pH sensor based on AuNPs/ITO membrane as extended gate field-effect transistor

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Abstract
In the present work, gold nanoparticles/indium tin oxide (AuNPs/ITO) thin films were analyzed for pH sensing application based on extended gate field-effect transistor (EGFET). The AuNPs were synthesized through pulsed laser ablation in liquid (PLAL) technique. Afterwards, the AuNPs were deposited onto ITO thin film by electrospinning method. The AuNPs were characterized using transmission electron microscope (TEM) and UV–Vis spectroscopy techniques. From the TEM analysis, the size of the spherical-shaped AuNPs was found to be in the range of 5–22 nm. The UV–Vis spectroscopy analysis revealed absorption peak at 518 nm, indicating purplish red color. The AuNPs/ITO thin films were also characterized using field emission scanning electron microscope (FE-SEM) and X-Ray Photoelectron Spectroscopy (XPS) technique. The depth of the films was 6.498 µm and the Au 4f doublet binding energy peaks of the photoelectrons at 83.79 and 87.45 eV. The current–voltage (I-V) curves indicated pH sensitivities values of 43.6 mV/pH and 0.6 μA1/2pH−1 with linear regression of 0.99 and 0.99 for pH voltage and current sensitivities, respectively. The hysteresis and drift characteristics of the prepared films were also done to investigate the stability and reliability of the films. The results of this work demonstrated that the AuNPs/ITO thin film is quite useful for the acidity and basicity detection.

1 Introduction

The pH sensors have gained extensive attention due to demand in numerous applications including water treatment, medicine, agriculture, and food processing [1–3]. A pH value is defined as the negative logarithm of hydrogen ions concentration H+ in the solution which indicated the hydrogen ion activity. A pH value determines whether the liquid is alkaline or acidic. The higher pH value indicates more alkaline liquid [4]. The pH can be expressed by Eq. 1.

\[
pH = - \log_{10}[H^+]
\]  

Substantial efforts aiming to sensitivity improvement of pH sensors have been devoted to enhance the sensitivity of the real-time monitoring of hydrogen ion concentration in a biochemical environment. Currently, several techniques are being used to determine the pH values. Among these, the electrochemical pH sensors have gained increasing interest in biochemical measurement due to their easy and low cost fabrication, fast response, long lifetime, highest sensitivity, and wide sensitivity range [2]. Recently, there is a great interest in the development of ion-sensitive field-effect transistor (ISFET) which combines the electrical field sensing of transistor and a chemical characteristic of the membrane [5]. However, the ISFETs have drawbacks including chemical instability, contact with solution, and sensitivity to the light [6, 7]. In contrast, an extended gate field-effect transistor (EGFET) provides many advantages as compared to ISFET that include an insensitivity of the device to the light and its use without having contact with the solution [7, 8]. In EGFET pH sensor, the gate of MOSFET is removed.

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and replaced with an ion-sensitive membrane such as TiO2 [9], ZnO [10], porous silicon [11], and ITO [12]. However; the sensitivity and stability of these sensors are still poor. Therefore, in this study, we fabricate ITO thin film and coat it with gold nanoparticles (AuNPs) to increase the sensitivity of the pH sensor.

2 Methodology

2.1 Fabrication of ITO thin film

Indium Tin Oxide (ITO) thin films of 200 nm thickness were grown on a commercial glass substrate (2cm × 2cm) using a radio-frequency (RF) sputtering of ITO target in argon (Ar) atmosphere. The base pressure of the chamber was maintained at 2 × 10⁻⁵ mbar while the working pressure of the deposition process was approximately 2 × 10⁻² mbar with flowing of high purity Ar gas (99.999%). The deposition of ITO film on glass substrate was carried out at 150W and at 0.6A°/s.

2.2 Synthesis of Au NPs

The AuNPs were produced using pulsed laser ablation in liquid (PLAL) technique. The rounded shaped gold plate of 99% purity and 0.5 mm thickness was immersed in the polyethylene oxide, C₇₇H₄₇O₃₄, (PEO) solution at room temperature. The solution was prepared by dissolving 200 mg of PEO in 10 mL of deionized water using a magnetic stirrer for an hour. The gold plate was cleaned by Branson in an ultrasonic bath and then washed with 20 mL acetone to remove contamination for 15 min at 40 °C. After immersing the gold plate in the solution 11 mm depth, it was ablated using Q-switched Nd:YAG laser of 1064 nm operated at 500 mJ, pulse duration 10 ns, and frequency of 10 Hz for 2000 pulses. A using lens of a focal length of 150 mm was used to focus the laser beam on the target.

2.3 Design and characterization of AuNPs/ITO thin film

Electrospinning was used to fabricate AuNPs on ITO thin films. The rate of injection was 1 mL/hr with a potential difference of 16 kV and the distance between the collector and syringe needle was 20 cm. The AuNPs on ITO thin films were annealed at 500 °C for 5 h to remove the polymer and impurities. The deposition parameters for the AuNPs/ITO thin films are given in Table 1.

The surface morphology analysis was investigated using field emission scanning electron microscope (FE-SEM). On the other hand, the composition of elements was identified using energy-dispersive X-ray (EDX). In addition, X-Ray photoelectron Spectroscopy (XPS) was investigated to analyze the surface chemistry of the prepared thin films including elemental composition and electronic state of the elements within the films.

2.4 Measurements processes

The measurement of the current–voltage (I-V) characteristic of AuNPS/ITO-EGFET performed using a Keithley 2400 apparatus with a similar method mentioned in ref [13]. The gate of a commercial n-MOSFET type (CD4007UBE—Texas Instruments) was replaced by the prepared thin film. The film was placed in a Teflon chemical cell and was connected to the copper base as shown in Fig. 1. This structure prevents the measurements from light exposure and electromagnetic disruption [14]. The Ag–AgCl reference electrode was immersed directly into the buffer solutions. The thermometer and pH meter probe were adjusted in the chemical cell to monitor the condition of the buffer solution. The temperature was fixed during the experiment because of the direct dependence of the electromotive force of the solution on the temperature as given by Nernst law [9]. Buffer solutions with pH ranges 2, 4, 6, 8, 10, and 12 were used to present the I–V characteristics of the sensor using two units of source meter (2400 source meter, Keithley Instruments, Inc., Cleveland, OH, USA). The source meters were connected to PC through GPIB-USB cable.

To study the stability and reliability of the prepared films, hysteresis and drift phenomenon were investigated. The hysteresis study was utilized by measure groups of $I_{DS} - V_{GS}$ plots in linear regime as explained in Sect. 3.3 with a fixed voltage of $V_{DS} = 0.3V$ for $pH = 7, 4$, and 10. The AuNPs/ITO thin film was immersed in an alternating cycles of pH buffer solutions i.e. $pH7 \rightarrow pH4 \rightarrow pH7 \rightarrow pH10 \rightarrow pH7$ for 4 min for each buffer solution. From each curve, the threshold voltage of $V_{GS}$ was constructed at fixed drain current $I_{DS} = 0.1mA$. The hysteresis curve was plotted as a relation of $V_{GS}$ vs. time in unit of mV/hr. In addition, the drift analysis was conducted with same measurements of $I_{DS} - V_{GS}$ plots in linear regime at $pH = 4, 7$ and 10 buffer solutions for 7 h and extract the threshold voltage for each 30 min.

| Table 1 Ambient parameters of the AuNPs/ITO thin films deposited using the electrospinning method |
|---|---|
| Substrate | Glass/ITO thin films |
| Solution | AuNPs in PEO |
| Flow rate | 2 mL/hour |
| Distance (capillary → collector) | 20 cm |
| Electric potential | 16 kV |
| Deposition time | 3 h |

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3 Result and discussion

3.1 NPs characterization

The optical and morphological analysis of the prepared nanoparticles were made using UV–Vis and transmission electron microscope (TEM) techniques. Figure 2 shows the UV–Vis spectrum, TEM image, and particle size distribution for AuNPs. The optical spectrum shows the surface plasmon (SPR) peak at 518 nm which can be described using the surface plasmon resonance (SPR) phenomenon [15, 16]. At this wavelength the electromagnetic field of the interacted light causing on coherent oscillations of conduction band electrons [17]. TEM analysis shows that the size of NPs ranges from 5 to 22 nm. This result is acceptable in scientific society [18]. Table 2 summarizes the properties of the NPs and compare these with the previous studies.

| Table 2  | Gold nanoparticles parameters |
|----------|------------------------------|
| Solvent  | Absorption peak (nm) | Size (nm) | Shape   | Ref        |
| Distilled water | 520          | 15–20     | Spherical | [19]       |
| Gum Arabic     | 540          | 12–18     | Spherical | [20]       |
| PEO            | 518          | 5–22      | Spherical | This study |

3.2 AuNPs/ITO thin film characterization

Figure 3 depicts the surface morphology of the fabricated AuNPs/ITO thin film. Figure 3a shows the top view of the prepared thin film in which the Au NPs distribute randomly on the ITO surface. Figure 3b demonstrates the cross section of a part of the prepared films with depth of Au NPS/ITO (6.498 µm), ITO (1.078), and Au-NPs layer (5.478 µm). Moreover, the XPS results of the AuNPs/ITO thin films are shown in Fig. 4.
The Au 4f doublet binding energy peaks of the photoelectrons are situated at 83.79 eV and 87.45 eV; respectively that corresponds to the chemical state of Au. It is reported that the binding energy is a function of the element, oxidation state, and electronegativity [21]. These two values are shifted to lower binding energy levels comparing to 86.7 and 90.1 eV.

**Fig. 3** a FE-SEM image of the top view of AuNPs/ITO thin film b film’s cross section and c EDX spectrum of the film

![Fig. 3](image)

**Fig. 4** XPS spectra of AuNPs/ITO thin film a wide scan and b narrow scan at 4f region

![Fig. 4](image)

**Fig. 5** a The $I_{DS}$-$V_{GS}$ curves for the prepared AuNPs/ITO pH-EGFET in the linear region for different pH buffer solution (pH = 2 to 12). b Plot of the $V_{GS}$ as a function of pH for the prepared samples. The $V_{DS}$ was kept constant at 0.3 V.

![Fig. 5](image)

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of pure gold due to oxidation of some NPs during the laser ablation when using nanosecond laser pulse [19].

3.3 AuNPs/ITO as EGFE T pH sensor

To test the pH sensitivity of the prepared films as pH-EGFET, the measurement performed in two regimes of current–voltage (I–V) curves. The first is at the linear regime of the drain-gate sensitivity with constant current; the second is at the saturation regime of the drain-source sensitivity at a fixed voltage (0.3 V). Figure 5 shows \( I_{DS} - V_{GS} \) curve at constant drain-source voltage \( V_{DS} = 0.3V \), linear region of the MOSFET. As shown in the figure, the curve is shifted to higher voltage when the hydrogen ions decrease i.e. when the electrolyte becomes more alkaline. Thus the threshold \( (V_T) \) depends directly on hydrogen ion concentration. The pH voltage sensitivity was calculated from the variation in gate-source voltage in \( mV/pH \) unit as shown in Fig. 4. The drain-gate sensitivity for prepared films are approximately 43.6 and 41 \( mV/pH \) based on the AuNPs/ITO and ITO films; respectively. The pH sensitivity for AuNPs/ITO is higher than those with different ITO structures [12]. On the other hand; the pH voltage sensitivity for AuNPs/ITO is better than that for pure ITO films. This result can be explained using site binding model [23, 24]. The AuNPs/ITO can be considered as ITO thin film with constant gate-source voltage at \( V_{GS} = 3 \) V. As the pH of the electrolyte increases from 2 to 12, the curves are shifted to lower drain-source current values. When the electrolyte becomes more alkaline, the \( OH^- \) ions increase leading the membrane surface to become negatively charged as explained above. The pH current sensitivity of the films can be computed from the variation of the drain-source current per unit pH in the unit of \( \mu A/pH \) using the following formula:

\[
\text{pH current sensitivity} = \frac{\Delta I_{DS}}{\Delta pH}
\]

(4)

Figures 6 shows the linear current sensitivity of both AuNPs/ITO and ITO thin films as a function of the pH values ranging from 2 to 12. The linear pH current sensitivity of AuNPs/ITO and ITO sensing membrane are noted to be 0.6 and 0.26 \( \mu A/pH \); respectively. Concurrently, this sensitivity and linearity of the films based on AuNPs/ITO has higher values than that for pure ITO thin films.

3.4 Sensing interpretation

The mechanism of the sensitivity of prepared films as a pH sensor can be explained using the site-biding model [23, 24]. The AuNPs/ITO can be considered as ITO thin film decorated by AuNPs. The thin film comprises a layer of surface sites. When these sites are immersed in an electrolyte, then these can accept or denote protons. In the acidic electrolyte, \( H^+ \) reacts with the film’s surface and the surface becomes positively charged. On the other hand; in
the alkaline medium, OH\(^-\) reacts with the surface, leading the surface to become negatively charged [10].

### 3.5 Stability and reliability

Figure 7a presents the hysteresis effect of the Au-NPs/ITO sensing membrane. This phenomena depends directly on the chemical interaction between the electrolyte ions (H\(^+\) and OH\(^-\)) and the surface sites of the sensing membrane [14]. It is observed from the Fig. 7a, for the loop pH 7 → pH 4 → pH 7, the hysteresis was 2.7 mV; while for the other loop pH 7 → pH 10 → pH 7, the hysteresis was 4.8 mV. This increase in hysteresis for the alkaline solution is due to the difference in diffusion of H\(^+\) and OH\(^-\) ions of the electrolyte. The H\(^+\) diffusion is faster than the OH\(^-\) diffusion which leads to the hysteresis in the alkaline medium higher than that for acidic one [11]. In this study, the net hysteresis was 7.5 mV which is slightly lower than the previous studies [11, 14]. Figure 7b presents the drift behavior in reference voltage of the prepared Au/ITO based on the EGFET pH sensor with respect to time for long-term stability. The drift phenomena is common on ion selective electrochemical sensor and the range of 3 -10 mV is quit acceptable [14, 25]. For drift characteristics, the long-term drift rate, which is the change in reference voltage per unit time (mV/h) was studied. Figure 7b reveals the drift rate for the sample at pH 4, 7, and 10. In this study, the total long-term drift rate at pH = 7 of the buffer solution was 1.85 mV/hr. The drift behavior initially increased dramatically at 2.9 mV/h on the range of [0–3.0] h, then the increase in the drift rate becomes slower. The initial fast drift could be due to the adsorption of the OH\(^-\), while the lower drift rate in the long-term is because of OH\(^-\) slow diffusion in buried sites of sensing membrane [14]. It is shown that (Fig. 7b), as the pH becomes higher, the drift rate increases due to the mobility of H\(^+\). The higher H\(^+\) concentration, the lower pH, leads to a slower speed rate [26]. This outcome matches the result of previous studies [27]. To study the practical stability of the prepared samples, the thin films were immersed in buffer solution at pH = 4 and 10 overnight. The sensor after 24 h still works with no significant degradation of the sensor surface.

Comparing to this study, lower drift rate of 1.5 mV/day (28) was achieved using two Indium Tin Oxide (ITO) electrodes as pH-sensitive material. While, the prepared Au/ITO film has lower long-term drift rate comparing to reported results on PdO [14] and CuO nanowires [25].

### 4 Conclusion

In summary, this study presented the usage of AuNPs/ITO thin film as a membrane for pH sensing based on the EGFET platform. The AuNPs/ITO membrane shows a higher value of voltage sensitivity at 43.6 mV/pH comparing to the ITO membrane. According to this study, when the ITO thin film is coated by AuNPs, the ITO surface sites become higher which results in increasing the charge accumulation leading to improvement in the pH sensing. This improvement in pH detection justifies the potential use of AuNPs/ITO as a pH sensor. The fabricated thin films showed good stability with a long-term drift rate of 1.85 mV/h at pH = 7 and found suitable for pH sensing applications.

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