



Electrochemical Nitrate Sensor Based on TiO₂-PVB Bilayer Composite Thin Film

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Abstract

A high level of nitrate (NO_3^-) ions from over-fertilization may affect plant growth and potentially harmful pollutant in drinking water. Thus, various materials used as sensing electrodes have been explored to detect these ions. In this study, a bilayer composite titanium dioxide-polyvinyl butyral (TiO₂-PVB) thin film could detect nitrate ions using an extended gate field-effect transistor (EGFET) method. The bilayer composite was deposited on indium tin oxide (ITO) coated substrate using a simpler sol-gel spin-coating method. The device showed sensitivity and linearity of 41.8 mV/dec and 0.6419 in the range of 10 to 100 ppm. In comparison to TiO₂ thin film which showed a sensitivity and linearity of 21.2 mV/dec and 0.6282. The addition of PVB thin film on top of the TiO₂ thin film did improve the nitrate sensing behavior. The surface morphology of both sensing electrodes was characterized using field-emission scanning electron microscopy (FESEM). Agglomerated particles were observed on the bilayer composite thin films, in contrast to the TiO₂ thin film which showed a smooth surface structure. The contact angle measurement was done between the droplet and the surface of the sensing electrode. The contact angle results supported the nitrate sensing performance of TiO₂-PVB bilayer composite thin film with 93.5° and showed a hydrophobic property, whereas the TiO₂ thin film showed hydrophilic property with 87.2°.

Keywords: Polyvinyl butyral, Titanium dioxide, Bilayer composite, EGFET nitrate sensor, Spin-coating

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1. Introduction

Nitrate is one of the nutrients in fertilizer needed for plant growth. However, over-fertilization may give an effect on the environment if it is applied in excess. For example, high level of nitrate ions may lead to the overgrowth of algae causing an oxygen depletion that is harmful for aquatic environment and may lead to water contamination and water-borne diseases [1-5]. Therefore, it is necessary to detect and monitor the nitrate levels. An electrochemical sensor is one of the methods that can be used to detect nitrate ions [6]. Commonly, electrochemical techniques for nitrate detection can be classified as voltammetry, amperometry, and potentiometry [7]. The difference between these techniques depends on the potential is applied. For example, potentiometric sensors consist of a reference electrode (RE) and sensing electrode

(SE) in which the result obtained from the potential difference between RE and SE immersed in a solution using the Nernstian relation. Besides, potentiometry is one of the electrochemical techniques that is easily adaptable for nitrate detection, particularly in complicated sample matrices like soil [7]. An ideal potentiometric sensor for a monovalent anion, such as NO_3^- at room temperature is expected to exhibit a -59.1 mV change for every factor of ten increase in NO_3^- concentration [2]. An extended gate field-effect transistor (EGFET) is one of the techniques in potentiometry method that offers a low cost, easy fabrication and insensitive to the light and temperature. Due to these advantages, the nitrate detection of the prepared sensing electrodes in this work was studied using the EGFET method.

There are several nanomaterials including metals, metal oxide, conductive polymers and carbon nanomaterials such as graphene have been studied as a modification of the electrode surface to improve the detection performance of nitrate [8-15]. Recently, several studies have shown that the metal oxides have the ability to be used as sensing electrodes such as zinc oxide (ZnO) and cobalt oxide (Co₃O₄) and copper oxide (CuO). For example, Bhargavi et al. have reported the use ZnO nanoparticles to determine the nitrate ion using cyclic voltametric sensor [10]. The device showed a linear response to nitrate ions over a concentration range from 0.1 to 2.0 mM with a low detection limit and high sensitivity of 10 nM and 39.91 $\mu\text{A}/\text{cm}^2 \text{mM}$, respectively. Another study done by Nguyen et al. have shown that the cobalt oxide nanoparticles (Co₃O₄ NPs) exhibited a Nernstian slope of -56.78 mV/decade for NO_3^- detection with a wide range of 10^{-7} – 10^{-2} M and a quick response time of 5.7 s [16]. So far, TiO₂ alone have not been reported as sensing electrode and have been commonly employed for nitrate detection by composite with other materials to improve device performance. For instance, Azahar et al. have reported on the graphene foam-based electrode modified by TiO₂ nanofiber [17]. The sensor showed sensitivity of $0.316 \text{ k}\Omega/\mu\text{M}/\text{cm}^2$, fast detection time ($\sim 87\text{s}$), and a high selectivity to nitrate ions even in presence of many interfering ions in the soil. Researchers have recently become interested in Ti-based electrodes because to their excellent efficiency and stability under extreme electrochemical conditions. Poly-pyrrole (PPy), polyaniline (PANI) and poly (3-octylthio-phene-2,5-diyl) (POT) are some of the conductive polymers that have been used for nitrate detection. Hashim et al. have shown the ability of Polyvinyl butyral (PVB) thin film as sensing electrode [6]. The thin film was deposited on ITO coated substrate using the sol-gel spin-coating method and tested at different nitrate concentrations of 0, 50 and 100 ppm. The device exhibited sensitivity and linearity of -40.9 mV/dec , 0.99936 which proved that this polymer also can be used as sensing electrode. Study on metal-oxide based sensor is still lacking for EGFET nitrate sensor. Thus, in this work, the TiO₂ and TiO₂-PVB bilayer composite thin film were employed as sensing electrodes for nitrate detection using EGFET method. The polymeric material, which is PVB was modified to the sensing electrode of TiO₂ thin film. The findings showed the bilayer composite has potential to be employed as sensing electrode for nitrate detection.

2. Materials and methods

In this work, a commercialized indium tin oxide (ITO) (size: $20 \times 20 \times 1.1 \text{ mm}$ (length \times width \times height) with a sheet resistance of $7\text{--}10 \Omega/\text{sq}$ was used as a substrate. Prior to the cleaning process, the ITO substrate was cleaned in methanol using an ultrasonic bath for 10 min. The same process was repeated using deionized (DI) water. The bilayer composite thin film was formed with Polyvinyl Butyral (PVB; Sigma Aldrich) on top of the TiO₂ thin film. **Figure 1** showed the cross-section of the prepared sensing electrodes used in this work. The TiO₂ solution was prepared using titanium isopropoxide (Ti [OCH(CH₃)₂]₄) (TTIP; 97%; Sigma Aldrich, Merck), glacial acetic acid (GAA; 98%; Friedemann Schmidt), triton X-100 (98%; R&M Chemicals) and ethanol absolute (99.8%; SYSTERM). The solution was stirred for 1 hour at room temperature.

The film was then deposited on the substrate with a spin speed of 3000 rpm for the 60s. Ten drops of the TiO₂ solution were dropped during the deposition process. The films were then dried in ambient air for 100 °C for 10 min before being annealed at 400 °C for 15 min. The PVB solution was prepared by dissolving PVB powder in a solution of ethanol and DI water with a ratio of 8:2. The PVB solution was deposited on top of TiO₂ thin film with a spin speed of 3000 rpm for the 60s. Lastly, the thin films were dried at 100 °C for 10 min. **Figure 2** shows the EGFET measurement setup used in this work. The nitrate detection was performed in the range of 10, 30, 50, 70, and 100 ppm using a serial dilution of the nitrate standard solutions nitrate nitrogen ($\text{NO}_3^- - \text{N}$) (Thermo Fisher Scientific; 100 ppm). The sensing electrode was connected to the gate of a commercialized MOSFET (CD4007UBE) using copper (Cu) wire as shown in the inset image in **Figure 2**. The Cu wire was placed on a bare ITO surface using silver paste and packaged with epoxy resin.

3. Results and Discussions

3.1. Nitrate Detection

Figure 3 represents the output voltage versus logarithmic nitrate concentration of TiO₂ and TiO₂ bilayer-composite thin films. The TiO₂-PVB bilayer composite thin film (**Figure 3 (b)**) shows better sensitivity behavior with 41.8 mV/dec and linearity of 0.6419 compared to the TiO₂ thin film. Meanwhile, the TiO₂ thin film showed sensitivity and linearity of 21.2 mV/dec and 0.6282. It can be seen that the addition of PVB thin film did improve both sensitivity and linearity values but still, further study needs to be done to achieve the Nernst equation. The potential difference between RE and SE immersed in a solution is correlated to ion concentration or ion activity achieved by Nernst Equation. The potentiometric sensors can be obtained by the slope of the linear regression as shown in Equation 1.

$$E = E^0 = 0.0592 V \log \frac{Q}{n} \quad (1)$$

Where E, E⁰, n, and Q are cell potential, standard cell potential, number of electrons, and reaction quotient, respectively. These findings suggested that the modification of the sensing electrode with PVB thin film did improve the nitrate sensing performance due to the presence of C = O sites in conducting polymer, PVB to sense the nitrate ions. This study was supported by Hashim et al., where they found that the sensing behavior of PVB thin film was better compared to the polyvinylpyrrolidone (PVP) thin film. The characteristics of PVB with the formula (C₈H₁₄O₂) include a functional group that contains oxygen which can be an excellent immobilization material for nano-functional components with fixing on sensor interface [6].

3.2. Morphological Characterization

The surface morphology of the thin films was characterized using field-emission scanning electron microscopy (FESEM) (JEOL JSM-7600F) with an operating voltage of 5 keV and a magnification of 10 k. **Figure 4** shows the surface morphology of TiO₂ and TiO₂-PVB bilayer composite thin film. The TiO₂ thin films showed a smooth surface morphology as shown in **Figure 4 (a)**.

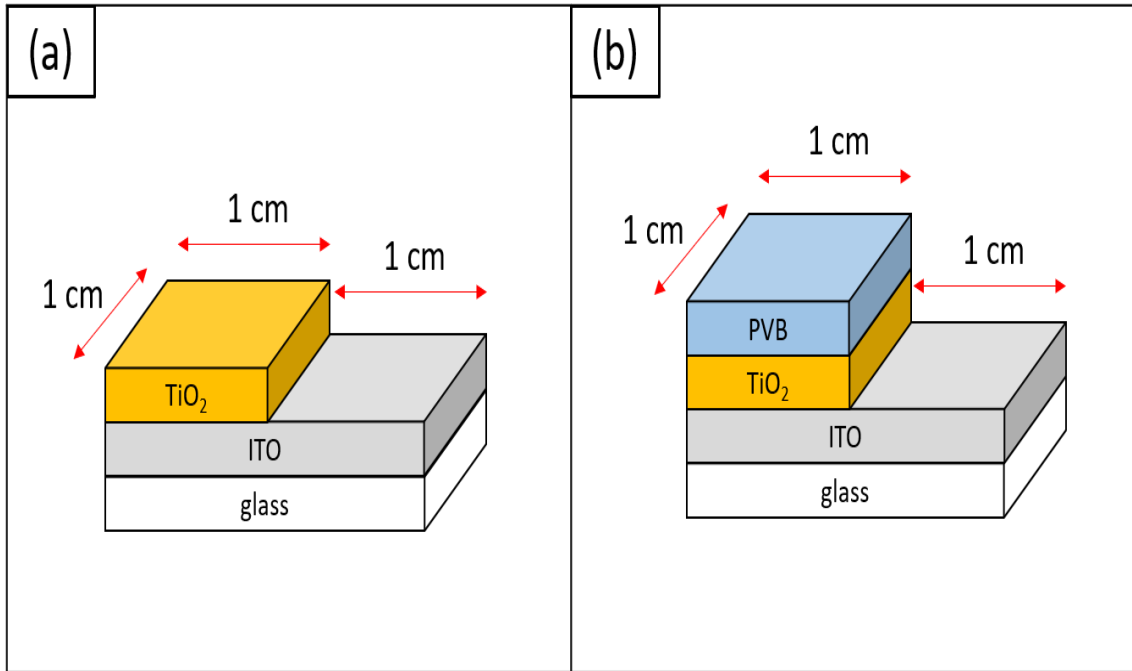


Figure 1. Cross-section of (a) $\text{TiO}_2/\text{ITO}/\text{glass}$ and (b) $\text{PVB}/\text{TiO}_2/\text{ITO}/\text{glass}$

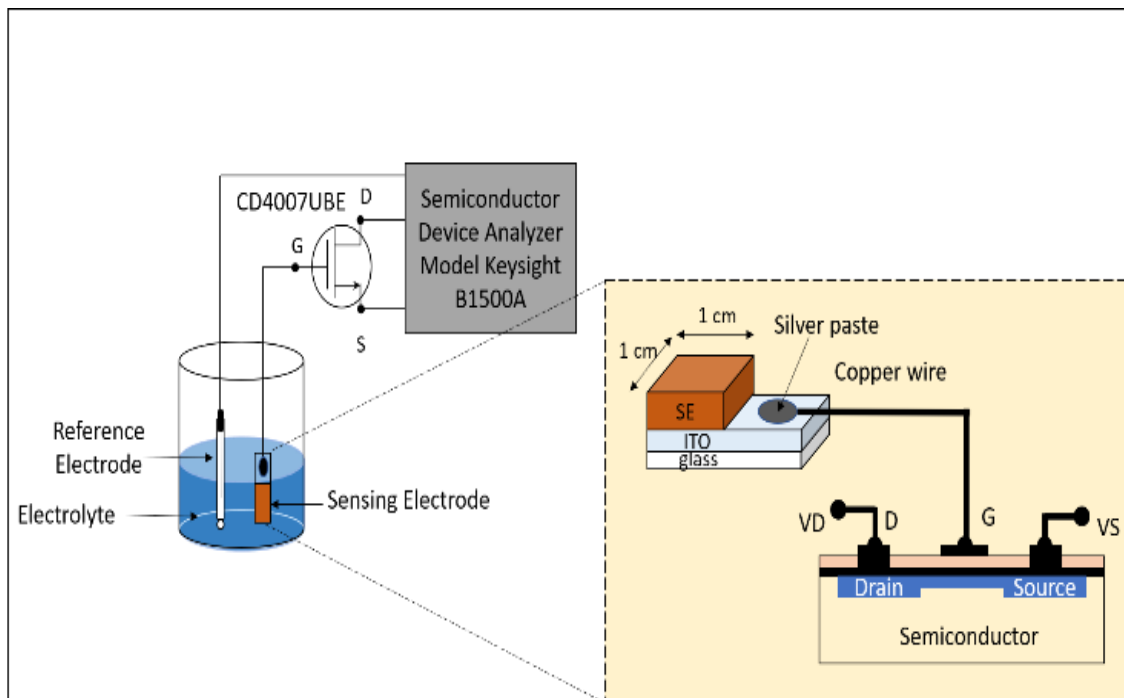


Figure 2. EGFET measurement setup

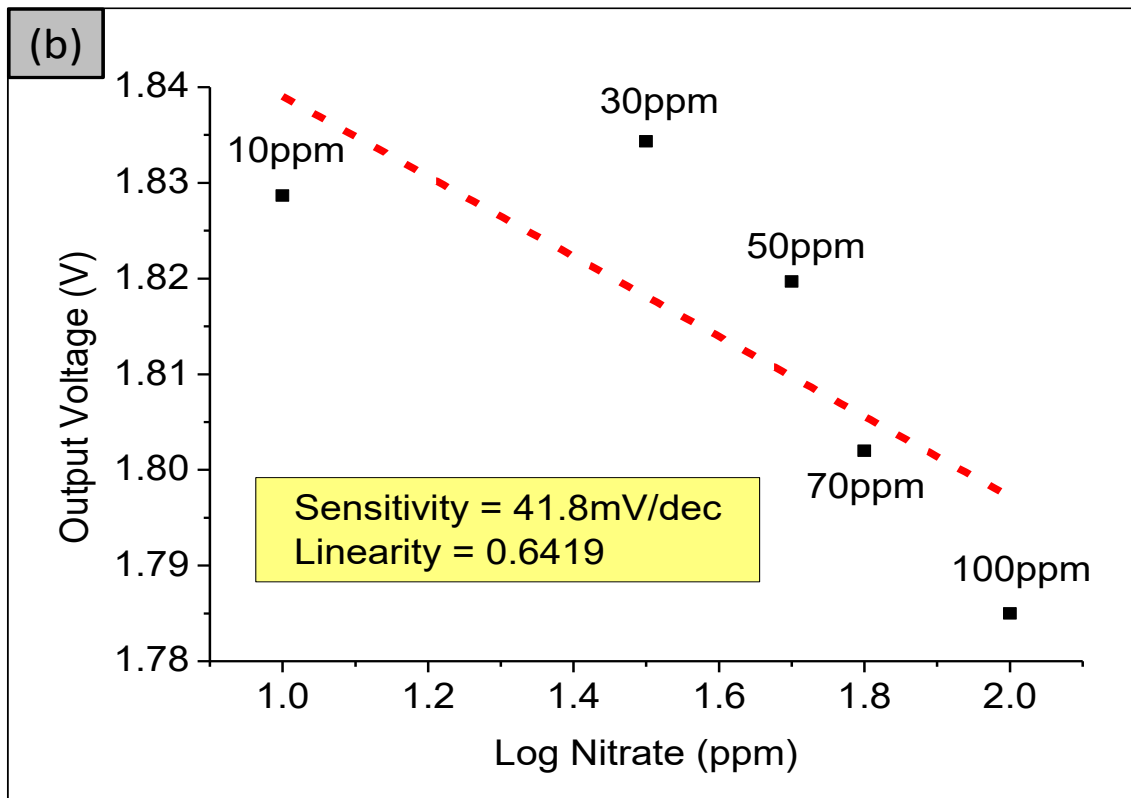
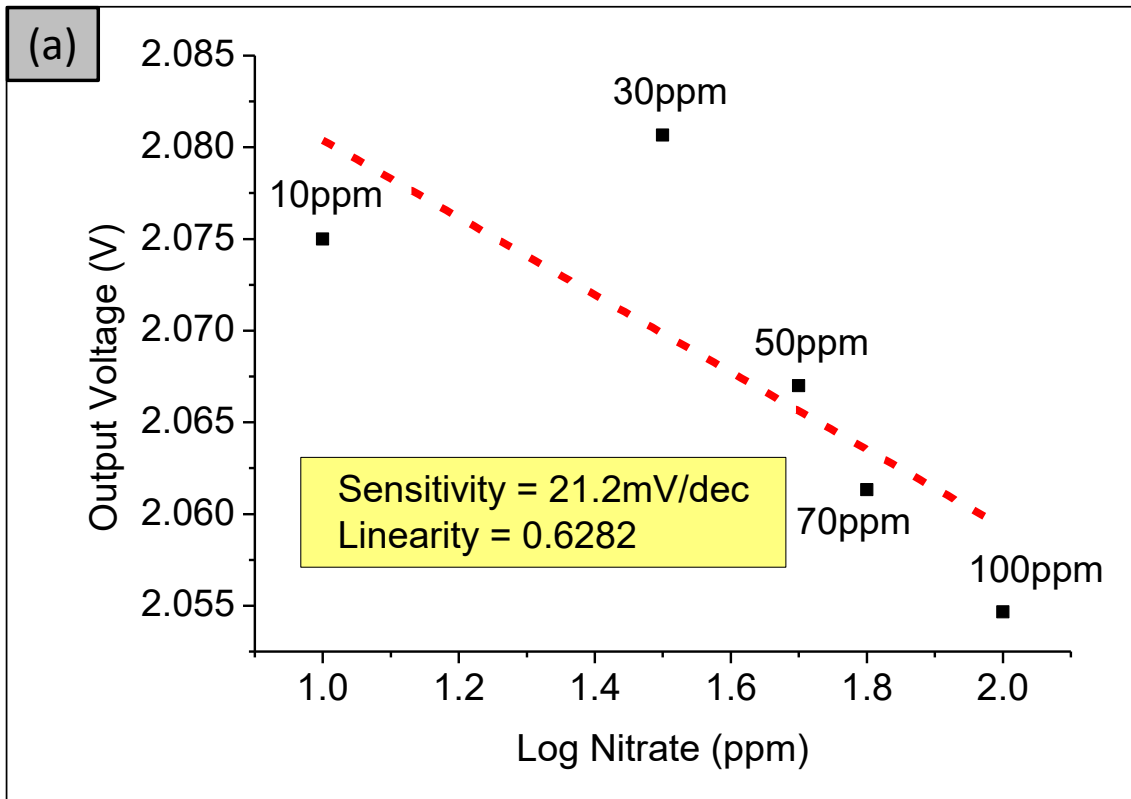


Figure 3. Output voltage of nitrate sensor and logarithmic nitrate concentration of (a) TiO₂ and (b) TiO₂-PVB bilayer composite thin film in the range of 10 – 100ppm

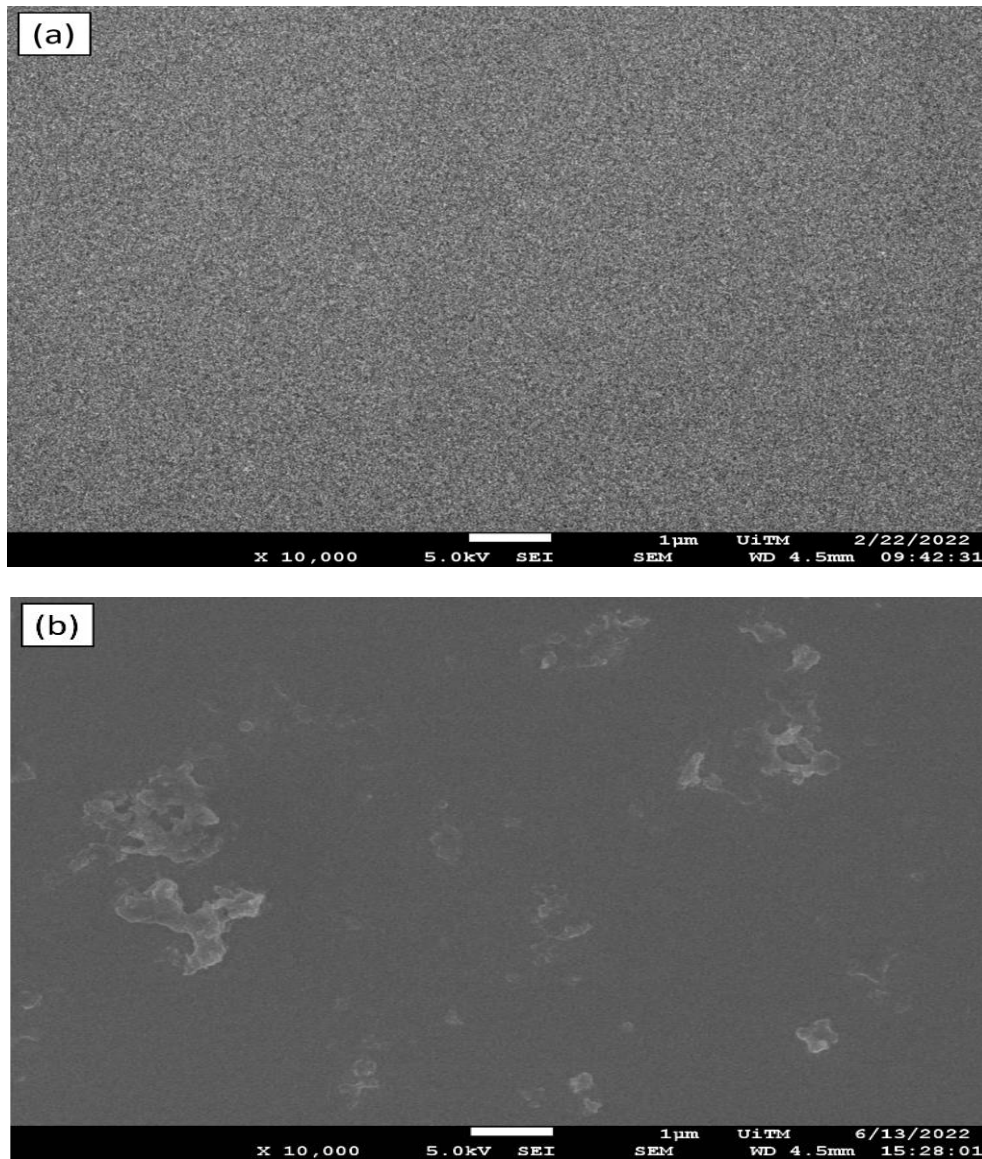


Figure 4. Surface morphology of (a) TiO₂ and (b) TiO₂-PVB bilayer composite thin film

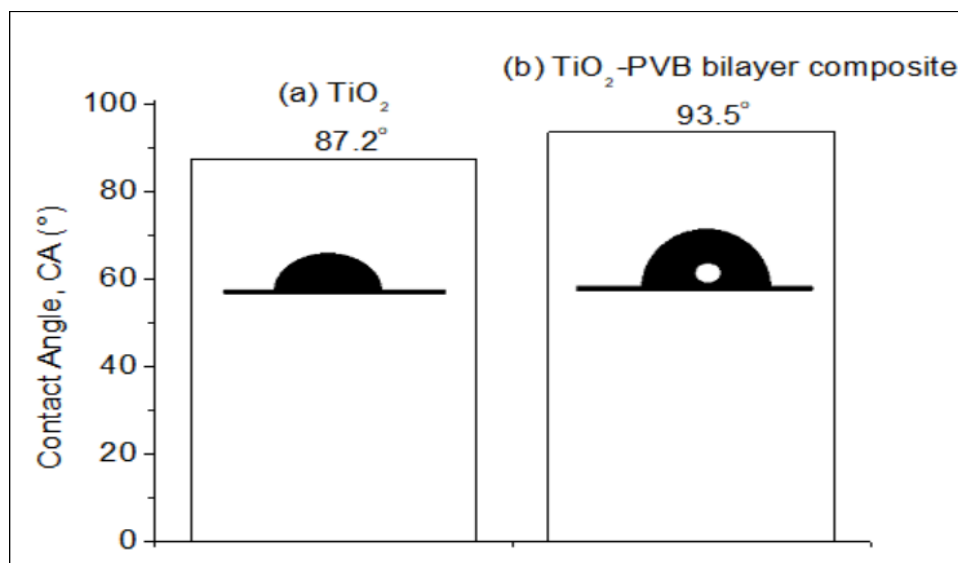


Figure 5. Contact angle measurement of (a) TiO₂ and (b) TiO₂-PVB bilayer composite thin film

However, a rough surface with undistributed agglomerate larger particle size was observed for the TiO₂-PVB bilayer composite thin film (**Figure 4 (b)**). It can be seen that the bilayer composite thin films are not well-dispersed, which contributes to the non-uniform surface structure.

3.3. Contact Angle

The contact angle (CA) of the samples was characterized using Video Contact Angle System (VCA3000S) which can capture an image of the droplet and automatically compute the tangent lines. A droplet of 1 μ l was placed on the surface of the sensing electrodes to test the CA. When the CA is less than 90°, the material is considered to be strong hydrophilicity. Meanwhile, when the CA is greater than 90°, the material has strong hydrophobicity. The TiO₂ thin films showed hydrophilic property with 87.2°, whereas the TiO₂-PVB bilayer composite thin film showed hydrophobic property with 93.5° as shown in Figure 5. It can be seen that the addition of PVB layer to the TiO₂ sensing electrode changes the hydrophilicity to hydrophobicity. Since the TiO₂ thin film prepared in this work showed a hydrophilic property, the water molecules can easily pass through the sensing electrode and form a water layer, which will significantly affect the sensing electrode's performance. Several studies have shown that the hydrophobic property is preferable for nitrate sensor [18-19]. Hydrophobic is known as a property of a substance that repels water. As suggested by Wakida et al., the hydrophobic sensor materials are superior in sensitivity and stability which improve the device performance [20].

4. Conclusions

In this study, TiO₂ and TiO₂-PVB bilayer composite thin films were deposited on ITO coated substrate using sol-gel spin-coating method. Both thin films were tested for nitrate detection using EGFET method in the range of 10, 30, 50, 70 and 100 ppm. The TiO₂ thin film showed sensitivity and linearity of 21.2 mV/dec and 0.6282. Meanwhile, the TiO₂-PVB bilayer composite thin film showed sensitivity of 41.8 mV/dec and linearity of 0.6419. The addition of PVB thin film on top of TiO₂ thin film did improve the nitrate sensing behavior by referring to the sensitivity and linearity values. Based on available literature, it was believed that the presence of C=O sites in conducting polymer, PVB was responsible to detect nitrate ions. This finding was supported by the contact angle results, where the TiO₂ thin film showed a hydrophilic property with 87.2°, whereas the TiO₂-PVB bilayer composite thin film showed a hydrophobic property with 93.5°. The surface morphology of the thin films was characterized using field-emission scanning electron microscopy (FESEM). It was found that the bilayer composite showed a rough surface with agglomerated particles size on the surface structure.

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