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ZnO Nanorods Prepared by Hydrothermal Method as a Nanosensor for Methanol Detection

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ABSTRACT: *Methanol which exerts negative influences on human health is widely found in industrial products. Metal oxides are well-studied for methanol detection but limited knowledge is available for zinc oxide (ZnO). In this study, ZnO nanorods (ZnONRs) were produced hydrothermally at a low temperature (80°C) with the aid of a ZnO seeds layer to create an electrode for methanol detection. The nanorods ranged from 62 nm to 90 nm in diameter. The nanorods aggregated in aligned patterns on the indium tin oxide (ITO) substrate. The resulting ZnONRs/ITO electrode showed a progressive positive response to methanol in increasing concentrations of 0.1 mM−5.0 M. The ZnONRs/ITO electrode exhibited a remarkable 0.30 $\mu AmM^{-1}cm^{-2}$ sensitivity with a 0.42 mM detection limit and a linear correlation coefficient (R^2) of 0.9327. The results thus proved the potential of ZnONRs/ITO electrode as a highly sensitive methanol sensor in an aqueous solution.*

Keywords: ZnO nanorods, hydrothermal, methanol, current voltage technique, sensitivity

1. INTRODUCTION

Environmental management authorities have expressed growing concern regarding the prevalence of volatile organic compounds (VOCs) in the environment. Industrial solvents such as acetone, formaldehyde, toluene, methanol, ethanol and acetone are hazardous VOCs that have raised growing concerns.[1] These compounds are widely used in various industrial and product manufacturing processes, causing their release into the environment. Methanol, also known as methyl alcohol or wood alcohol, is a colourless, flammable and volatile liquid with a faint alcoholic odour that serves as a vital industrial chemical and fuel source.[2,3]

Methanol can be found in various products such as paints, glues, adhesives, varnishes and cleaning solutions. It is widely used in solvent production, fuel blending, formaldehyde synthesis and as a raw material for chemical and material production. Methanol is miscible with water, alcohol and most organic solvents. Nevertheless, methanol has a broad detrimental effect on humans, including irritation of the eyes, skin and respiratory tract, as well as the potential to cause birth defects in the central nervous system.[4] The development of a simple and reliable methanol sensor is essential to rule out consumers' exposure to methanol. Semiconducting metal oxide sensors are widely used for detecting and monitoring the presence of pollutants in the environment. These sensors are based on the principle of electrical conductivity changes that occur when certain metal oxide materials come into contact with specific target pollutants.[5] Their simple construction, minimal production cost, practical application robustness and adaptability to a broad variety of hazardous analytes make them the most promising choice for sensing applications. The majority of research has been focused on iron oxide (Fe_2O_3), tin oxide (SnO_2), titanium oxide (TiO_2) and tungsten oxide (WO_3).[6–8]

Among metal oxides, zinc oxide (ZnO) is a highly versatile semiconducting metal oxide that finds applications in various fields such as optics, electronics, electromagnetic shielding, catalysis and chemical sensing.[9] Its exceptional chemical stability, cost-effectiveness, low toxicity and resilience in practical applications make it particularly attractive for chemical sensing purposes. In addition, ZnO is a n-type semiconducting with a wide bandgap of 3.37 eV.[10,11] This bandgap enables it to efficiently interact with target gases, including VOCs. In recent years, various nanostructures of ZnO, such as nanorods, nanoparticles, nanosheets and nanowires, have been extensively studied and demonstrated to possess high sensitivity and selectivity towards VOCs.[12] Rahman et al., fabricated a methanol sensor using a hybrid silver oxide (Ag_2O_3)-doped zinc

oxide nanoparticle (ZnONPs) and undoped Ag_2O_3NPs, which acted as efficient mediators to detect methanol using I-V method.[13,14] In another study, Faisal et al., developed undoped ZnONPs and they found that the electrode was sensitive to the methanol in aqueous solution.[15] However, the fabricated electrodes were aggregated with nanoparticles and time consuming.

Among the different ZnO nanostructures, ZnO nanorods (ZnONRs) have gained attention due to their extensive utilisation in sensing applications.[16] This is attributed to their large active surface area, non-toxic nature, chemical stability and high conductivity, which facilitate direct electron transfer to the target molecules. Hydrothermal methods, sputtering and pulse vapour deposition are the common techniques to fabricate ZnONRs.

Among these methods, hydrothermal methods offer advantages such as being cost-effective, compatible with various substrates, environmentally friendly and allowing for precise control over nanorod properties.[17] Furthermore, this method provides aqueous-based processes with high affordability, versatility and a controlled growth environment, thus is an attractive choice for large-scale production of high-quality ZnONRs for chemical sensing applications.[18] On the other hand, sputtering can be expensive and may result in non-uniform film deposition due to uneven target erosion, while pulse vapour deposition exhibits a slower deposition rate. Despite the great potential of ZnONRs, there is limited knowledge available regarding methanol detection in aqueous solutions using simple and reliable current-voltage (I-V) techniques that incorporate redox reactions with ZnONRs.

In our study, we demonstrated the successful synthesis of ZnONRs using a hydrothermal technique at a low temperature. The current response resulting from methanol oxidation in an alkaline medium, where ZnONRs exhibited excellent electrocatalytic activity was measured. Our findings provide valuable insights into the potential application of ZnONRs as sensitive methanol sensors in aqueous solutions. The originality of this study is in the quantitative analysis of the aligned ZnONRs in terms of linear dynamic range, sensitivity, detection limit and methanol detection capability in aqueous solution utilising the I-V method. ZnONR serves as an electrode modification on indium tin oxide (ITO) electrode, speeding up charge transfer and enhancing absorption capacity towards methanol to enhance catalytic activity for detection efficiency.

2. MATERIALS AND METHODS

2.1 Preparation of ITO Substrate

In this study, ITO electrodes were utilised as substrates to grow ZnONRs. The ITO substrates were prepared by cutting them into 2 cm × 1 cm squares. To ensure proper growth of ZnONRs, the ITO substrates were subjected to a series of pre-treatment steps. Firstly, they were soaked in a 1:4:20 mixture of ammonium hydroxide, hydrogen peroxide and distilled water for 20 min. Subsequently, the substrates were heated at 60°C. Afterward, the ITO electrodes were cleaned using distilled water and submerged in 2-propanol before being oven-dried.

2.2 Synthesis of ZnO Seed Solution

The synthesis of ZnO seeds for ZnONRs growth was carried out using the sol-gel method. Zinc acetate dihydrate was dissolved in 15 mL of methanol and rapidly stirred for 20 min at 60°C. Then, 15 mL of ethanolamine solution was added to the mixture, which was continuously agitated for 2 h at 65°C. This mixture was kept at room temperature for 24 h.[19] The resulting solution containing ZnO seeds was drop-casted onto the ITO substrates, and this procedure was repeated three times. The coated ITO electrodes were annealed in a 500°C furnace for 2 h during annealing process.

2.3 Hydrothermal Method for ZnONRs Growth

The ZnONRs/ITO electrodes were further treated hydrothermally to enhance their properties. They were immersed in a solution containing 0.1 M zinc nitrate [$Zn(NO_3)_2$] and hexamethylenetetramine (HMT) in deionised water. The hydrothermal treatment was carried out in a screw-capped container for 4 h at low temperature of 80°C. After the treatment, the electrodes were washed with distilled water and dried in an oven for 30 min. The morphology and structure of ZnONRs/ITO electrodes were investigated using field emission scanning electron microscopy (FESEM) (Germany) and X-ray diffraction (XRD) (Germany). The elemental composition and purity of the synthesised ZnONRs/ITO electrodes were analysed using energy-dispersive X-ray spectroscopy (EDX) (Germany). The wettability of the surface samples was measured with a contact angle goniometer (Finland). All measurements were carried out for 30 s after the water droplet was positioned to ensure a consistent contact angle. The resulting ZnONRs/ITO electrodes were then utilised as the working electrodes for methanol sensing. A schematic representation of the entire procedure can be found in Figure 1.

2.4 Detection of Methanol Using the I-V Method

A methanol sensor based on the ZnONRs/ITO electrode was developed for the detection of methanol in an aqueous solution. A three-electrode system and electrochemical methods were employed for this purpose. Throughout the experiment, a 0.5 M phosphate-buffered saline (PBS) solution with a constant volume of 25 mL was used as the electrolyte. To obtain a I-V curve of methanol, the solution was prepared with various concentrations of methanol analyte ranging from 0.10 mM to 0.70 mM. The current response of the ZnONRs/ITO electrodes to different methanol concentrations was measured.

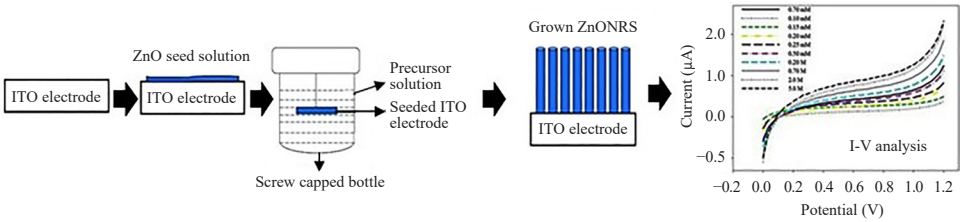


Figure 1: Schematic diagram of ZnONRs/ITO electrode fabrication using the hydrothermal method.

3. RESULTS AND DISCUSSION

The contact angle is a key parameter that provides information about the interaction between a solid surface and a liquid, typically water. The contact angle represents the degree of wetness or the ability of the liquid to spread on the solid surface.[20] The ZnONRs/ITO electrode displayed a hydrophilic behaviour (water contact angle < 90°) with a static water contact angle of 62°. In comparison, the bare ITO electrode exhibited a higher static water contact angle of 73° (see Figure 2). The hydrophilic properties of the ZnONRs/ITO electrode can be attributed to its fabrication in an aqueous solution at a low temperature. This process generated thermally stable hydroxyl groups (-OH) within a temperature range of 50°C to 400°C on the surface, which contributed to its enhanced hydrophilicity.[21] As high wettability is usually associated with a short contact angle, both ZnONRs/ITO and ITO electrodes displayed high wettability, with the ZnONRs/ITO electrode having higher wettability.

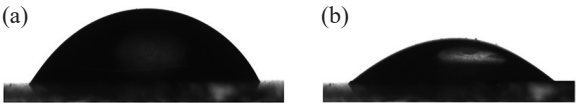


Figure 2: Static contact angle of (a) ITO and (b) ZnONRs/ITO electrodes.

The well-defined hexagonal ZnONRs arrays grown on the ITO substrate showed a uniform diameter along their entire length. The ZnONRs were vertically oriented, exhibiting a small diameter and a high-density distribution across the entire substrate surface. The diameter of the ZnONRs ranged from 62 nm to 90 nm, indicating the successful synthesis of nanorods with controlled dimensions at 100,000X magnification (see Figure 3). Inset image shows the growth of ZnONRs in perpendicular on the ITO electrode. The growth length of the ZnONRs on the electrode measures approximately 1.74 ± 0.002 µm, as depicted in Figure 3(b). This fabrication process has proven effective to produce well-structured ZnONRs arrays on the ITO substrate to assure good crystallinity and alignment for various applications, such as sensing, catalysis and optoelectronics.

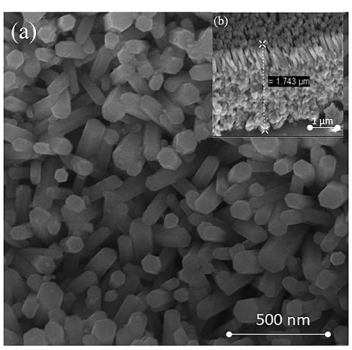


Figure 3: (a) FESEM image of hexagonal ZnONRs and (b) The inset image is the cross-section image of ZnONRs grown on ITO electrode.

The discernible peaks in the XRD pattern correspond to the hexagonal ZnO, and their positions can be matched with the lattice constant values of a = 3.25 Å and c = 5.21 Å. These peaks also corresponding to the ICDD 79-2205.[19] The peaks observed at [010], [002] and [011] in the ZnONRs/ITO electrode align with the nanorod morphology, validating the presence of nanorods on the ZnO/ITO electrode. This concurrence supports the indication of preferential growth on the basal plane, as evidenced by the FESEM images. The samples consisted solely of the pure hexagonal ZnO phase due to the absence of a peak representing Zn (see Figure 4).

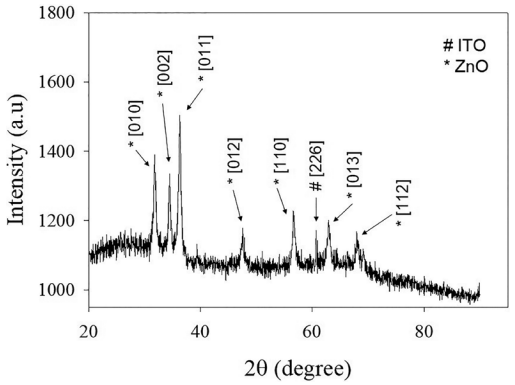
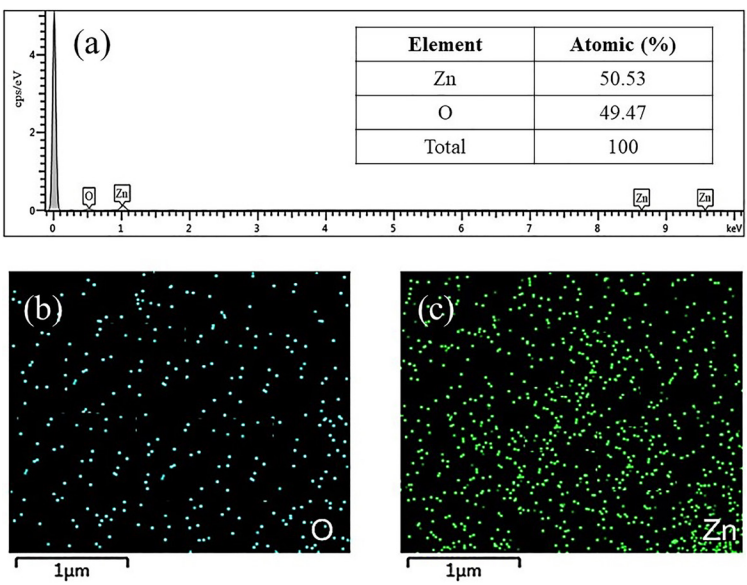


Figure 4: XRD spectrum of the ZnO nanorods.

The ZnONRs/ITO electrode consisted of Zn and O in equal proportions (1:1 ratio) as shown in Figure 5(a). This composition matched the stoichiometric formula of ZnO, suggesting the presence of a well-balanced combination of O and Zn atoms in the material as depicted in Figure 5(b) and (c), respectively. The elements such as indium and tin were missing in EDX results due to they are present in as electrode and beneath the surface being analysed, their signals may not be strong enough to be detected. Moreover, EDX is more sensitive to elements present on or near the surface of the electrode.



Element	Atomic (%)
Zn	50.53
O	49.47
Total	100

Figure 5: (a) Energy dispersive X-ray and (b)-(c) elemental mapping of ZnONRs/ITO electrode.

The current response of the ZnONRs/ITO electrode in a 0.5 M PBS solution was investigated to study its electrochemical behaviour towards methanol in an aqueous environment. As the target methanol is introduced into the solution, a drastic change in surface current is observed, indicating the electrochemical reaction occurring at the electrode interface [see Figure 6(a)]. To create a concentration gradient, the cell was initially filled with 25.0 mL of 0.5 M PBS solution, followed by the gradual addition of methanol in different concentrations from a stock solution, drop by drop. The concentration gradient enabled the construction of a current-voltage curve to evaluate the sensitivity and detection limits of the ZnONRs/ITO electrode towards methanol in aqueous solutions.

The current response of the ZnONRs/ITO electrode exhibited an increasing trend as the concentration of the target methanol increases from 0.1 mM to 5.0 M at room temperature [see Figure 6(b)]. This observation suggests the presence of active sites on the electrode surface, which interacted with methanol molecules and thus contributed to the amplified current response with increasing analyte concentrations. The sensitivity of the electrode, determined from the slope of the calibration curve of the current response at a fixed electric potential of +0.5 V, was estimated to be 0.30 $\mu A\ mM^{-1}cm^{-2}$. This value indicates the extent to which the current output of the electrode changed per unit change in methanol concentration. The ZnONRs/ITO electrode exhibited a linear dynamic range spanning from 10 mM to 5 M, indicating a consistent and direct proportional response of the electrode to varying methanol concentrations [see Figure 6(c)]. The high linear correlation coefficient of 0.9327 supports the linear relationship between the measured current and methanol concentration besides emphasising the electrode's accuracy in reflecting changes in methanol concentration. The electrode demonstrated a low detection limit of 0.42 mM, highlighting its exceptional sensitivity to detect even a trace amount of methanol. Upon exposure to air or liquid, the ZnONRs/ITO electrode underwent a process wherein oxygen molecules are adsorbed onto its surfaces, resulting in ionisation.[22] This ionisation occurred through the capture of electrons from the conduction band, leading to the formation of O^- or O^{2-} ions.[23] The occurrence of these reactions at the interface of air or liquid can be attributed to the low carrier concentration, which subsequently increased the resistance of the sensors. As the electron concentration that served as the charge carrier, decreased, a depletion layer emerged, increasing the resistance of the ZnONRs/ITO electrode.[24] Nevertheless, the introduction of methanol into the system caused the methanol molecules to react with the adsorbed oxygen species on the surface of the ZnONRs/ITO electrode (see Figure 7). The presence of adsorbed oxygen species was crucial for methanol sensing as the electrode interacted with the absorbed oxygen species upon exposure to methanol, resulting in the release of trapped electrons back into the conduction band.

The trapped electrons were liberated back into the conduction band, resulting in an increased electron concentration and a subsequent decrease in the resistance of the ZnONRs/ITO electrode. The conductivity of the ZnONRs/ITO electrode increased and the remarkable sensitivity of the ZnONRs/ITO electrode towards methanol was showcased. The analytical parameters of the fabricated sensor are presented in Table 1 as a comparison to other related works.

Table 1: Comparative investigations of analytical performance in methanol sensing based on various hybrid or composite nanomaterials.

Electrode	Sensitivity ($\mu Acm^{-2}\ mM^{-1}$)	Limit of detection	Linear dynamic range	Method	Ref
Ag_2O_3-ZnONPs/μ-chip	7.917	71 μM	0.25 μM–0.25 M	I-V	13
ZnONPs/GCE	0.9554	0.11 mM	0.25 mM–1.8 M	I-V	15
Ag_2ONPs/GCE	2.65	36.0 μM	0.12 mM–1.2 M	I-V	14
ZnONRs/ITO	0.3	0.42 mM	10 mM–5 M	I-V	This work

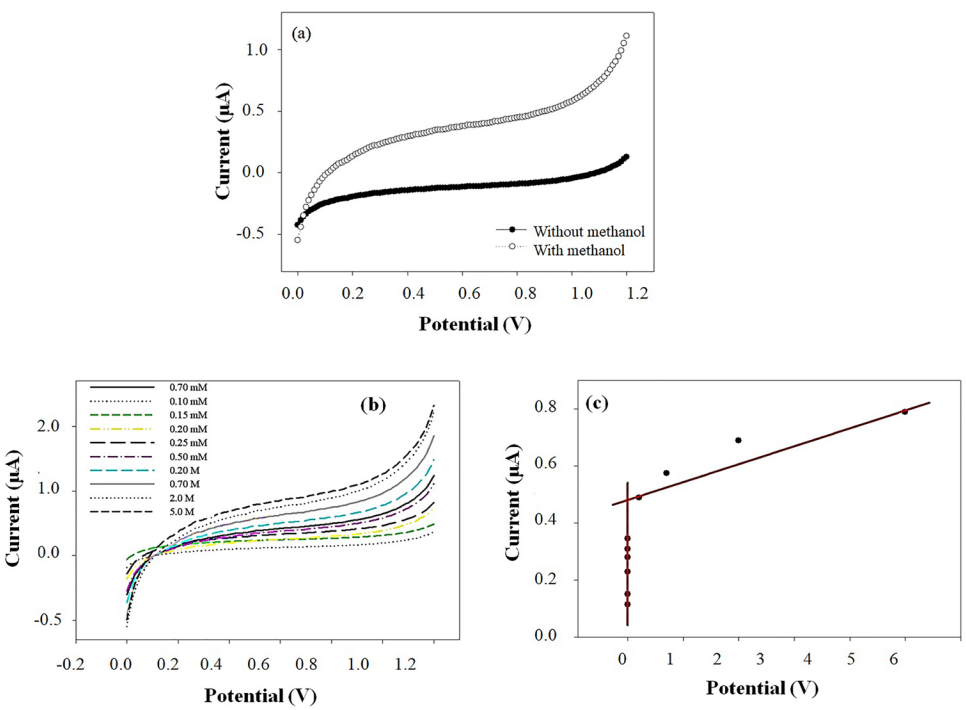


Figure 6: Current-voltage (I-V) responses of ZnONRs/ITO electrode (a) with and without methanol, (b) in increasing methanol concentration in 0.5 M PBS solution and (c) on a calibration plot at +0.5 V.

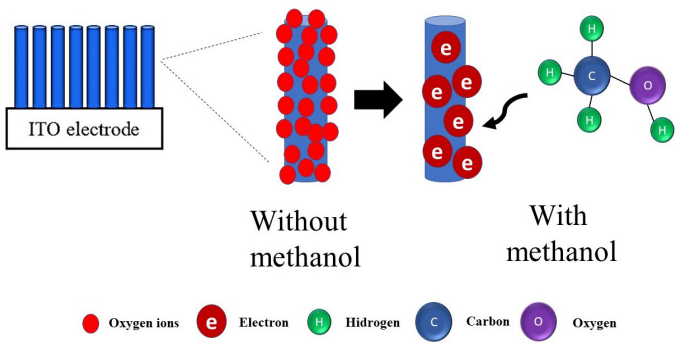


Figure 7: Sensing mechanism of ZnONRs/ITO electrode with and without methanol at room temperature.

4. CONCLUSIONS

In conclusion, ZnONRs/ITO electrodes were successfully prepared by a simple hydrothermal method at a low temperature. The fabricated ZnONRs exhibited a well-defined crystalline structure of wurtzite hexagonal phase with average diameters of 62 nm to 90 nm, showed excellent 0.30 $\mu AmM^{-1}cm^{-2}$ sensitivity with the 0.42 mM detection limit towards methanol and a linear correlation coefficient (R^2) of 0.9327. The ZnONRs/ITO electrode showed great potential as a highly sensitive methanol sensor for environmental sensing.

5. ACKNOWLEDGEMENTS

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