Optimized Low-Temperature Gas Sensing Performance of Cu_2O-ZnO Heterostructured thin films

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1. ABSTRACT

The gas-sensing performance of Cu_2O-ZnO nanocomposites synthesized via different methods is systematically evaluated at low operating temperature conditions. Cu_2O-ZnO was grown on FTO substrates with electrodeposited p-type Cu_2O films and n-type ZnO films coated by the Successive Ionic Layer Adsorption and Reaction (SILAR) method or electrodeposition. Before the gas sensing studies, the films were characterized with contact angle measurements (CAM). At 70 ℃, the LPG sensitivity of the Cu_2O/ZnO composites, where ZnO layers were SILAR grown for dipping times of 30 s, 1 min, and 5 min on Cu_2O showed an increase of ~ 5 % compared to the pure Cu_2O. The electrochemical deposition of ZnO on Cu_2O was not successful due to the formation of CuO. The ZnO-Cu_2O heterostructures exhibited varying gas-sensing behaviors depending on the deposition time. The ZnO-Cu_2O film deposited for 10 minutes displayed a predominantly p-type response, while the film deposited for 15 minutes showed an unstable n-type gas sensor response (~10%) after repeated measurements. Contact angle measurements indicated that the Cu_2O-ZnO nanocomposite film had a partially wetting nature, which significantly improved the gas sensor responses by 100% to 200% across an operating temperature range of 30°C to 100°C. In this heterostructure, Cu_2O acted as a visible-light harvester, playing a crucial role in the gas-sensing mechanism. This study demonstrated successful room-temperature gas sensor operation under white light illumination.

2. INTRODUCTION

Sensors based on heterostructures have shown appreciable responses at room temperature due to their unique chemical interactions, the adsorption of gases, and changes in electronic binding energies in the composite. However, most of the traditional semiconductor gas sensors operate at extremely high temperatures. This condition is an unavoidable requirement due to its effectiveness in removing the accumulated water vapor resulting during the sensing process. Given its high power consumption, this scientific gap should be addressed to promote a new generation of low temperature-highly sensitive gas sensors.

Literature on the ZnO/SnO_2 composites reports, that ZnO nanorods act as active light absorption centers whilst SnO_2 nanoparticles on the surface increase the surface area and the chemisorption ability of the gas. The responses of all sensors to gas were found to enhance under UV light illumination. In particular, the sensor's response has increased from 13.4% without UV light illumination to 1266 % under UV light illumination [1].

The NO_2 gas response of ZnO/SnO_2 sensors showed a dependence on the relative humidity at room temperature, and a negative impact of moisture leading to a decreased response in the dark. However, with UV light irradiation, the film surface physisorbed water has been decomposed by the photo-generated charges and increased the gas response than that in the dark at the same relative humidity.

On the other hand, ZnO limits its light absorption to the UV region due to its large bandgap of 3.37 eV [2]. As an example, semiconductor heterostructures, particularly p-n junctions like Cu_2O/ZnO, are key to enhancing photo-electrochemical (PEC) performance and solar cell efficiency. This is due to their ability to control the electronic structure at the interface and the achievement of favorable energy band alignment. Moreover, ZnO nanomaterials with their rich morphologies, high electron mobility, and large exciton binding energy (60 meV), have been extensively studied.

Here, Cu_2O with a narrower bandgap of 2.2 eV, is often combined with ZnO to extend the light absorption range into the visible region, thereby improving PEC performance [2]. The Cu_2O thin films are typically grown as a p-type semiconductor due to the copper vacancies within its crystal lattice. The concentration of charge carriers in Cu_2O can be controlled by adjusting the pH of the electrolyte during electrodeposition [3]. This provides a method to manipulate the electronic properties at the interface of the Cu_2O/ZnO heterostructure. To the best of the authors' knowledge, the efficiency of Cu_2O/ZnO composite material-based gas sensors that are operating at low temperatures have not been reported, yet, but will open up a new chapter in gas sensors.

In this study, Cu_2O-ZnO heterostructures are grown with electrodeposited p-type Cu_2O films and n-type ZnO films coated by the Successive Ionic Layer Adsorption and Reaction (SILAR) method, and electrodeposition. The paper focuses on the gas sensing efficiencies of such differently grown heterostructures, Cu_2O/ZnO (ZnO on Cu_2O), and ZnO/Cu_2O **(**Cu_2O on ZnO) and finding the most suitable/optimal sensor platform at room temperature. Moreover, this work characterizes the sensors based on their surface and bulk particle structure and roughness, and optical and electrical properties.

3. EXPERIMENTAL DETAILS

3.1 Materials and Methods

Electrochemical deposition (ECD) of Cu_2O, on FTO substrates was done inside a two-electrode chemical cell by considering the parameters realized to be influential in previous works [4]. With a Cu counter electrode, an FTO glass substrate was deployed as the working electrode, which was carefully washed with detergent and followed by distilled water, and finally surface treated with acetone by ultra-sonication to improve Cu_2O film adhesion. FTO glass substrates were deployed as the working electrode. A surface area of ~ 1×1.5 cm^2 of the FTO was immersed in the aqueous solution mixture of 3.5 M lactic acid (Sigma–Aldrich, purity - 99.0%) and 0.45 M cupric sulfate (Sigma–Aldrich, purity - 99.0%). The pH of the electrolyte was adjusted to pH 10. The temperature of the electrolyte was maintained constant at 60°C and Cu_2O thin films were potentiostatically electrodeposited at - 730 mV versus the anode/counter electrode. The deposition duration varied from 5-30 min to obtain the optimum film thickness and

surface morphology that matches the Cu_2O/ZnO heterostructure. After the deposition, films were washed with distilled water and dried in normal air at the room temperature.

$$2Cu^{2+} + 2OH^- + 2e^- \leftrightarrow Cu_2O + H_2O \quad (1)$$

The chemical reaction involved in this process is given in Eq. (1).

Electrochemical deposition of ZnO, on FTO substrates was done inside a two electrode chemical cell having Zn anode under experimentally observed fine film deposition conditions. Electrolyte consists of a 0.1 M $Zn(NO_3)_2$ (Sigma–Aldrich, purity - 99.0%) aqueous solution with 5.6 pH level. Pristine ZnO has been observed to deposits under -800 mV potential at 60 ºC with varying fabrication durations from 5-30 min. The general scheme of electro-precipitation of ZnO thin films from nitrate baths is supposed

$$Zn(NO_3)_2 \rightarrow Zn^{2+} + 2NO_3^- \quad (2)$$

$$NO_3^- + H_2O + 2e \rightarrow NO_2^- + 2OH^- \quad (3)$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \quad (4)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (5)$$

Overall expression of the reaction is given in Eq. 6.

$$Zn(NO_3)_2 + 2e \rightarrow ZnO + NO_2^- + NO_3^- \quad (6)$$

as follows [5].

Electro-reduction of nitrate to nitrite ions generates hydroxide ions at the cathode. Thereafter, zinc ions precipitate with the hydroxyl anions and dehydrate on cathode (FTO) surface as explained in Eq. 2-5.

However, the ECD of ZnO film on the electrochemically deposited Cu_2O films

$$Cu(NO_3)_2 + ZnO \rightarrow CuO + Zn(NO_3)_2 \quad (7)$$

(Cu_2O/ZnO) results in a blackish CuO layer following the reaction given in Eq. 7.

The SILAR method was also utilized to fabricate ZnO on pre-electrodeposited p-Cu_2O films to develop Cu_2O/ZnO heterojunctions. A NH_4OH solution was added dropwise using a regular pipette (1 drop= 30 µl) to a 10 ml of 0.1 M $Zn(SO_4)$ (Sigma–Aldrich, purity - 99.0%) aqueous solution. This results in a precipitate/foggy solution. By adding few more drops (altogether ~ 10-15 drops) of ammonia, this precipitate dissolves forming a clear solution. However, adding more drops/high ammonia concentration could result in a reduction or dissolution of Cu_2O. As explained in Eq.8, the Zinc-amine complex is produced when NH_4OH is added to the $ZnSO_4$ aqueous solution.

$$Zn(SO)_4 + 2\,NH_4OH \rightarrow [Zn(NH_3)_4]^{2+} \quad (8)$$

To deposit different thicknesses of ZnO layers, the electrodeposited Cu_2O films was immersed (once) in the Zinc-amine solution for different dipping durations of 1 min, 5

$$[Zn(NH_3)_4]^{2+} + H_2O \rightarrow Zn^{2+} + NH_4{}^{2+} + OH^- \quad (9)$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \quad (10)$$

min, 10 min, 15 min, and 30 min. At this point, the complex firmly sticks to the Cu_2O surface as a foggy $Zn(OH)_2$ layer followed by the reaction in Eq.9-10.
Longer the immersed time, the solution turned blue (color of Cu^{2+} ion), indicating a

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (11)$$

possible dissolution of Cu_2O layer. Then the film was taken out, rinsed with deionized water, and heat treated at 100 ℃ for 10 minutes to oxidize the $Zn(OH)_2$ to ZnO (Eq.11).

Material characterization

Using the sessile drop method with double distilled water drops of 5 µl, the surface tension was measured via Contact Angle Measurements (CAM). Using a digital microscope (2MP 1000x 8 LED USB Digital Microscope Endoscope), the contact angle values of separate 30.0 µl distilled water droplets placed on the left Cu_2O and right ZnO sides of the film were observed. After settling under normal atmospheric conditions for approximately 5 to 10 minutes, the contact angles were captured and measured using ImageJ 1.54d/Java 1.8.0_345 software. Surface morphologies of the films were characterized via scanning electron micrographs (SEM, Zeiss EVO 15 LS), and the electrical characterization was conducted by AC impedance spectroscopy using AUTOLAB Model PGSTAT 302 potentiostat/galvanostat using three-electrode electrochemical cell containing Cu_2O deposited FTO substrate as the working electrode, platinum counter electrode, and Ag/AgCl as the reference electrode in 0.1 M NaAc electrolyte. The optical energy band gaps were characterized using the UV-visible spectrophotometer (Genesys 10s UV-Vis).

Gas sensitivities of the deposited p-n junctions were measured by introducing to a continuous LPG: air flow at different operating temperatures. Here the heterostructures' surface impedance across two points was observed via two identical FTOs (for Cu_2O-ZnO heterojunctions-FTO conducting sides are placed on each layer with a 5 mm gap) as shown in Fig 1. The output electrical resistivity of the film surfaces was measured using a computer-interfaced dual channel multimeter (GW INSTEK GDM-9060/9061). Data was collected in 1 s time intervals.

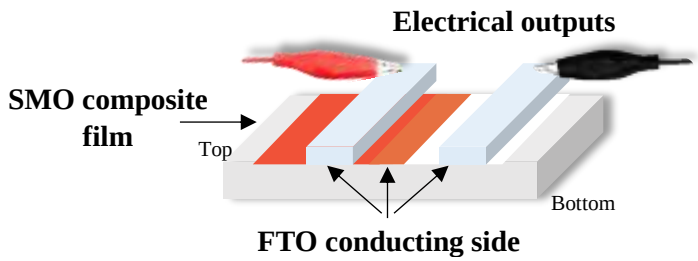

Figure 1: Schematic diagram illustrating the strategy used to make electrical contact on the film surface for LPG sensor/impedance measurement.

In the gas sensing measurements, the film containing gas chamber that was set to the selected operating temperature (30 ℃ - 100 ℃) was initially flushed with 100 cc min^{-1} compressed air flow rate for a few minutes. Thus, settling the film in the ambient sensing conditions. Here, the film resistance was allowed to reach a stable level R_a. Then, a constant LPG rate of 0.2 $lmin^{-1}$ was injected, until the films reach a steady state maximum R_g(with a tolerance of ±0.1% of the measurement). After that, the LPG flow was stopped and let the film recover to its ambient conditions under compressed air flow. The response and recovery times were measured as the times the sample took to reach or drop 90% of the maximum change. For the considered sensing temperature, this process was repeated several times continuously. Here, in order to check the performance, films underwent temperatures ranging from 30°-70° C with 10℃ steps. During the gas sensing process, the films were exposed to natural light (4.43 kW/m^2 - 5.64 kW/m^2) to investigate the impact of the photovoltaic effect of the Semiconductor Metal oxide (SMO) films utilized for gas sensing performance.

4. RESULTS AND DISCUSSION

4.1 Cu_2O(ECD)-ZnO(ECD) Heterostructures

The heterostructure formation of p-Cu_2O and n-ZnO has been achieved by depositing on an effective area of ~ 1×2 cm^2 (~ 1×1 cm^2 area of each pristine layer) of the films, where each layer overlap at the middle. As illustrated in Fig 2(a)**,** the ECD of ZnO film for 5 min on the ECD Cu_2O film (Cu_2O/ZnO) resulted in a blackish CuO layer following the Eq. 7. However, this layer does not appear when the Cu_2O film is deposited after/on the ZnO (ZnO/Cu_2O) film (Fig 2 b-c). Therefore, in order to check the characteristic differences accompanied by these Cu_2O/ZnO and ZnO/Cu_2O (overlapped layers) heterostructures were utilized as discussed below.

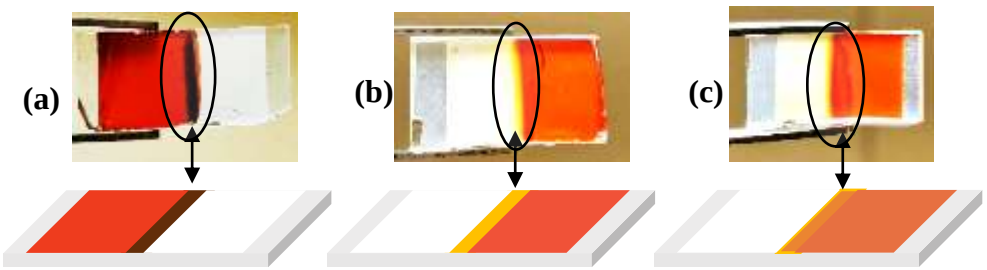

Figure 2: Electrochemically deposited heterostructures with overlapped (a) ZnO 5 min layer, on Cu_2O 30 min layer, (b) Cu_2O 15 min layer on ZnO 5 min layer, and (c) Cu_2O 10 min layer on ZnO 5 min layer.

The surface adhesive nature of each film was analyzed using the sessile drop method, by the Contact Angle Measurement (CAM) of a 10 µl droplet placed on both ZnO and Cu_2O sides of the film (Fig. 3). Here, the ZnO layers had a wetting nature which was consistently identified as a low contact angle of approximately 25°. When placing the

distilled water droplet on ZnO, it quickly spread across the film resulting in an uneven droplet. In comparison, on the Cu_2O side, with decreasing deposition time from 15 to 10 min, the CAM has been increased from wetting (30°-60°) to partially wetting (60°-90°). A high CAM value of 83.6° was observed on the $Cu_2O_{30\ min}$ film surface.

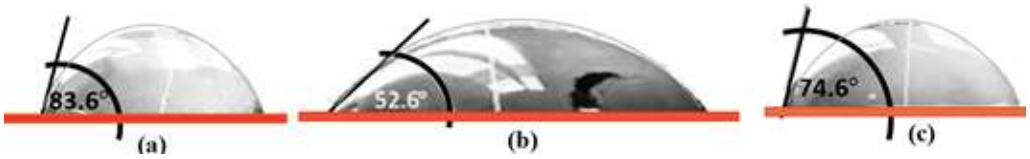

Figure 3: CAM on the Cu_2O side of a) Cu_2O 30 min – ZnO 5 min b) ZnO 5 min-Cu_2O 15 min, and c) ZnO 5 min - Cu_2O 10 min junctions.

LPG sensitivity of ZnO(ECD)-Cu_2O(ECD) Junctions

In general, Cu_2O once exposed to LPG shows a p-type sensing pattern where resistance decreases with the introduction of a reducing gas. ZnO shows an n-type behavior where the opposite happens with the reducing gases. The first sample of Cu_2O 30 min–ZnO 5 min heterostructure, initially started responding to the reducing gas and gradually increased the resistance showing a prevailing n-type sensing behavior. After a certain time, the response stability didn't take place and, once the LPG was stopped, the film didn't recover to its original/ambient resistance at any given temperature. This was suspected to result from the black CuO intermediate layer.

The ZnO 5 min - Cu_2O 15 min junction was first tested at 35 ℃. The heterostructure also displayed a prevailing n-type sensing pattern with ~10% maximum response, 30s response time, and 120 seconds recovery time. With repeated cycles, the junction showcased an increasing recovery period as shown in Fig 4(a). The longer the gas exposed time, the heterostructure showed inconsistent response, with increased response and recovery periods due to the two layers' structural and conductivity changes that occurred with exposure. With time, at much higher temperatures, the junction stopped recovering.

On the other hand, when the film thickness of the Cu_2O was decreased by limiting the deposition to 10 minutes, ZnO 5 min-Cu_2O 10 min junction showed a p-type sensing pattern with an average LPG response of ~9% as illustrated in Fig. 4(b) Having a maximum response time of 2 min and recovery time 1 min, ZnO 5 min-Cu_2O 10 min junction also displayed the same instability with higher temperature (>50 ℃).

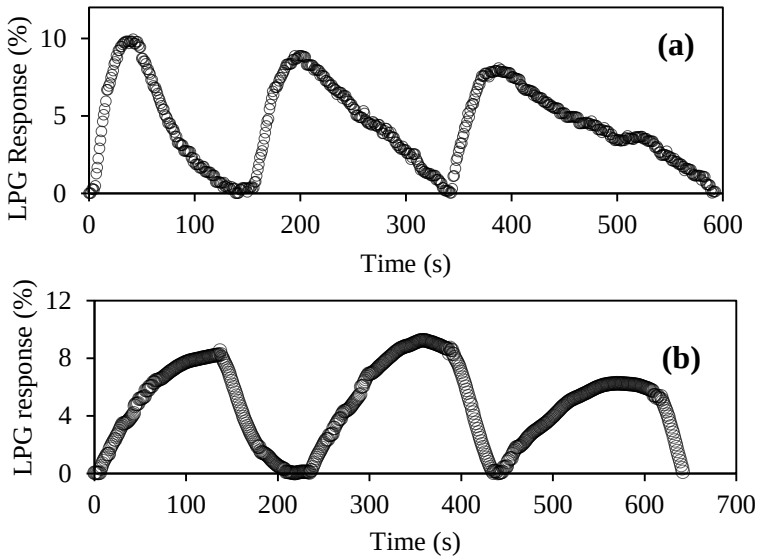

Figure 4: LPG response of (a) ZnO 5 min-Cu_2O 15 min junction at 35℃ and (b) ZnO 5 min-Cu_2O 10 min junction at 50℃ .

4.2 Cu_2O(ECD) / ZnO(SILAR) Heterostructures

The Cu_2O films electrochemically deposited for 30 min at pH 10 on FTO were directly subjected to ZnO SILAR growth with shorter dipping times of 30 s, 1 min, and 5 min to check the LPG sensitivity of the heterojunction. These newly deposited Cu_2O/ZnO heterojunctions were first characterized based on their contact angle which determines the adhesive nature of the film during the gas adsorption and desorption. The observed results depicted in Fig.5 shows an induced increase in the surface wettability by ZnO introduction. This slight wetting nature has been greatly reduced with increasing dipping time, indicating a possible slower response and quick recovery.

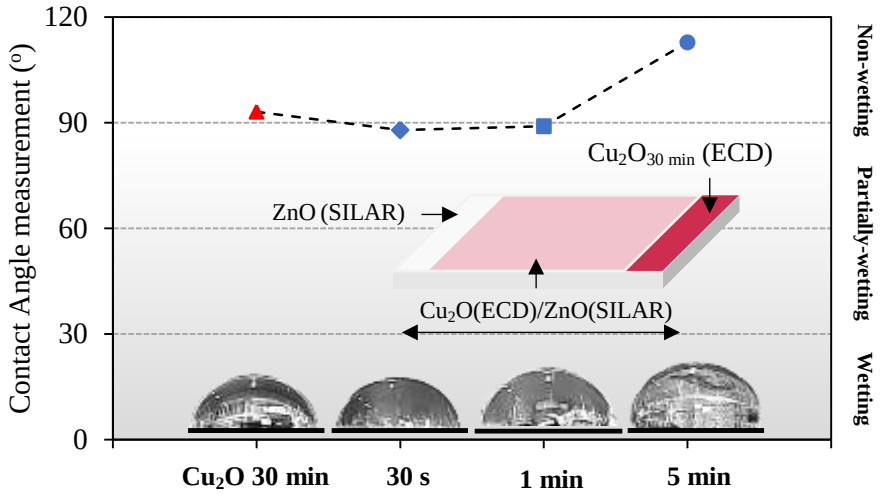

Figure 5: Contact angle measurement variation across pristine Cu_2O 30-min and Cu_2O(ECD)/ZnO(SILAR) heterostructures fabricated with 30 s, 1 min, and 5 min dipping time of SILAR cycles.

LPG sensitivity of Cu_2O(ECD)/ZnO(SILAR) heterostructures

The Fig. 6 illustrates a ~ 2% change in LPG sensitivity at 70℃ due to the ZnO growth on Cu_2O. In comparison, increasing dipping time has maintained a stable response percentage with varying response and recovery times as expected with their respective contact angle measurements. Evidently, at 5 min SILAR dipping time, recovery/ gas desorption is faster due to its lowest surface adhesive nature. But overall, this change in gas sensitivity is not significant enough and contains fluctuations in the sensor output resistance. Therefore, Cu_2O/ZnO heterojunctions fabricated with ZnO layer grown by SILAR method on top of ECD Cu_2O layer need further rectifications.

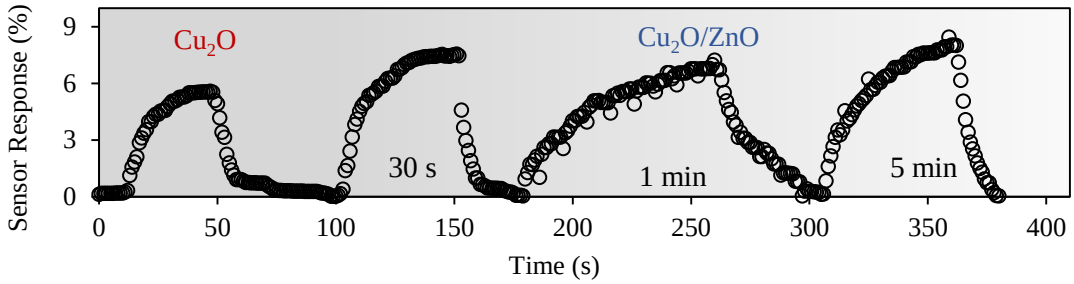

Figure 6: LPG sensitivity of Cu_2O/ZnO with ZnO deposited by SILAR process with dipping times of 30 s, 1 min, and 5 min on p-Cu_2O films.

4.3 ZnO(ECD)/Cu_2O(ECD) Heterostructures

ZnO/Cu_2O heterojunctions were grown sandwiched in an effective area of ~2×1.5 cm^2 on FTO using electrodeposition technique. Following the optimal deposition conditions found with the testing samples, the Cu_2O and ZnO layers were ECD for a 5 min duration each to minimize the interfacial thickness and increase the contribution of the base ZnO layer more in the gas sensing process. After the synthesis of the ZnO layer, the sample was heat treated at 90℃ -100℃ temperature for 5 min to get an even, less wetting film. This step was repeated after the Cu_2O deposition. To compare the CAM, characteristics of Cu_2O, ZnO/Cu_2O, and ZnO layers, a separate sample was synthesized as shown in Fig. 7**,** with ~ 2×0.75 cm^2 on FTO.

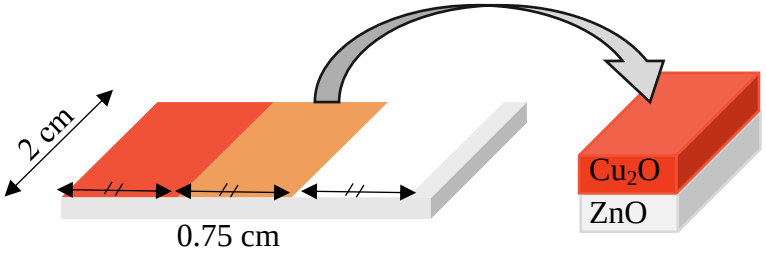

Figure 7: Schematic illustration of the Electrochemically deposited Cu_2O-ZnO/Cu_2O-ZnO (starting from the left) layers on FTO.

The identified CAM values of Cu_2O, ZnO/Cu_2O, and ZnO layers are displayed in Fig. 8**.** The partially wetting behavior of Cu_2O, and relative wetting nature of ZnO have been induced in an intermediate wettability in the heterojunction with 47.6° contact angle

value. The possible high wetting nature accompanied by the ZnO layer is avoided here by heat treating the ZnO (base) film. In this sense, the ideal CAM value of the junction could be able to provide high gas adsorption that possibly penetrates through the junction and reaches the ZnO base.

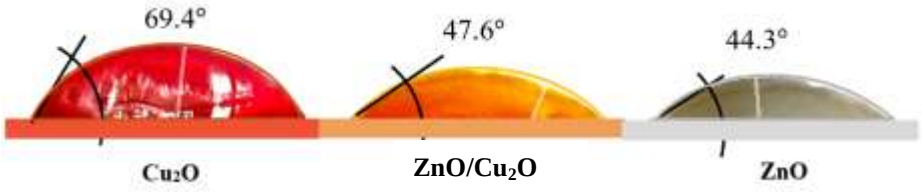

Figure 8: Contact angle variation of a 30 µl distilled water drop placed on the Cu_2O, ZnO/Cu_2O, and ZnO layers ECD on FTO substrates.

LPG sensitivity of ZnO(ECD)/Cu_2O(ECD)

When Cu_2O-ZnO is exposed to UV-vis / natural light (4.43 kW/m² - 5.64 kW/m²), then a significant number of electron-hole pairs will be generated, leading to the excitation of electrons from the valence band (VB) of Cu_2O to its conduction band (CB). This will result in an increased electron flow to the conduction band of ZnO, where photo-generated electrons will react with oxygen molecules in the air (Eq. 12), forming additional photo-induced chemisorbed oxygen species at the interface [6].

$$O_{2(ad)} + e^-(h\nu) \rightarrow O_2{}^-(h\nu) \qquad (12)$$

At one point, the adsorption and desorption of oxygen molecules on the surface of the heterostructure gradually reach a stable equilibrium state (R_a). Upon exposure to LPG at room temperature, the hydrocarbon molecules react with the photo-induced oxygen ions at the ZnO/Cu_2O interface and get reduced as a result of the trapped electrons being transported back to ZnO CB as given in Eq. 13. Therefore, under white light, sufficiently large energy causes an increase in the adsorption and desorption of the gas, and improve response and recovery rate [1,2,7-9].

$$O^{2-} + C_nH_{2n+2} \rightarrow CO_2 + H_2O + 2e^- \qquad (13)$$

The gas response was tested with simultaneous heat treatment of the sensor platform under operating temperatures ranging from room temperature 30 ℃ to 100 ℃. Compared with the Cu_2O maximum LPG responses (<40%) obtained with previous studies [3] under covered dark conditions, the Cu_2O showed pronounced photo responses of 60 % under white light illumination. Moreover, it has also been experimentally observed that the previously unreachable low-temperature operation is possible up to the room temperature level (30 ℃) under white light.

Respectively, ZnO/Cu_2O heterostructures displayed extraordinary gas response of over 100% with the improved visible light absorption brought by Cu_2O and efficient interfacial charge transport. As identified by the sensor responses in Fig. 9(a), Cu_2O seems to be minimally involved in gaseous interactions but actively working as the sensors' visible-light harvester, producing photo-generated electrons.

On the other hand, thermal excitation has induced a great increase in the photo-excited electron kinetic energy that enhances the number of LPG/O_2-film interactions. With this newly gained energy, the electrons create an additional resistance drop with oxygen ionosorption and resistance increases with LPG adsorption (Fig. 9**)**. Thereby increasing sensitivity and recovery time with the temperature. It is to be noted that (as in Fig. 9b), these two combinations can cause a more than 200 % LPG response percentage at greater temperatures such as 100 ℃.

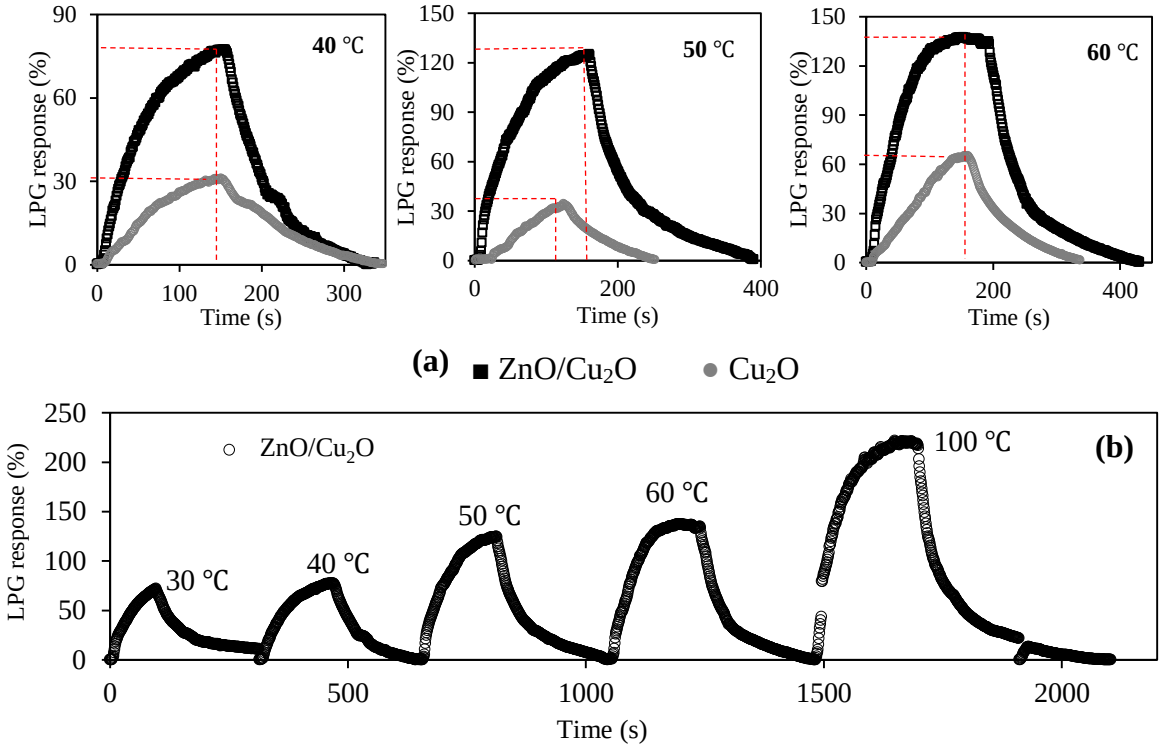

Figure 9: LPG response (a) comparison of Cu_2O and ZnO/Cu_2O heterostructure, and (b) LPG response variation of ZnO/Cu_2O at different temperatures.

5. CONCLUSION

This research investigates the performance of copper oxide-zinc oxide (Cu_2O-ZnO) nanocomposites as gas sensors, particularly focusing on their ability to detect gas at low temperatures. The nanocomposites were prepared by combining p-type Cu_2O with n-type ZnO on an FTO conductive substrate. Two fabrication methods, including electrodeposition and SILAR technique, were utilized to synthesize ZnO on Electrodeposited Cu_2O. The study identified the inability to process with samples ZnO electrodeposited on a Cu_2O layer due to the formation of CuO. The gas sensing experiments of ZnO-Cu_2O heterostructures (deposited side-by-side layers) exhibited an interesting behavior. At shorter deposition times (10 minutes), the sensor showed a p-type behavior that changed to an n-type behavior at longer deposition times of Cu_2O (15 minutes), even though the response was unstable. The partially wetting nature of the ZnO_{ECD}/Cu_2O_{ECD} (sandwiched layers) nanocomposite films contributed to improved gas sensing responses compared to Cu_2O or ZnO. Here the key finding was the role of Cu_2O as a visible light harvester in the ZnO_{ECD}/Cu_2O_{ECD} heterostructure for gas sensing. This

enabled the sensor to operate effectively at room temperature under white light illumination. Displaying a gas response of about ~ 100% at room temperature, which could exceed 200% with higher operating temperatures (above 100°C), making this sensor a promising candidate for practical applications.

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