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Effect of annealing temperature for structural, electrical, and ammonia sensing properties of pristine ZnO and ZnO/SiO_2 nanoparticles

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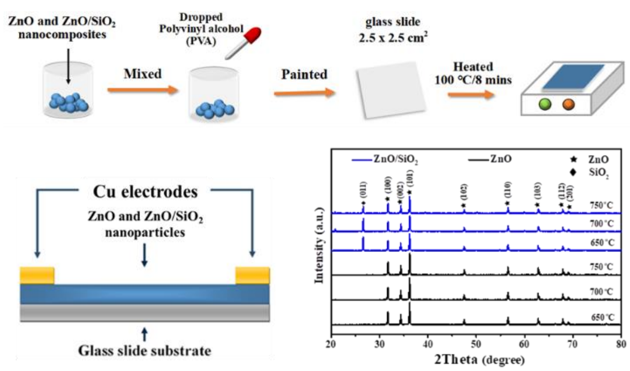
Abstract

The main objective of this research was to study the electrical and gas-sensing properties of Zinc oxide (ZnO) nanoparticles. The samples were divided into two conditions in the preparation process. In the first condition, ZnO powder was annealed at temperatures of 650, 700, and 750 °C for 2 h, while the second condition involved mixing ZnO powder with SiO_2 powder and annealing at temperatures of 650, 700 and 750 °C for 2 h. The characteristics of the prepared samples were studied by scanning electron microscopy (SEM) and the X-ray diffraction technique (XRD). The SEM images showed the agglomeration of the particles with micron-sized diameters. In addition, the XRD patterns of all samples exhibited the hexagonal structure of ZnO. Assessment of the electrical properties of the samples was carried out by forward bias from 0 – 15 V and reverse bias from 0 V to -15 V. The I – V characteristic curves showed diode-like rectifying behavior. The gas-sensing property of the samples was investigated by using ammonia gas, and ZnO nanoparticles annealed at 750 ºC for 2 h were found to have the highest sensitivity.



Keywords: ZnO; ZnO/SiO_2; ZnO nanoparticles; electrical properties; Gas sensing properties

Introduction

Ammonia is a volatile organic compound (VOC) gas that is toxic to human health. The chemical formula of ammonia is NH_3. At room temperature, ammonia is a colorless gas with a very pungent smell. Ammonia is widely used in various industries such as industrial refrigeration, ice manufacturing, pharmaceuticals, and the food industry, all of which closely relate to daily life. The leakage of ammonia presents a significant health hazard. Accordingly, studies concerning gas leakage detection have been conducted attentively. The leakage of toxic gases can be detected by sensors fabricated from various materials such as polymers, covalent organic frameworks, metal oxide semiconductors, nanocomposite materials, thin films, and heterojunction materials. These materials offer benefits including low cost, high performance, and high stability. Sensors can be designed to detect at low temperatures and high sensitivity [1 – 6]. Zinc oxide (ZnO) nanomaterials have received significant attention from researchers and scientists due to their numerous beneficial properties such as high sensitivity, good selectivity, low cost, operation at low temperatures, fast response and short recovery time [7 – 8]. Normally, ZnO nanomaterials are synthesized by methods such as co-precipitation, chemical vapor deposition (CVD), physical vapor deposition (PVD), sputtering, sol-gel, precipitation, hydrothermal, and spin coating [9]. Moreover, various synthesis methods can be employed to synthesize different ZnO nanostructures such as nanorods, nanowires, nanoparticles, nanorings, nanotubes, and nanosheets.

Recent studies have been conducted to investigate ZnO nanostructure-based gas sensors. Cao Cheng et al. fabricated a ZnO/CuO heterojunction by using the hydrothermal method. The ZnO/CuO heterojunction shows high performance for ammonia gas detection at room temperature. The ZnO/CuO heterojunction has been reported to exhibit a detection limit as low as 0.39 ppm, as well as fast response and recovery time [10]. Mingjia Bai et al. synthesized a ZnO nanorod/SnO_2 film heterojunction in one step by using the chemical vapor deposition (CVD) process. The ZnO nanorod/SnO_2 film heterojunction demonstrates a highly selective and responsive value for NO_2 gas sensing [6]. Moreover, Tongwei Yuan et al. fabricated the n-ZnO/p-Co_3O_4 heterojunction materials by using the ion-etching method. It has excellent gas sensing performance to carbon monoxide (CO) gas and has a high response value with Rg/Ra = 35.40 at 50 ppm for CO gas [11]. The ZnO/CuO nanoflower on graphene printed on paper substrates, prepared by the hydrothermal method, demonstrates a higher sensitivity for ammonia (4.90%) gas at a low concentration of 5 ppm at room temperature. This work was reported by Mohanraj Jagannathan et al. [12]. In addition, Mehrdad Asgari et al. fabricated SiO_2/ZnO core/shell nanostructures using a facile ultrasonic-assisted deposition-precipitation method, resulting in a highly selective and sensitive sensor for ethanol gas at low temperatures [13]. Later, Susan Samadi et al. synthesized ZnO@SiO_2/rGO core/shell nanocomposites using the sol-gel-assisted hydrothermal method. The ZnO@SiO_2/rGO core/shell nanocomposites exhibited excellent sensitivity to 1-propanol with a concentration of 300 ppm at ambient temperature [14].

In this work, the authors present ZnO and ZnO/SiO_2 nanoparticles that were annealed at various temperatures of 650, 700, and 750 °C under an air atmosphere. The samples were measured for sensitivity to ammonia gas at room temperature, and the electrical and sensitivity properties of the ZnO and ZnO/SiO_2 nanoparticles were reported.

Materials and Methods

Preparation of ZnO nanoparticles and ZnO/SiO_2 heterojunction nanocomposite materials

The samples were prepared under two conditions. In the first condition, one gram of ZnO powder was annealed at temperatures of 650, 700, and 750 °C, respectively. In the second condition, ZnO powder was mixed with SiO_2 powder at a weight ratio of 1:0.50. Afterward, the mixture was annealed at temperatures of 650, 700, and 750 °C for 2 h, respectively.

Characterization of the samples

After the temperature of the furnace was cooled to room temperature, the samples were taken out for further measurements. The morphology was determined by scanning electron microscopy (SEM), and the crystal structures were characterized by the X-ray diffraction

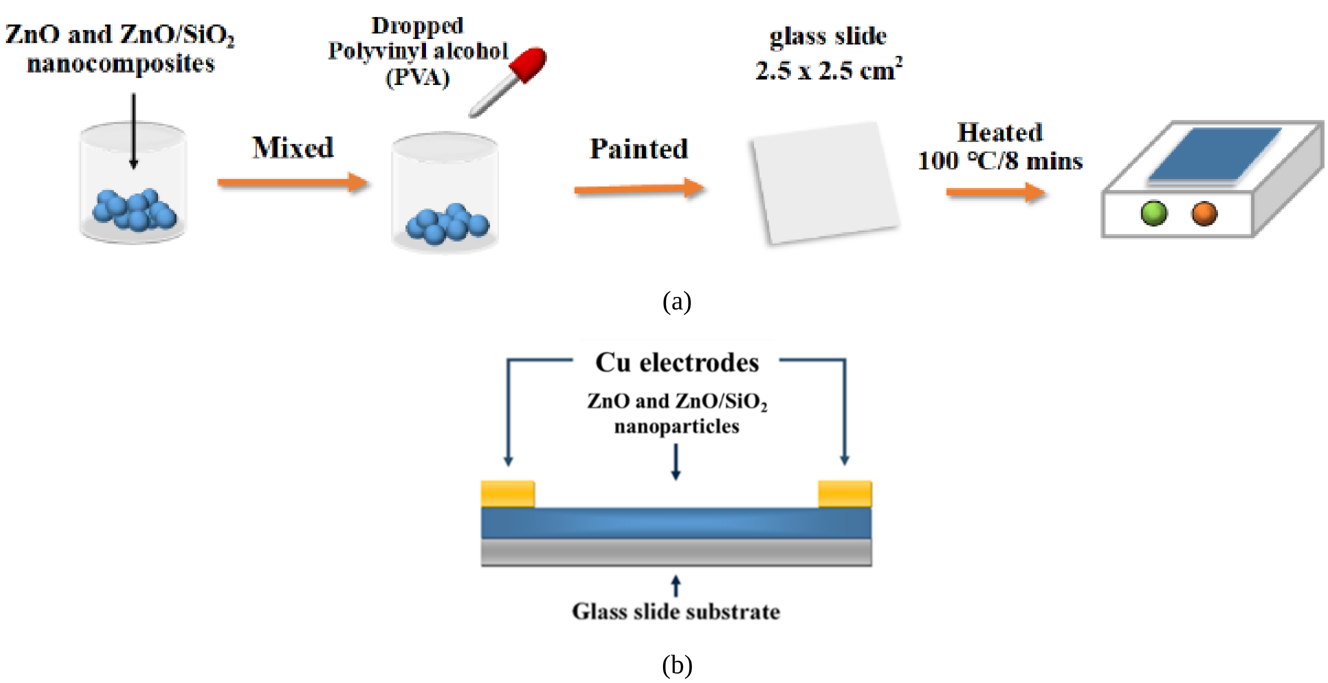
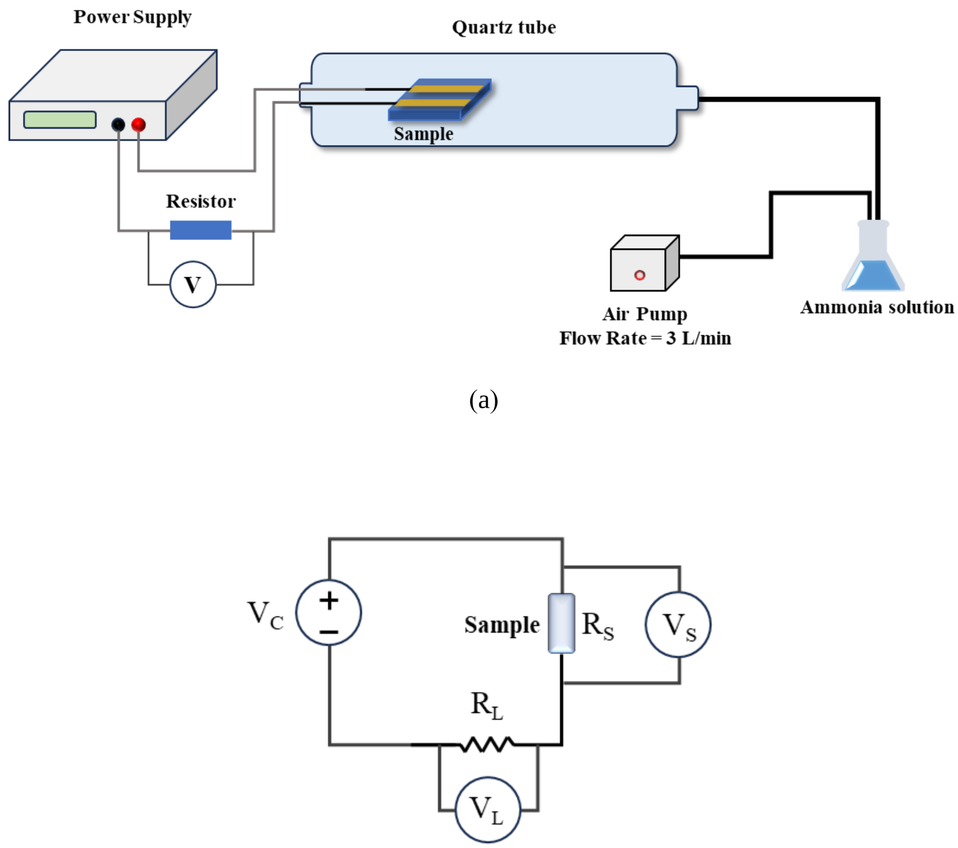


Fig. 1 (a) – (b) Fabrication of the samples for I-V characteristics and ammonia gas sensor measurement**.**



(b)

Fig. 2 (a) Diagram of a detection test system and **(b)** an electrical circuit for gas detection.

(XRD) technique (X'Pert MPD, Philips) using Cu Kα radiation at a wavelength of 1.5406 angstroms.

Fabrication of samples to assess I-V characteristics and ammonia sensor measurement

Fig. 1 shows the fabrication of samples for assessment of I-V characteristics and ammonia gas sensor measurement. Firstly, the glass slides with dimensions of 2.50 × 2.50 cm^2 were used as substrates. The ZnO and ZnO/SiO_2 samples were mixed with polyvinyl alcohol (PVA) [15]. Afterwards, the samples were heated on a hot plate at a temperature of 100 °C for 8 minutes. Subsequently, the electrical properties of the samples were studied by I–V curve characteristics. Finally, the sensitivity properties were measured under an ammonia atmosphere at room temperature for 300 s. Fig. 2(a) – (b) shows the gas detection test system and electrical circuit used for this test. In the gas sensitivity test, the V_L value is measured using an electrical circuit, as shown in Fig. 2(b). Next, the V_S value from Eq. (1) is calculated. Finally, the R_S value is determined using Ohm's Law.

$$V_C = V_L + V_S \qquad (1)$$

Sensitivity can be calculated by the following eq. (2) – (3).

$$S = \frac{R_a}{R_g} \quad \text{when } R_a > R_g \qquad (2)$$

and

$$S = \frac{R_g}{R_a} \quad \text{when } R_g > R_a \qquad (3)$$

where S is sensitivity, R_g is sensitivity under ammonia atmosphere and R_a is sensitivity under air atmosphere [15 – 17].

Results and Discussions

The crystal structures of ZnO and ZnO/SiO_2 nanoparticles were investigated using the XRD technique. In Fig. 3, the XRD patterns of the samples are demonstrated. The results show the phases of ZnO nanoparticles in black lines and ZnO/SiO_2 nanoparticles in blue lines. The XRD patterns of ZnO nanoparticles exhibit planes of (100), (002), (101), (102), (110), (103), (112), and (201), corresponding to peaks at 31.74°, 34.38°, 36.21°, 47.48°, 56.54°, 62.78°, 67.87°, and 69.01° (JCPDS NO. 01-076-0704) [18 – 19], respectively. Moreover, the crystal system of the ZnO nanoparticles is hexagonal. In terms of ZnO/SiO_2 nanoparticles, the XRD patterns in blue lines show a peak of SiO_2 at 26.63°. This peak corresponds to a plane of (011). Moreover, the crystallite size of ZnO and ZnO/SiO_2 nanoparticles can be calculated using the Scherrer eq., as shown in eq. (4).

$$D = \frac{k\lambda}{\beta\cos\theta} \tag{4}$$

The crystallite sizes of ZnO nanoparticles are 466.22, 466.87, and 471.13 nm, while the crystallite sizes of ZnO/SiO_2 nanoparticles are 462.66, 460.71, and 476.45 nm in diameter. These sizes correspond to heating temperatures of 650, 700, and 750 °C, respectively. Considering the size of the crystals, it was observed that there were slight variations in their sizes.

The morphology of the samples was investigated using the SEM technique. Fig. 4 (a-f) shows ZnO and ZnO/SiO_2 nanoparticles. The ZnO and ZnO/SiO_2 nanoparticles are approximately 200 – 500 nm in diameter. Additionally, the results show that the ZnO and ZnO/SiO_2 nanoparticles have an asymmetric shape but are not uniformly distributed. The I-V characteristic curves of ZnO and ZnO/SiO_2 nanoparticles are shown in Fig. 5. The results demonstrate a non-linear relation and diode-like rectifying behavior [20].

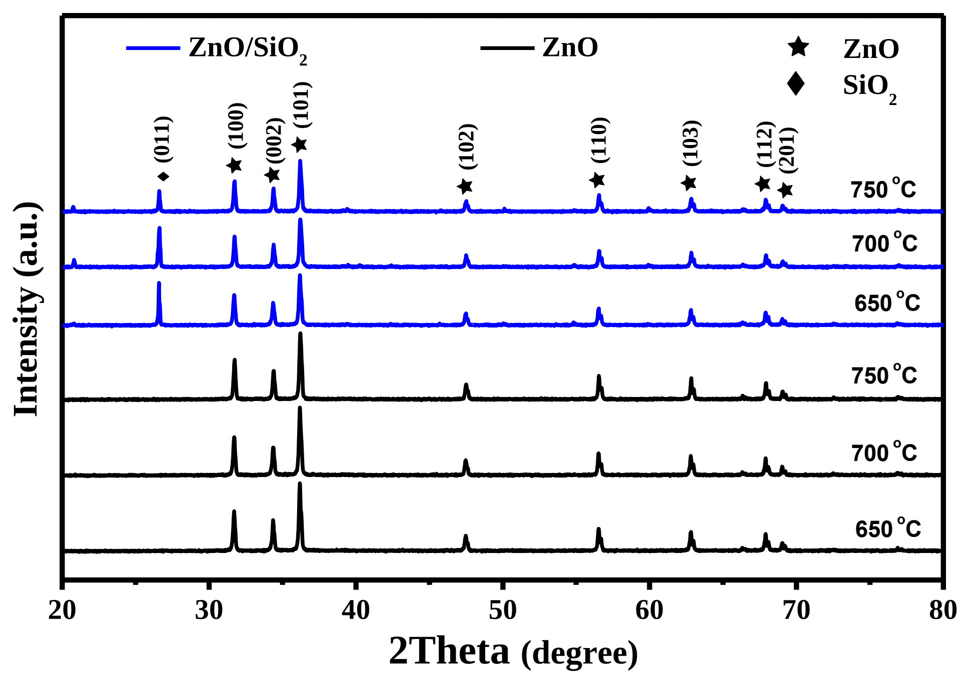


Fig. 3 XRD patterns of ZnO and ZnO/SiO_2 nanoparticles annealed at temperatures of 650, 700 and 750 °C

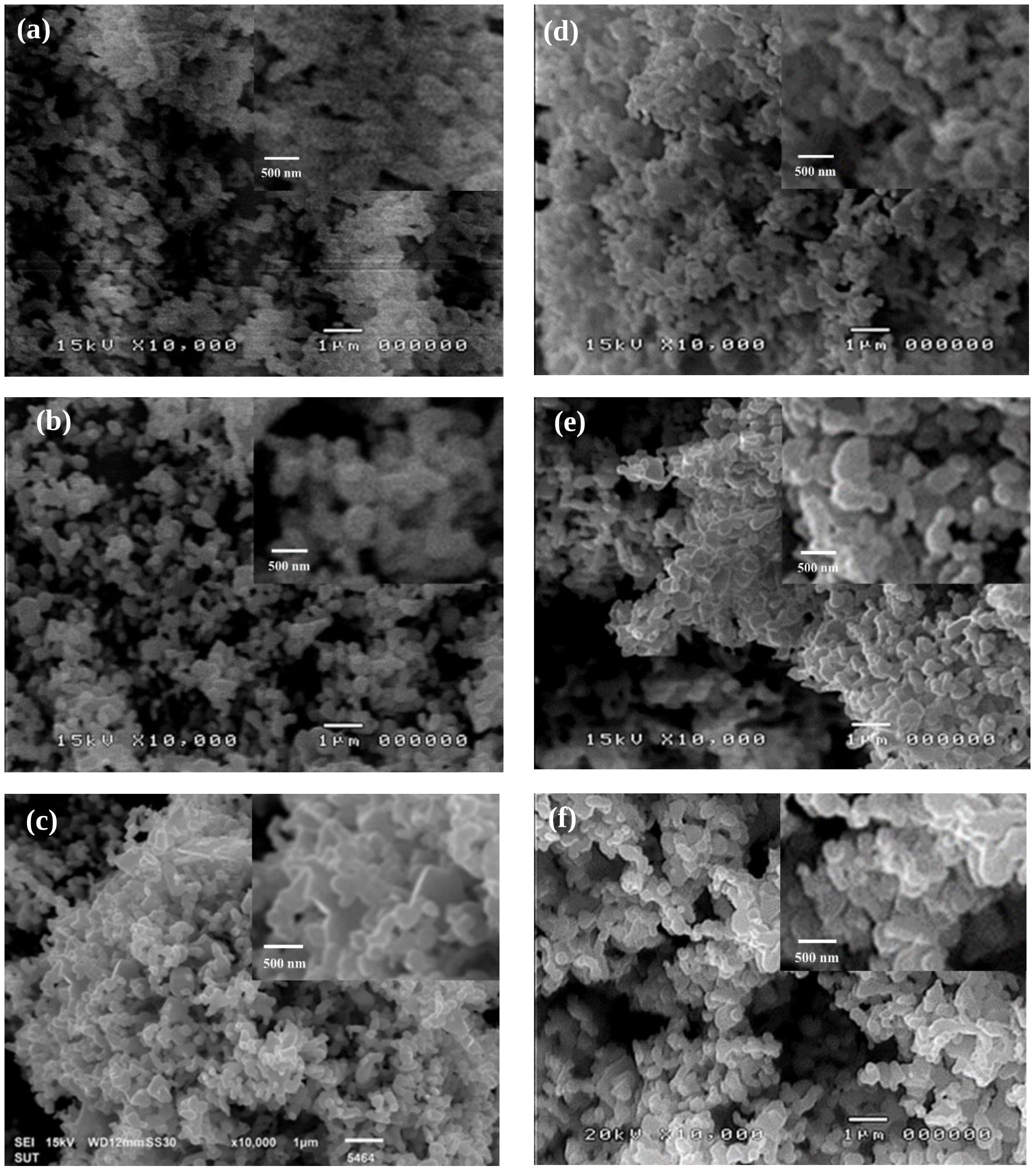


Fig. 4 (a) – (c) Morphology of ZnO nanoparticles annealed at temperatures of 650, 700, and 750 °C, and (d) – (f) the morphology of ZnO/SiO_2 nanoparticles annealed at temperatures of 650, 700 and 750 °C

Fig. 6 (a) shows the sensitivity of ZnO and ZnO/SiO_2 nanoparticles at room temperature under ammonia atmospheres for 300 s. The results indicate that the sensitivity of ZnO nanoparticles is higher than that of ZnO/SiO_2 nanoparticles [13]. The highest sensitivity values for ZnO nanoparticles at heating temperatures of 650, 700, and 750 °C, are 23.73, 22.49, and 24.22 for 300 s, respectively. The highest sensitivity values for the samples during 300 s of testing are not significantly different. For less than 50 s, however, the sensitivity of ZnO nanoparticles at a heating temperature of 700 °C depicts the fastest response.

Furthermore, the sensitivity of ZnO/SiO_2 nanoparticles is less than that of ZnO nanoparticles, but their sensitivity lines are smoother than those of ZnO nanoparticles (Fig. 6 (b) – (c)). The combination of ZnO and SiO_2 may improve the smoothness of the sensitivity curves, though further studies are required. The smoothness of the sensitivity curves indicates increased sensitivity in relation to the time of exposure to ammonia gas. Meanwhile, the sensitivity curve of ZnO nanoparticles decreased in some range. Based on the experimental results, it can be said that the ZnO nanoparticles sensor is less stable than the ZnO/SiO_2 nanoparticles sensor.

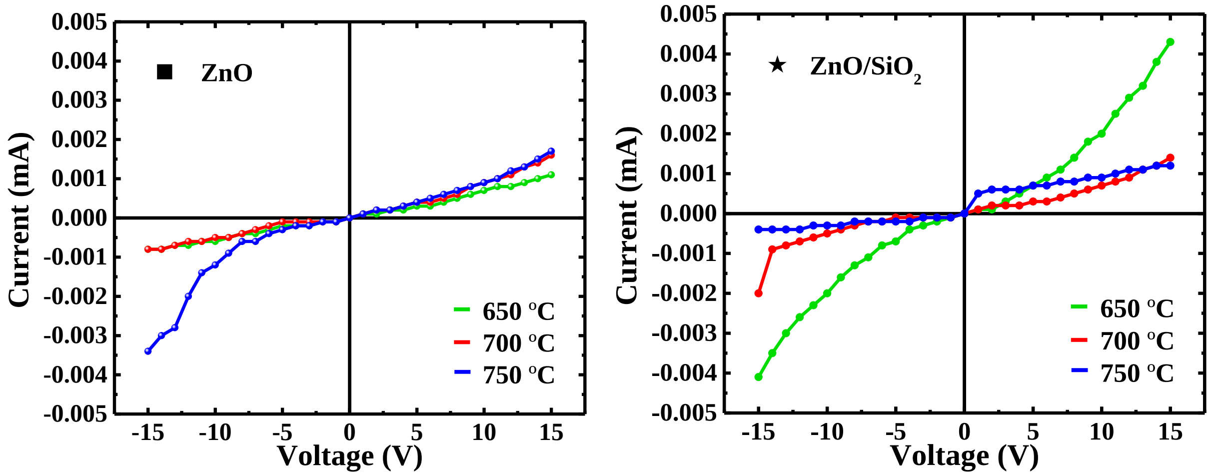


Fig. 5 I-V characteristics curves of ZnO and ZnO/SiO_2 nanoparticles annealed at temperatures of 650, 700, and 750 °C.

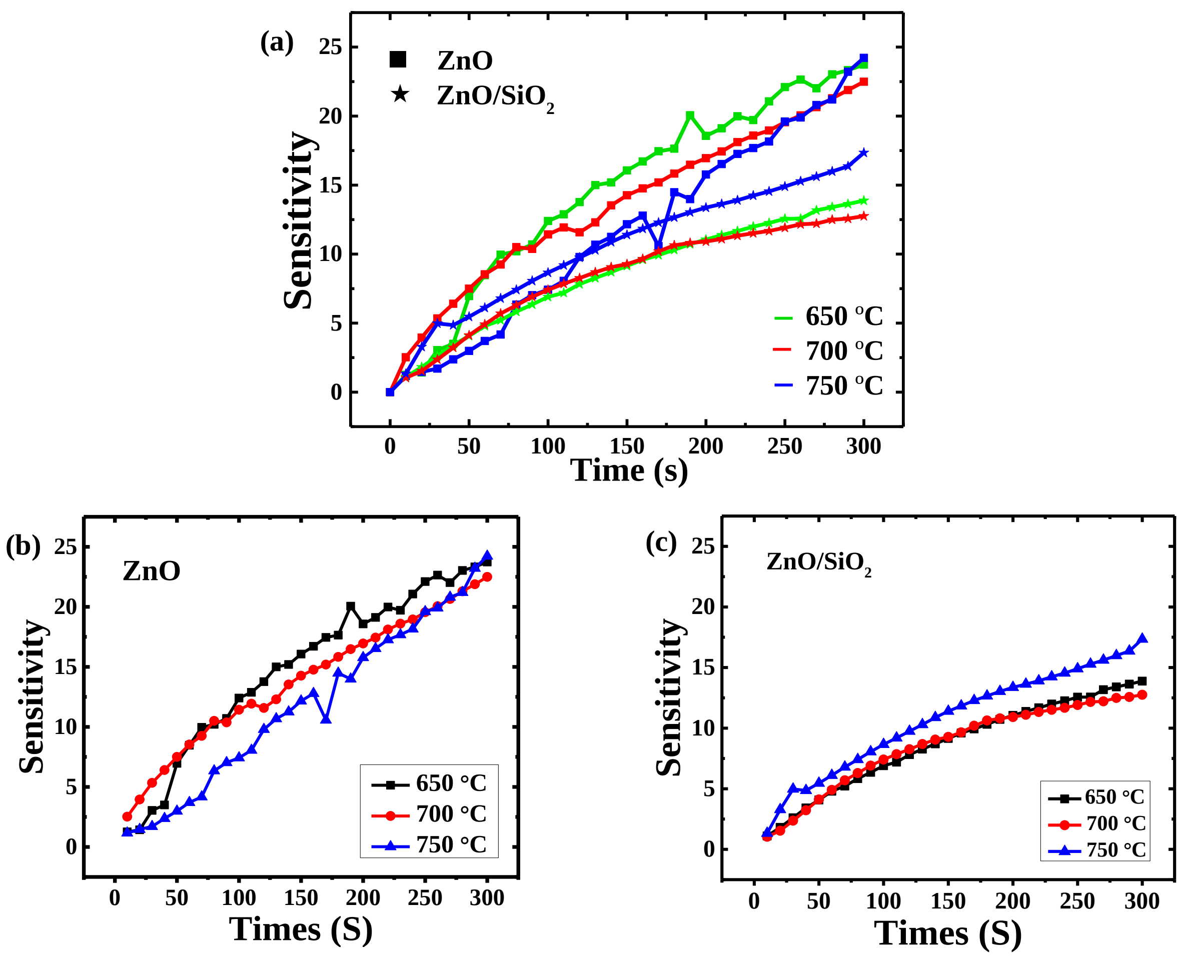


Fig. 6 Sensitivity of ZnO and ZnO/SiO_2 nanoparticles annealed at temperatures of 650, 700, and 750 °C.

Conclusion

ZnO and ZnO/SiO_2 nanoparticles were annealed at temperatures of 650, 700, and 750 °C in an air atmosphere. The current–voltage characteristics showed diode-like rectifying behavior. The ZnO nanoparticles showed a higher sensitivity to ammonia gas compared to the ZnO/SiO_2 nanoparticles. However, the ZnO/SiO_2 nanoparticles showed a smoother linear sensitivity for ammonia sensing at room temperature. The smooth curves indicate a relative increase in sensitivity with time of exposure to ammonia gas. Meanwhile, the sensitivity curve of ZnO nanoparticles decreased at certain periods.

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