



Enhanced humidity sensing performance using Sn-Doped ZnO nanorod Array/SnO₂ nanowire heteronetwork fabricated via two-step solution immersion



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ABSTRACT

A unique heteronetwork consisting of crystalline tin-doped zinc oxide nanorod arrays and rutile tin oxide nanowires (SZO/SnO₂) was fabricated for the first time using a two-step solution immersion method at a low temperature and immersion time (2 h) for humidity sensing applications. The average diameter and thickness of the SZO are approximately 95 and 730 nm, respectively. The diameter of the SnO₂ nanowires ranges from 60 nm to 120 nm, and the length of the nanowire is approximately 10 μm. The SZO/SnO₂-based humidity sensor exhibits high stability and superior humidity sensing performance compared with the SZO-, SnO₂-, and ZnO/SnO₂-based sensors with a sensitivity of 67.8. Results demonstrate that the unique architecture of SZO/SnO₂ heteronetwork can enhance the humidity sensing capabilities of the nanowires.

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1. Introduction

The regulation of humidity level in the surroundings is a huge challenge considering the possible adversities that may occur due to uncontrollable humidity. Currently, a huge demand for using humidity sensors, especially in medical, agricultural, industrial, and food processing industries, is observed. Low processing cost, high sensitivity to humidity changes, long-term stability, and rapid response/recovery time remain to be the main interests of humidity sensor development. Thus, researchers have implemented various types of materials for humidity sensing applications, in which zinc oxide (ZnO) and tin oxide (SnO₂) are considered among the best materials because of their astounding properties and versatility. Furthermore, the manipulations of the ZnO/SnO₂ heterostructures improve the performance of devices [1,2]. The present research focused on fabricating a relative humidity (RH)-type humidity sensor utilizing Sn-doped ZnO nanorod arrays/SnO₂ nanowires (SZO/SnO₂) as the sensing membrane. The heteronet-

work film was prepared through a two-step low-temperature solution immersion method at low immersion time of 2 h. To the best of our knowledge, the application of SZO/SnO₂ through the above-mentioned method for humidity sensing is scarcely reported.

2. Experimental procedure

A SZO/SnO₂ heteronetwork was synthesized on a glass coated aluminum-doped ZnO seed-layer film. The seed layer preparation is described in a different paper [3]. For the SZO preparation, 0.1 M zinc nitrate hexahydrate, 0.1 M hexamethylenetetramine, and 0.001 M tin (IV) chloride pentahydrate were dissolved in deionized (DI) water before sonication at 50 °C for 30 min. Then, the solution was aged at room temperature for 3 h and transferred into a vessel containing a seed layer-coated substrate. The vessel was immersed into a water bath tank at 95 °C for 1 h. The resulting SZO sample was cleaned, dried, and annealed at 500 °C for 1 h. Undoped ZnO film was also prepared using similar procedure but without Sn-doping. The SnO₂ nanowires were deposited onto the SZO film through the following procedures: first, a 0.05 M tin (IV) chloride pentahydrate, 0.1 M sodium hydroxide, 125 ml ethanol, and 125 ml DI water were mixed and vigorously stirred for 1 h. Then, the prepared solution was transferred into a vessel, and then

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the SZO-coated substrate was immersed into the solution at 25 °C for 10 min. The SnO₂ nanowires were also deposited onto undoped ZnO film and bare glass substrate for comparison. Next, the film was annealed at 500 °C for 1 h. The structural properties of SZO and SZO/SnO₂ were characterized by using field emission scanning electron microscopy (FESEM; JEOL JSM–7600 F), energy dispersive X-ray spectroscopy (EDX; Oxford Instruments), and X-ray diffraction (XRD; PANalytical X'Pert PRO). The optical properties of SZO and SZO/SnO₂ were investigated using ultraviolet–visible spectroscopy (Varian Cary 5000). The sensor performance of SZO, SnO₂, ZnO/SnO₂, and SZO/SnO₂ was characterized using a humidity chamber (ESPEC-SH261) equipped with a sensor measurement system (Keithley 2400).

3. Results and discussion

The surface morphology and cross-sectional images of SZO are depicted in Fig. 1(a) and (b). Highly dense and well-aligned nanorod arrays were uniformly deposited on the substrate with an average diameter and thickness of approximately 95 and 730 nm, respectively. Fig. 1(c) and (d) illustrate the surface morphology of SZO/SnO₂ at 1,500× and 50,000× magnifications, respectively. The images reveal that the SnO₂ nanowires are arbitrarily oriented on the SZO with multiple directions, thereby enhancing the surface area and porous channels of the film, in

the process. The diameter of the nanowires ranges from 60 nm to 120 nm. The cross-sectional images of the SZO/SnO₂ in Fig. 1 (e) and (f) show that heteronetwork was formed between SZO and SnO₂, with the length of the nanowires extended up to 10 μm. The EDX spectrum in Fig. 1(g) shows the heteronetwork film consisting of O, Zn, and Sn with an atomic percentage of 45.58%, 51.79%, and 2.63%, correspondingly.

Fig. 2(a) displays the XRD plot of the films. The diffraction peaks of the SZO film are assigned to the hexagonal wurtzite structure (JCPDS No. 36-1451). The magnified XRD pattern in Fig. 2(b) confirmed that the SnO₂ crystal successfully grew, in which the diffraction peaks correspond to the tetragonal rutile structure of pure SnO₂ (JCPDS No. 41-1445). Fig. 2(c) presents the transmittance properties of the SZO and SZO/SnO₂ films at a wavelength ranging from 350 to 800 nm. The average transmittances of the SZO and SZO/SnO₂ films at a visible region (400–800 nm) are 70% and 9%, respectively. The transmittance was significantly reduced after the SnO₂ deposition due to the increment in film thickness, thereby leading to the enhancement of optical scattering. Fig. 2 (d) illustrates the absorbance spectra of the films. The SZO/SnO₂ film exhibits intense absorbance than the SZO film at the UV region below 400 nm.

Fig.3(a)–(d) present the humidity sensing response of the SZO-, SnO₂-, ZnO/SnO₂-, and SZO/SnO₂-based humidity sensors, respectively, at the humidity level ranging from 40% to 90% RH at 5 V bias.

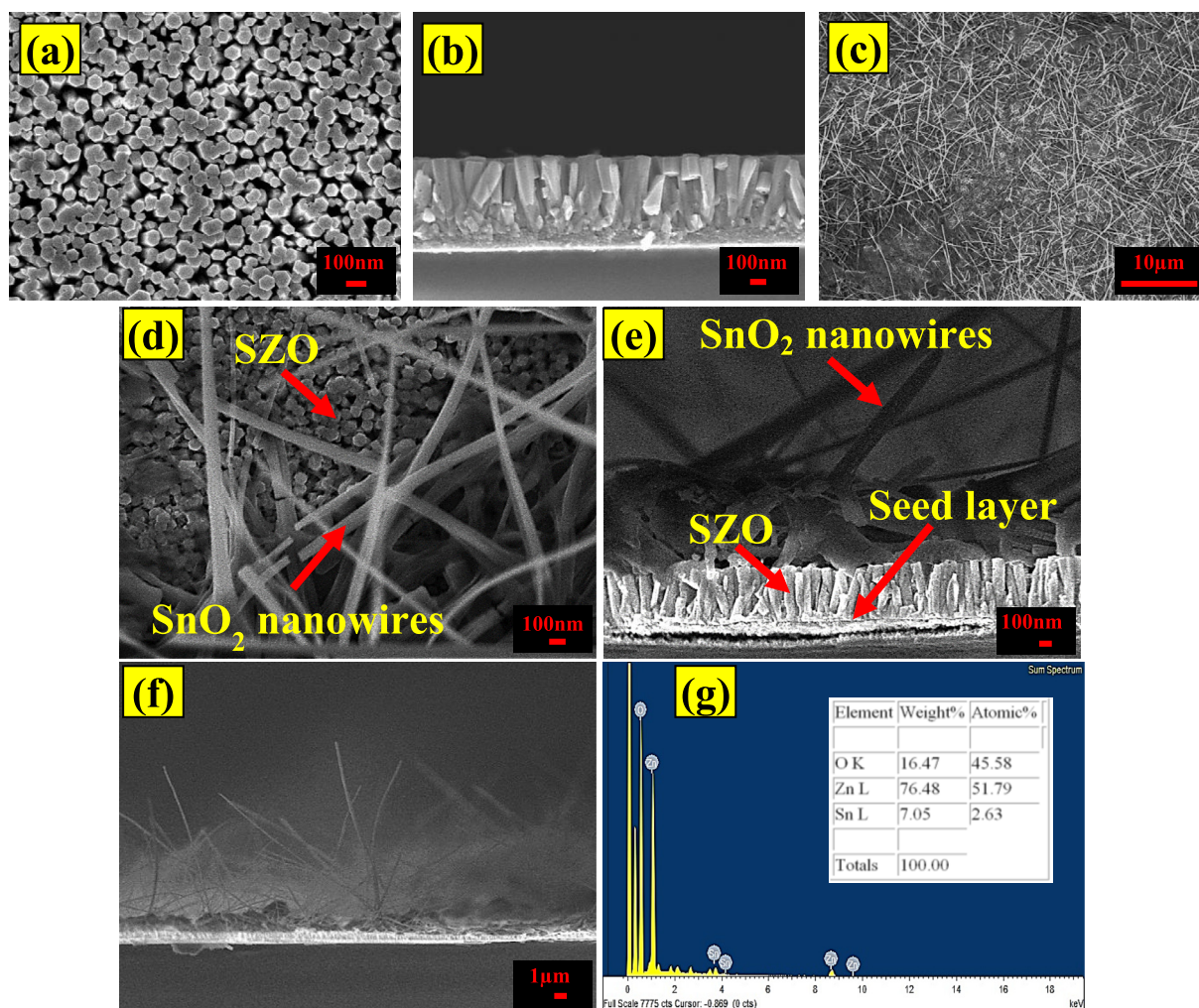


Fig. 1. (a) Surface morphology of SZO at 50,000× magnification. (b) Cross-sectional image of SZO at 50,000× magnification. Surface morphology of SZO/SnO₂ at (c) 1,500× and (d) 50,000× magnifications. Cross-sectional image of SZO/SnO₂ at (e) 30,000× and (f) 3,000× magnifications. (g) EDX spectrum of SZO/SnO₂.

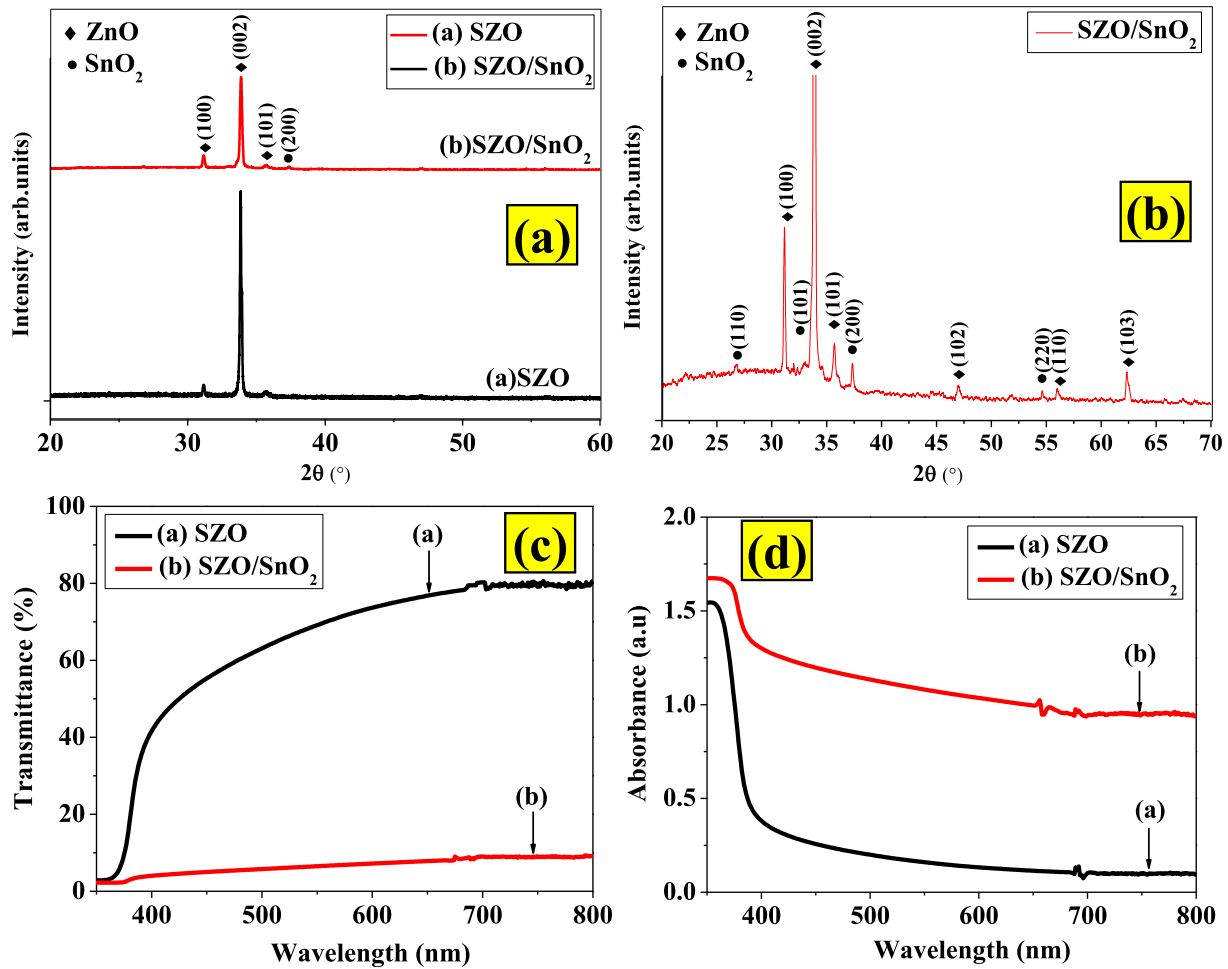


Fig. 2. (a) XRD patterns of SZO and SZO/SnO₂ films. (b) Magnified XRD plot of the SZO/SnO₂ film. (c) Transmittance and (d) absorbance spectra of the SZO and SZO/SnO₂ films.

The sensitivity of the sensors is determined by the following equation:

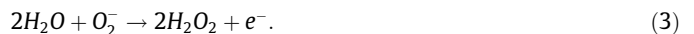
$$S = \frac{R_a}{R_{rh}}, \quad (1)$$

where R_a is the resistance of the sensor under exposure to the initial humidity level, and R_{rh} is the resistance of the sensor at the exposed humidity level. The R_a/R_{rh} values of SZO, SnO₂, ZnO/SnO₂, and SZO/SnO₂ are $4.68 \times 10^8/1.45 \times 10^8$, $1.41 \times 10^8/8.91 \times 10^6$, $1.09 \times 10^8/3.25 \times 10^6$, and $99.01 \times 10^6/1.46 \times 10^6 \Omega$, correspondingly, thereby generating sensitivity values of 3.2, 15.8, 33.5, and 67.8, respectively. The excellent humidity sensing performance of SZO/SnO₂ may be attributed to the substantial enlargement of surface area provided by the SnO₂ nanowire layer, as observed in the FESEM images. Subsequently, the pore channels between the nanorod and nanowire films facilitate additional adsorption sites to water molecules. Based on previous studies, the appearance of a heterojunction between two consecutive films contributes to enhancing the surface area, improving electron transfer, and reducing possibilities of the electron–hole recombination [4–6]. At low humidity levels, oxygen from the environment adsorbs on the sensor surface and traps free electrons, thereby resulting in the formation of adsorbed oxygen ions as expressed by the following equation [7]:



Water molecules react with the sensor surface through a chemisorption process when RH is increased. In addition, water

molecules react with the adsorbed oxygen ions to release free electrons in the process, which can be described by the following relation:



Therefore, the electrical conduction of the sensor is increased. Water molecules are continuously adsorbed on the sensor surface and form hydrogen bonds with the primary chemisorbed water layers when RH is further increased. The secondary water layers decompose into H_3O^+ and OH^- ions because of the electrostatic field of the primary water layer. Furthermore, H_3O^+ ions can be hydrated and produce H^+ ions. These ions become the main charge carriers, which increases the conductivity of the sensor. The processes can be expressed as follows:



At this stage, the sensing conduction is dominated by the movement of the proton, which hops along the series of water molecules called Grotthuss chain. At extremely high RH, capillary condensation occurs whereby the porous channels between nanorods and nanowires are filled with water. Consequently, the conduction ions freely move between the nanostructures and increase the electrical conduction of the sensors. The surface area and porous channels are enhanced due to the deposited SnO₂ nanowire layer on top of the SZO layer. High charge density regions are also induced in

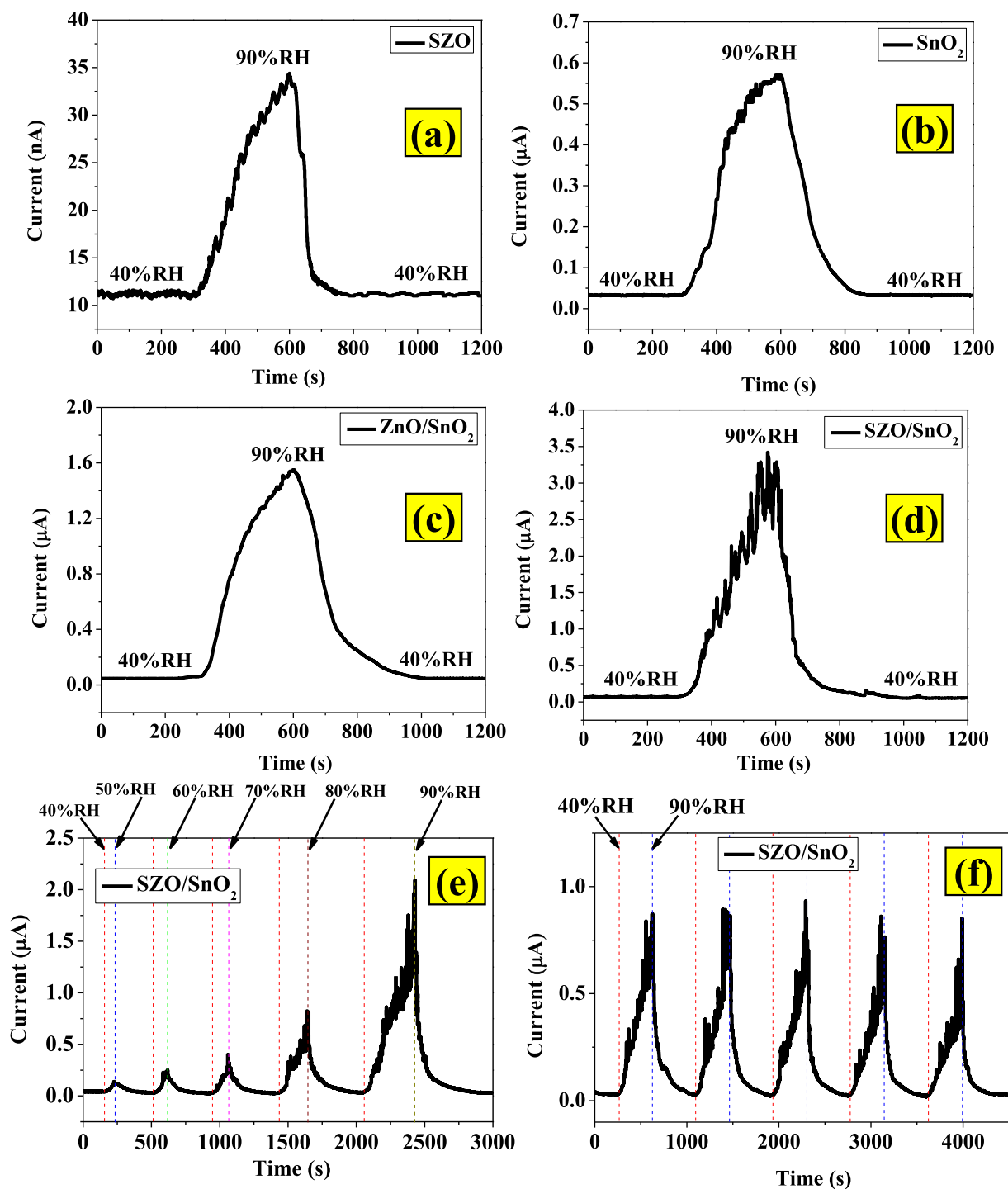


Fig. 3. Humidity sensing responses of (a) SZO-, (b) SnO₂-, (c) ZnO/SnO₂-, and (d) SZO/SnO₂-based humidity sensors. Humidity sensing responses at (e) different RH. (f) Repeatability behavior of the SZO/SnO₂-based humidity sensor.

the heteronetwork film because of the presence of Sn⁴⁺ and Zn²⁺ species, which provide active surface centers for water adsorption. Therefore, generating electrical conduction through Grotthuss chain and capillary condensation are exaggerated, resulting in the remarkable humidity sensing performance of the SZO/SnO₂-based sensor than the SZO-based sensor. The fabrication of bilayered ZnO/SnO₂-based humidity sensors utilizing the nanorod array-nanowire heteronetworks are rarely reported in the literature. However, the fabrications on ZnO/SnO₂-based composite humidity sensors using different configurations and nanostruc-

tures have been reported in the previous studies [8,9]. For example, Misra and co-worker fabricated SnO₂-doped ZnO pellets (disc-shaped pellet with diameter of 12 mm and thickness of 2 mm) by mixing SnO₂ powder into ZnO powder to form SnO₂-ZnO compound structures [9]. The highest humidity sensitivity based on these nanocomposite pellets under humidity level ranging from 15% to 95% RH was 32 MΩ/% RH.

Fig. 3(e) depicts the humidity sensing response of SZO/SnO₂ at five humidity levels ranging from 50% to 90% RH. The sensitivities of 50%, 60%, 70%, 80%, and 90% RH are 2.4, 4.7, 7.9, 16.3, and 67.8,

respectively. This result denotes that the SZO/SnO₂-based humidity sensor is sensitive to the different levels of humidity. Fig. 3(f) displays the stability behavior of the SZO/SnO₂-based humidity sensor, measured by repeatedly exposing the film to 40% and 90% RH for five cycles. The repeatable responses with the identical pattern were observed in the plot, indicating that the sensor exhibits a stable humidity sensing.

4. Conclusion

A unique configuration of SZO and SnO₂ nanowire heteronetwork was successfully synthesized using a two-step solution immersion at low immersion time for humidity sensing applications. The average diameter and thickness of SZO are approximately 95 and 730 nm, respectively. The diameter of the SnO₂ nanowires ranges from 60 nm to 120 nm, and the length is approximately 10 μm. The SZO/SnO₂-based humidity sensor demonstrates high sensitivity to humidity with a value of 67.8, which is significantly higher than bare SZO. These results are attributed to the enhanced surface area and porous channels induced by a unique SZO/SnO₂ heteronetwork film.

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