

Micro Humidity Sensor with High Sensitivity and Quick Response/Recovery Based on ZnO/TiO₂ Composite Nanofibers *

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ZnO/TiO₂ composite nanofibers are synthesized by an electrospinning method and characterized by x-ray diffraction, scanning electron microscopy, and transmission electron microscopy. A micro humidity sensor is fabricated by spinning the precursors of these nanofibers on a ceramic substrate with Ag-Pd interdigitated electrodes. Humidity sensing investigation reveals that this micro sensor offers high sensitivity and quick response/recovery at an operating frequency of 100 Hz. The corresponding impedance changes more than four orders of magnitude within the whole humidity range from 10% to 90% relative humidity (RH), and the response and recovery times are about 4 and 12 s, respectively. The maximum hysteresis is around 2% RH. The humidity sensing mechanism is also discussed based on the nanofiber structure and morphology.

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Humidity sensors are increasingly in demand for personal safety, environmental monitoring, industrial control, and national security because of their small size, low cost, and compatibility with microelectronic technology.^[1,2] Materials for humidity sensors are generally organic polymer thin films or metal oxide nanoparticles,^[3] and these naturally have their own characteristics. Organic polymer films pose many challenges owing to their weak mechanical strength and poor physical or chemical stability.^[4–6] Meanwhile, metal oxide nanoparticles (such as ZnO, TiO₂, SnO₂, and In₂O₃) often suffer from long response and recovery times,^[7] which are mainly due to the aggregation growth among them.^[8,9]

In the last decade, one-dimensional (1D) nanostructures, such as nanowires, nanorods, nanotubes, and nanofibers, have become a focus of intensive research because their physical and chemical properties can be improved in this way.^[10–17] In the sensor field, the small diameter, large surface-to-volume ratio, high density of surface sites, and anti-aggregation characteristics of these 1D nanostructures make them strong candidates for fabricating high performance humidity sensors.^[18–24] Hitherto, a serial of humidity sensors based on metal oxide nanofibers with good humidity sensing properties have been reported.^[25] However, most of them are obtained by grinding the nanofibers to form pastes, and then coating the pastes on substrates.^[26] These processes will surely destroy the material structure and morphology, and decrease the sensor performance accordingly.

Electrospinning is a unique technique that offers a relatively facile and versatile method for the large-

scale synthesis of 1D nanofibers that are exceptionally long in length, uniform in diameter, large in surface area, and particularly diversified in composition.^[24] In this Letter, we present a simple and effective route for the synthesis of ZnO/TiO₂ composite nanofibers. A micro humidity sensor is fabricated by spinning the fiber precursors on the sensor substrate. Excellent humidity sensing properties, such as high sensitivity, quick response/recovery and small hysteresis, are observed in our investigation. The results offer a possible route to employ nanofibers for fabricating practical micro humidity sensors.

Zinc nitrate, tetrabutyl titanate, acetic acid, ethanol, and poly (vinyl pyrrolidone) (PVP, molecular weight 1.3×10^6) were supplied by Beijing Chemical Co. in China. N,N-dimethylformamide (DMF) was bought from Tianjin Tiantai Chemical Co. All chemicals were analytical grade and used as received without further purification. Sensor substrates were bought from Beijing Elite Tech Co. Ltd.

The electrospinning process in the present experiment is similar to that described previously for metal oxide nanofiber synthesis.^[27] In a typical procedure, 2 g of tetrabutyl titanate was mixed with acetic acid (4 mL), ethanol (10 mL), and PVP (0.6 g) in a glove box under vigorous stirring for 30 min. Simultaneously, 0.75 g zinc nitrate was added into a solvent of DMF (6 g), ethanol (10 mL), and PVP (1.2 g) in the other glove box under vigorous stirring for 6 h. Subsequently, both of them were mixed together under stirring for 6 h. The obtained mixture was loaded into a glass syringe and connected to a high-voltage power supply. A voltage of 18 kV was applied between the

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cathode (a flat aluminum foil) and anode (glass syringe) at a distance of 20 cm. The sensor substrate (6 mm×3 mm, 0.5 mm in thickness) with a mask was placed on the aluminum foil. There were four pairs of Ag-Pd interdigitated electrodes (both the width and distance were 200 μm) on the sensor substrate, and the electrodes could be calcined at 850°C without any resistivity change. After spinning, the mask was removed and the substrate was calcined at 600°C for 3 h in air to convert the precursor into crystalline ZnO/TiO₂ composite nanofibers.

The crystal structures of the nanofibers were determined by x-ray powder diffraction (XRD) using an X'Pert MPD Philips diffractometer (Cu Kα x-radiation at 40 kV and 50 mA). The morphologies of the nanofibers were viewed by a scanning electron microscope (SEM, SSX-550, Shimadzu). Transmission electron microscopy (TEM, Model JEM-2000EX, JEOL) was performed with an accelerating voltage of 200 kV.

Humidity sensing properties were measured by a CHS-1 T (Chemical Humidity Sensor-1 Temperature) intelligent humidity sensing analysis system (Beijing Elite Tech Co., Ltd., China). The voltage applied in our studies was ac 1 V, and the frequency varied from 50 Hz to 100 kHz. Two stretch probes were pressed onto the sensor electrodes as lead wires. Humidity ambience for testing the frequency and hysteresis characteristics was generated by using a double-flow humidity source in the analysis system. Two flows with different relative humidity (RH) (3% and 99% RH) were flowed into a test chamber with very precise control to form the target RH condition. Response and recovery characteristics were tested by switching the sensor between two chambers with LiCl (RH value 11% RH) and KNO₃ (RH value 95% RH) saturated salt solutions, respectively.^[28] There were also a standard humidity sensor and a thermometer in our system to monitor the RH value in the chamber and the operating temperature of the sensor, respectively.

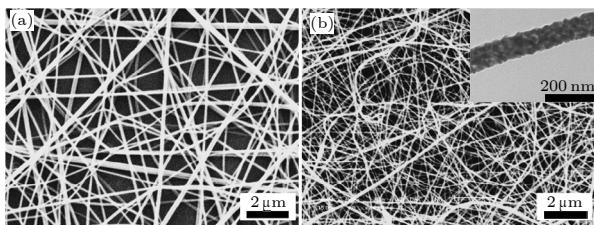


Fig. 1. SEM images of the precursor (a) and calcined nanofibers (b). Inset: a corresponding TEM image.

Figures 1(a) and (b) show the SEM images of the precursor (zinc nitrate/tetrabutyl titanate/PVP fibers) and the ZnO/TiO₂ composite nanofibers, respectively. After calcination, the fiber becomes thinner than the precursor, indicating the removal of the PVP template. From Fig. 1(b) it can be seen that

the final product is dominated by the nanofibers with lengths of several tens of micrometers and diameters ranging from 70 to 120 nm. The average diameter of the nanofibers is about 90 nm. The features of an individual ZnO/TiO₂ composite nanofiber were examined by TEM (inset in Fig. 1(b)). As can be seen, the nanofibers are made up of ultrafine particles with an average diameter of about 20 nm.

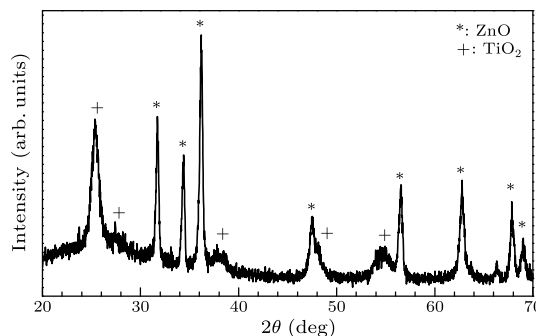


Fig. 2. XRD pattern of ZnO/TiO₂ composite nanofibers.

Figure 2 shows the XRD pattern of ZnO/TiO₂ composite nanofibers. The sample is polycrystalline in nature. All diffraction peaks can be perfectly indexed as the hexagonal wurtzite structure for ZnO and the tetragonal anatase-rutile crystal system for TiO₂,^[28,29] suggesting the high crystallinity of the nanofibers after calcining at 600°C for 3 h. No characteristic peaks for impurity are observed. It should also be noted that TiO₂-based materials with different crystallographic structures (anatase, rutile, and brookite) exhibit various physical and chemical properties.^[30] TiO₂ nanofibers with anatase-rutile mixed structures are expected to be the ideal materials for humidity sensors due to the dissociating promoting effect.^[29] Thus the composite nanofibers with mixed TiO₂ structures in this case may also be considered as good candidates to show high sensitivity.

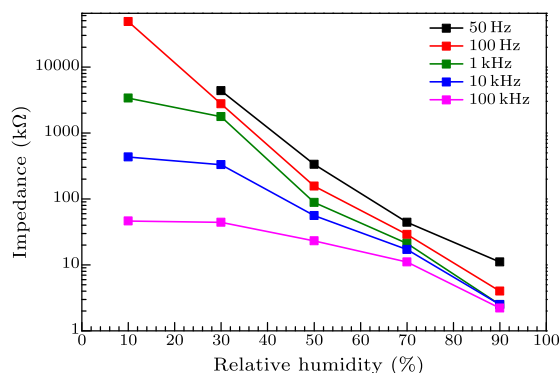


Fig. 3. Variations in sensor impedance as a function of RH at different frequencies.

Figure 3 shows the impedances of the as-fabricated sensor under various RH conditions at different frequencies. The impedance curves are found to de-

crease with increasing RH at each frequency. The largest impedance change may appear at 50 Hz, but the electric signal is out of the testing range of our measurement (over 100 M Ω) at 10% RH. Such high impedances at this frequency will need complex amplifying circuits and strict testing conditions for applications, thus leading to low practicability.^[31] Therefore, we move our focus to the characteristic curve at 100 Hz, which owns both high impedance change (high sensitivity) and good linearity. It can be found that the impedance decreases more than four orders of magnitude within the whole humidity range from 10% to 90% RH at this frequency, indicating a high humidity sensitivity of this micro sensor. The impedance turns flat at high frequency, which is due to the fact that the adsorbed water cannot be polarized at higher frequencies.^[29]

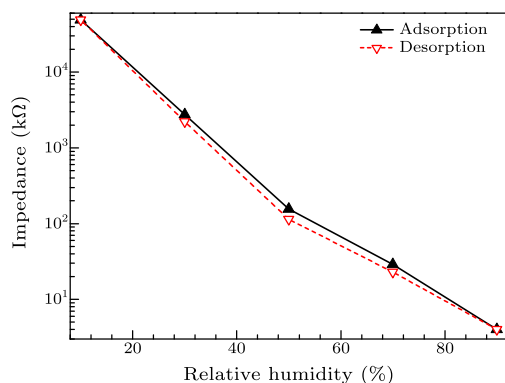


Fig. 4. Sensor hysteresis measured at 100 Hz.

Sensor hysteresis is examined to obtain some information about the reliability. As shown in Fig. 4, the impedance on desorption process is slightly lower than that of the absorption process, and based on the desorption process of the absorbed water in the humid membrane, it is slower than that of the absorption process. The maximum hysteresis is around 2% RH at about 50% RH, indicating good reliability of the micro humidity sensor.

Response and recovery behaviors are important characteristics for evaluating the performance of sensing materials. To test the response/recovery times accurately, we use a saturated-salt-solution humidity source instead of the double-flow humidity source (which needs more time to balance). The time taken by the sensor to achieve 90% of the total impedance change is defined as the response time in the case of adsorption or the recovery time in the case of desorption. From Fig. 5 we can see that the impedance becomes stable within 4 s after it is exposed to 95% RH, and returns to the original values within 12 s after the condition is replaced by 11% RH. Thus the response time (humidification from 11% to 95% RH) and recovery time (desiccation from 95% to 11% RH) are about

4 and 12 s, respectively. As humidity sensors usually operate at room temperature, their response and recovery times are relatively long. Many humidity sensors need several minutes to reach steady states, and the response and recovery times of the order of several tens of seconds are considered high speed with the current technology.^[7] This sensor exhibits very short response/recovery times, mainly due to the fiber structure and morphology. The details are discussed below.

The qualitative mechanism to explain the humidity sensing properties of metal-oxide based sensors was presented in many earlier papers.^[1,26,32] Briefly, the increase in conductivity with increasing RH is based on the reaction on the surface (surface mechanism). At low RH, the tips and defects of the metal oxides present a high local charge density and a strong electrostatic field, which promote water dissociation. The dissociation provides protons as charge carriers of the hopping transport. At high RH, one or several serial water layers are formed among metal oxides, and electrolytic conduction between sensing materials takes place along with protonic transport and becomes dominating in the transport process.

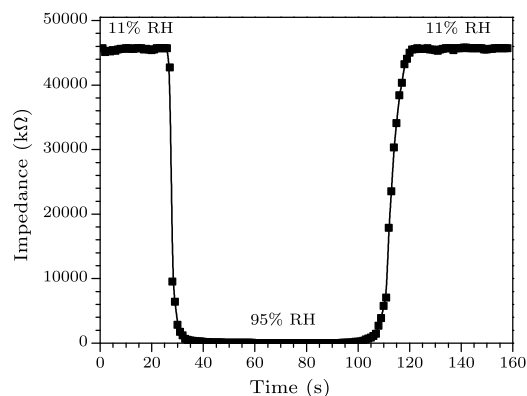


Fig. 5. Response and recovery characteristics of the sensor measured at 100 Hz.

TiO₂ is a traditional sensing material that has been proved to be sensitive to many gases and humidity. Researchers usually use alkali compounds (such as LiCl, KCl, and NaCl) to enhance the humidity sensing properties of TiO₂ owing to the high solubility of these alkali compounds.^[29] However, the high solubility may also lead to a large hysteresis and a poor long-term stability for these humidity sensors. The present sensor exhibits high sensitivity to RH without any alkali dopants, which can be explained by considering the fiber structure and morphology. TiO₂ with mixed structures produces more defects in the nanofibers, leading more H₂O molecules to dissociate.^[29,32] Simultaneously, ZnO is also a humidity sensing material, which can increase the amount of tips and defects in the nanofibers further.^[1] Adding ZnO in TiO₂ has been proved to be an effective sensing enhancing

method because of the coupling transport in the interface of these two different materials. Reports relating this effect are widely found for metal oxide-based nanoparticles or thin films (especially for $\text{SnO}_2\text{-ZnO}$ and $\text{In}_2\text{O}_3\text{-ZnO}$),^[33,34] and we think that this coupling transport may also take place in 1D nanofibers.

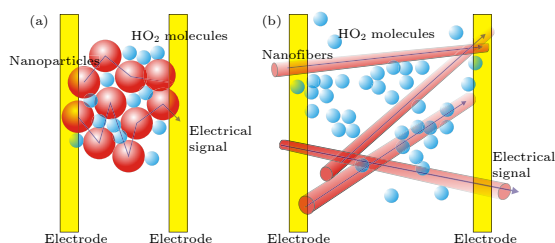


Fig. 6. Schematic illustration of the humidity sensing mechanism of nanoparticles (a) and nanofibers (b).

Moreover, the present sensor is fabricated without any grinding, thus the fiber morphology can be completely preserved on the sensor surface. Compared with nanoparticle materials (Fig. 6(a)), the net-like structure of nanofibers combined with their much larger holes makes the absorption of water molecules on the surface of the material easy (Fig. 6(b)).^[35] On the other hand, the large surface-to-volume ratio of 1D nanofibers and the congruence of the carrier screening length with their lateral dimensions make them highly sensitive and efficient transducers of surface chemical processes into electrical signals.^[35] All of these factors eventually lead to the high humidity sensing properties of the as-fabricated micro sensor.

In conclusion, a micro humidity sensor is fabricated by spinning the precursors of ZnO/TiO_2 composite nanofibers on a sensor substrate directly. After calcination, the sensor exhibits high humidity sensing properties in our investigation. The impedance changes more than four orders of magnitude within the whole humidity range from 10% to 90% RH. The response and recovery times are about 4 and 12 s, respectively. The maximum hysteresis is around 2% RH. These results make the as-fabricated sensor a good candidate for practical applications. Moreover, the experimental process may offer a possible route to employ electrospinning in micro sensor fabrication.

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