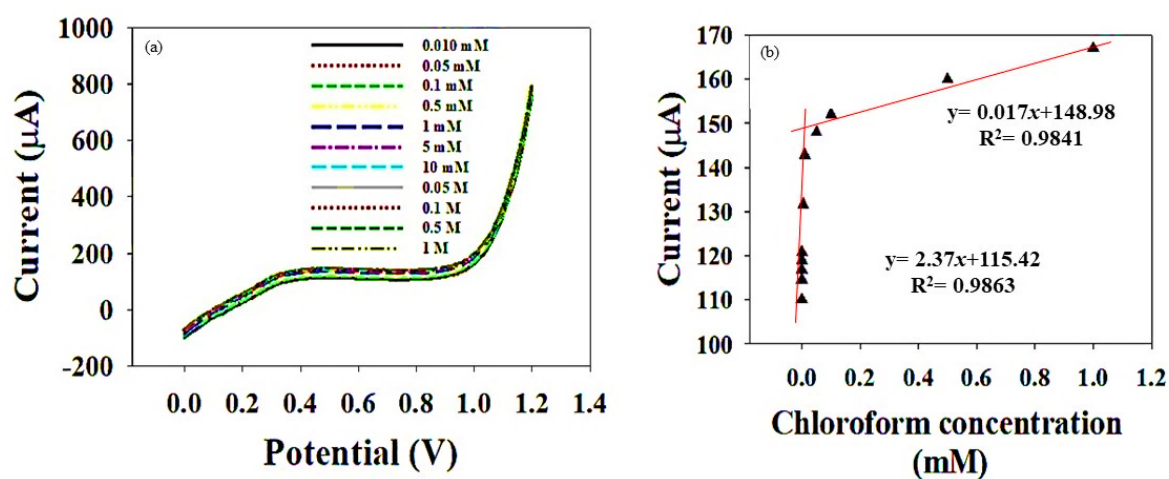


FIGURE 8. The electrochemical behaviour via the I-V response of the modified ZnONRs/ITO electrode at (a) different chloroform concentrations and (b) the linear calibration curve

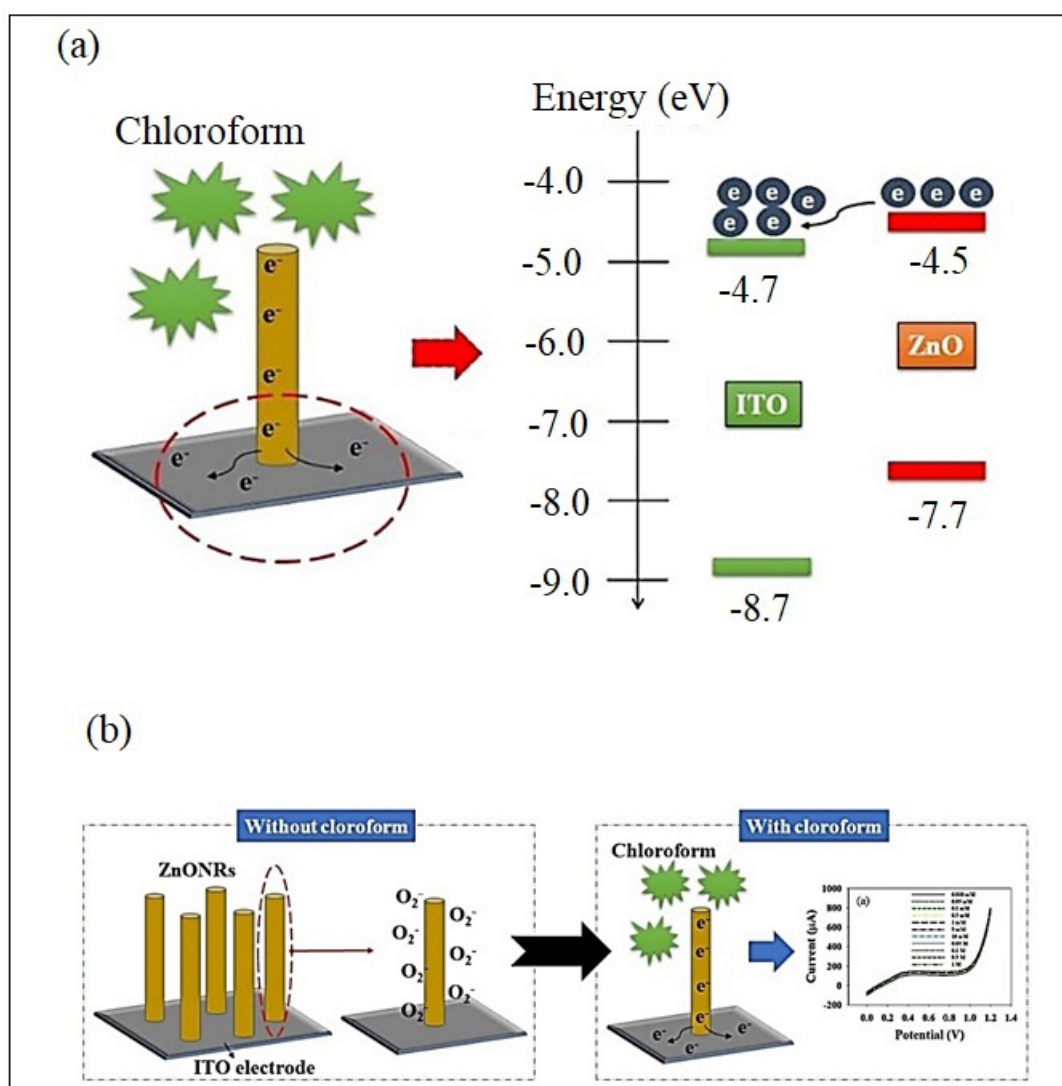


FIGURE 9. Schematic representation of the (a) energy bandgap of the chloroform sensor comprising the undoped modified ZnONRs/ITO electrode and (b) the sensing mechanism of the modified ZnONRs/ITO electrode with and without chloroform

REPEATABILITY AND REPRODUCIBILITY OF THE MODIFIED ZnONRs/ITO ELECTRODE FOR CHLOROFORM SENSING IN REAL SEAWATER SAMPLES

The modified ZnONRs/ITO electrode efficiently detected the presence of chloroform in real seawater samples and ultimately approved the reliability and appropriate outcome of the I-V method. Table 1 presents the overall results within a 0.010-10 mM calibration range.

The fabrication of the modified ZnONRs/ITO electrode requires two vital features comprising

repeatability and reproducibility to ensure that the sensor provides accurate and consistent chloroform measurement. Under optimised PBS conditions (0.1 M, pH 7), the repeatability of a single ZnONRs/ITO electrode for 10 successive measurements recorded a Relative Standard Deviation (RSD) of 1.41%, while the reproducibility assessment achieved an RSD of 2.61% for 5 successive measurements, as depicted in Figure 10(b) and 10(c), respectively. The RSD measures the precision level of the analysed data in percentages. A

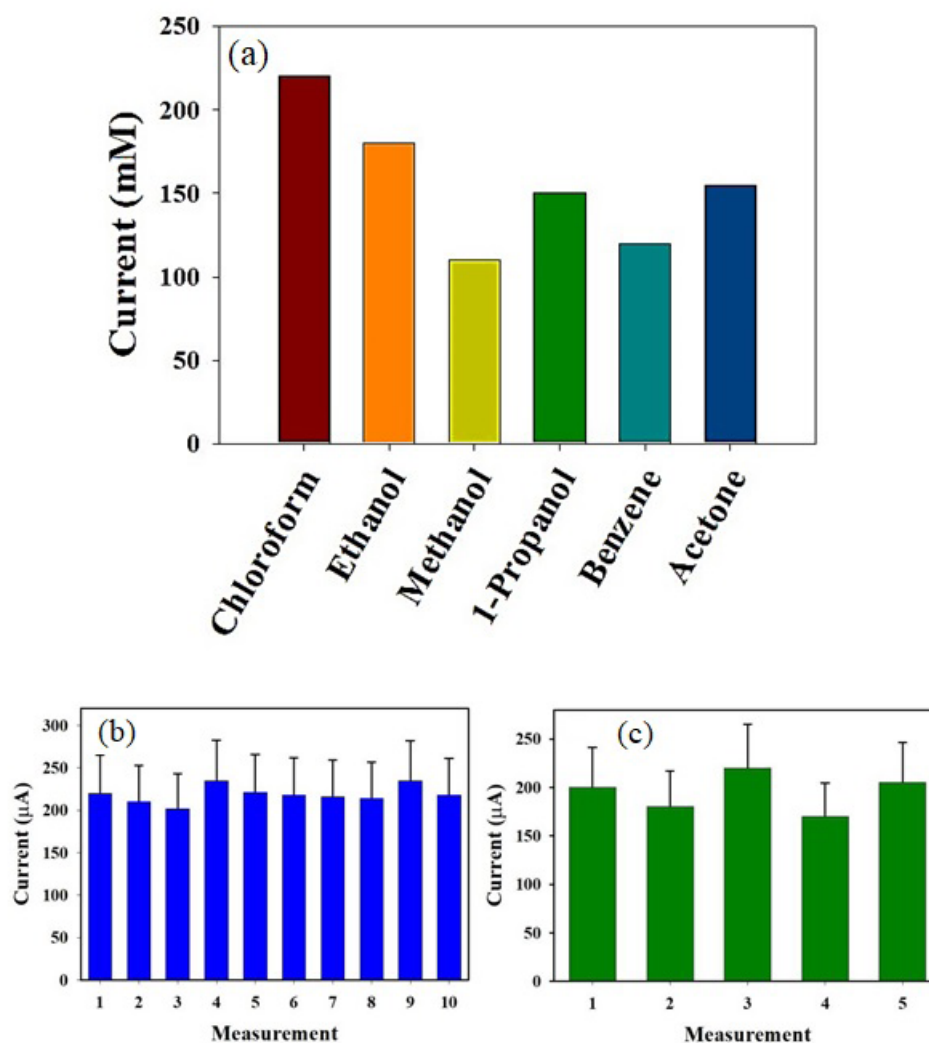


FIGURE 10. (a) Selectivity analysis of the modified ZnONRs/ITO electrode for the detection of 1 mM chloroform mixed with various analytes at +0.4 V and assessment of the (b) repeatability (n = 10) and (c) reproducibility (n = 5) of the modified ZnONRs/ITO electrode under optimal PBS solution conditions with 1 mM chloroform

5% or less RSD value indicates a good performance method and vice versa (Benavides et al. 2021). Based on the obtained results, the low RSD values implied the outstanding repeatability and reproducibility of the modified ZnONRs/ITO electrode, which also reflected the well-dispersed attachment of ZnONRs on the surface of the ITO electrode. Therefore, the compatible matrix of the electrode for nanoparticles decoration through surface modification ensured sufficient stability during the aqueous-phase detection.

The performance of the modified ZnONRs/ITO electrode as a chloroform sensor was comparable to that

of other fabricated metal-oxide electrodes in recently published works, as tabulated in Table 2. The enhanced surface area and excellent electrical conductivity of ZnONRs, which were contributed by the morphology of the ZnONRs directly grown on the electrode substrate, provided an edge over other recently reported electrodes, including a wider linear range and high sensitivity for chloroform detection. As a result, the electrical response of the modified ZnONRs/ITO electrode was significantly improved and can be applied to detect chloroform in VOC sensors as well as in real seawater samples.

TABLE 1. Peak potential and concentration parameters for chloroform sensing in real seawater samples using the modified ZnONRs/ITO electrode

Parameter	Unit	Value
Peak potential	V	+0.4
Concentration	mM	18.2 ± 0.18

TABLE 2. Comparison of chloroform sensors developed using metal-oxide electrodes from past studies

Electrode	Limit of detection	Sensitivity ($\mu\text{A}/\text{cm}^2 \cdot \text{mM}$)	Linear dynamic range	Reference
ZnONRs/ITO	1.50 μM	2.11	0.010–10 mM	This Work
	0.14 mM	0.015	0.01–1.0 M	
NiO/MWCNT NPs /GCE	0.1034 nM	917.7	3.5 nM–0.35 mM	[42]
CuONSs/AgE	0.08 mM	1.497	0.13 mM–0.66 M	[43]
$\beta\text{-Fe}_2\text{O}_3\text{NPs}/\text{GCE}$	4.4 μM	2.179	12 μM –12 mM	[44]
ZnONCs	6.67 μM	0.478	12 μM –12 mM	[45]

CONCLUSIONS

This study successfully demonstrated the fabrication of modified ZnONRs/ITO electrodes for chloroform sensing applications. Under optimal PBS solution conditions of 0.1 M at pH 7, the modified ZnONRs/ITO electrode showed unique surface characteristics, including the well-dispersed growth of ZnONRs on the surface of the ITO electrode and hydrophilic behaviour, as indicated by the WCA value of 66.39°. Furthermore, the modified ZnONRs/ITO electrode exhibited exceptional chloroform detection based on the electrochemical performance, where the electrode recorded high sensitivity of up to 2.11 $\mu\text{A}/\text{cm}^2 \cdot \text{mM}$ and 0.14 $\mu\text{A}/\text{cm}^2 \cdot \text{mM}$ within the 0.010-10 mM and 0.01-1.0 M linear response range, respectively. When applied in real seawater samples, the modified electrode achieved reliable repeatability and reproducibility of 1.41% ($n = 10$) and 2.61% ($n = 5$), respectively, while the limit of detection was 1.5 μM .

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