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Humidity sensing properties of KCl-doped ZnO nanofibers with super-rapid response and recovery

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ABSTRACT

KCl-doped ZnO nanofibers are synthesized via an electrospinning method and characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The humidity sensing properties of these nanofibers are investigated by screen-printing them on a ceramic substrate with a pair of Ag–Pd interdigitated electrodes. The experimental results show that the 5.7 wt% KCl-doped ZnO nanofibers hold super-rapid response and recovery, high response value, good reproducibility, linearity, selectivity, and stability at 100 Hz. Especially, the response time and recovery time is only about 2 and 1 s, respectively. These results demonstrate the potential application of KCl-doped ZnO nanofibers for fabricating high performance humidity sensors.

1. Introduction

Chemical sensors play a major role in environmental sensing, personal safety, industrial production, and national security, with economic impact in medicine, agriculture, and in the automotive and aerospace industries [1–3]. Most chemical sensors operate on the basis of modification of electrical properties of an active element, normally a metal-oxide film, brought about by the adsorption of an analyte on the surface of the sensing film [4–6]. In recent years, one-dimensional (1D) nanostructure materials have received considerable attention due to their remarkable optoelectronic and electronic properties [7–10]. In particular, 1D metal-oxide semiconductor (e.g., SnO_2, ZnO, TiO_2, and In_2O_3) nanostructures are very interesting from the point of view of application in chemical sensors [11]. Of these, ZnO is recognized as one of the key functional metal-oxide semiconductors owing to its outstanding optical, electrical and piezoelectrical properties [12]. Recently, a series of 1D ZnO nanostructures, such as nanorods, nanotubes, nanowires, and nanobelts have been successfully synthesized and applied in chemical sensors [13]. Their excellent sensing characteristics are based on the high surface-to-volume ratio (a higher surface area provides more sites for analyte molecules adsorption), which means these molecules can be effectively adsorbed on the surfaces of the sensing materials [14–16]. At the same time, 1D nanostructures can facilitate fast mass transfer of the analyte molecules to and from the interaction region as well as require charge carriers to transverse the barriers introduced by molecular recognition along the 1D nanostructures [11].

Among the chemical sensors, the humidity sensor plays an important role in libraries, museums, hospitals, and food storage [17–20]. In recent decades, researchers have developed humidity sensing architectures that use changes in capacitance, frequency, refractive index, and impedance as sensing mechanisms [21–23]. And many kinds of sensing materials including metal oxides, polymers, and polyelectrolyes have been employed to serve these applications [24–26]. An excellent humidity sensor should have the following characteristics: high response value, broad range of operation, good reproducibility, quick response and recovery, and low cost. One parameter of particular importance is the time required to respond to changes in humidity. As the humidity sensors are usually operated at room temperature, the response and recovery times are relatively long. Many humidity sensors need several minutes to reach steady state [18,20], and the response and recovery times in the order of several tens of seconds are considered high speed with current technology [27–30]. However, humidity sensors with response and recovery times in the range of a second will be crucial for numerous applications including management of patients undergoing anaesthesia, pulmonary function diagnostics, and semiconducting process control [31]. Previously, we have reported the humidity sensor based on flower-like ZnO nanorods.

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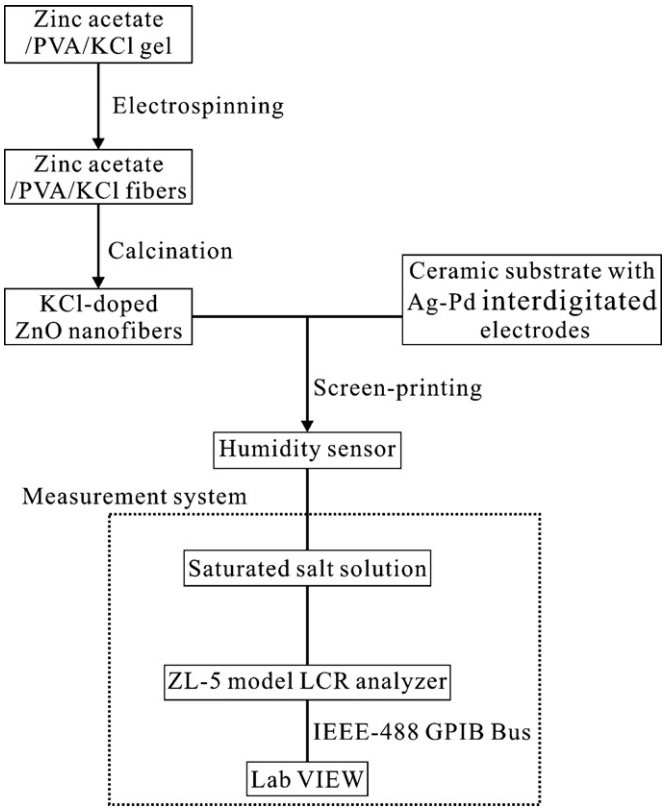

Fig. 1. A block diagram of the sensor fabrication and measurement.

This sensor exhibits quick response time (5 s) and recovery time (10 s), but its linearity cannot be improved by doping materials [32]. We have also reported the humidity sensing properties of KCl-doped TiO_2 nanofibers with rapid response time (3 s) and recovery time (4 s), and good linearity [33]. However, the sensing characteristics (e.g., response, recovery, linearity, selectivity, and stability) still need to be improved.

In this paper, we demonstrate a simple and effective route for the synthesis of KCl-doped ZnO nanofibers with super-rapid response (about 2 s) and recovery (about 1 s) to humidity. ZnO has been chosen as the functional material for its high sensing performance [16]. At the same time, the addition of potassium ions (K^+) is used to increase the carrier concentration [34], thereby resulting in the improvement of the humidity sensing performance [35,36]. We believe our method can offer a powerful platform to understand and design high performance humidity sensing materials.

2. Experimental

2.1. Preparation of materials

Pure ZnO nanofibers and KCl-doped ZnO nanofibers with three different contents (4.3 wt%, 5.7 wt%, and 8.3 wt%) were synthesized through an electrospinning method (Fig. 1). Briefly, 3 g of zinc acetate aqueous solution (16.7 wt%), containing an appropriate amount of KCl, was dropped slowly into an aqueous solution containing 7.6 g of poly (vinyl alcohol) (PVA, MW = 75,000) with 0.01 g of Triton-X100 added. After stirring for 12 h, a viscous gel was obtained. Then, the as-obtained gel was loaded into a glass syringe and connected to a high-voltage power supply. An electric field of 18 kV was applied between the cathode (a flat aluminum foil) and anode (syringe) at a distance of 20 cm [37]. Then calcination (600 °C in air for 5 h) was used to remove the organic constituents of PVA and convert the precursor into crystalline ZnO.

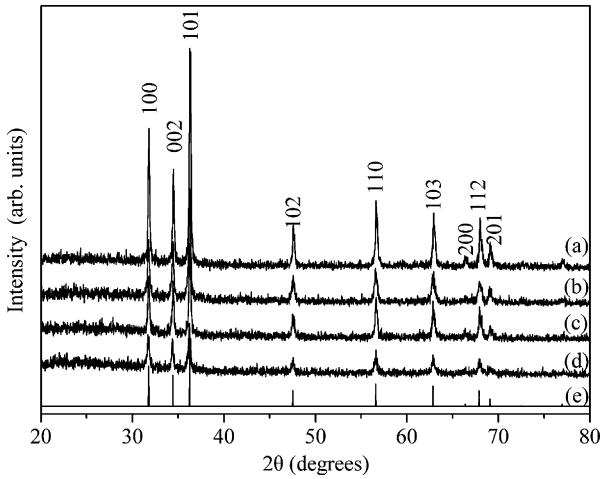

Fig. 2. XRD patterns of (a) pure, (b) 4.3 wt%, (c) 5.7 wt%, and (d) 8.3 wt% KCl-doped ZnO nanofibers, and (e) JCPDS card #36-1451.

2.2. Measurement

The ZnO nanofibers were mixed with deionized water (with a resistivity of 18.0 MΩ cm^{-1}) in a weight ratio of 100:25 to form a paste. The paste was screen-printed on a ceramic substrate (6 mm × 3 mm, 0.5 mm in thickness) with a pair of Ag–Pd interdigitated electrodes (electrode width and gap: 0.15 mm) to form a film with a thickness of about 200 μm, and then the film was dried in air at 60 °C for 5 h. Finally, the humidity sensor was obtained after aging at 95% relative humidity (RH) with a voltage of 1 V, 100 Hz for 24 h for the improvement of stability and durability.

The humidity sensing characteristics were measured on a ZL-5 model LCR analyzer (Shanghai, China). The data were collected by a computer automatically through an IEEE-488 GPIB Bus (82350A GPIB, Agilent, America). Special application software was developed using the LabVIEW environment (Version 7.1) to govern the work of the whole system. The voltage applied in our studies was AC 1 V, and the frequency varied from 40 Hz to 100 kHz. The sensor was placed in several chambers with different RH levels at an operating temperature of 25 °C. These chambers were made of glass, 17 cm in height and 10 cm in diameter. The six different saturated salt solutions were LiCl, $MgCl_2$, $Mg(NO_3)_2$, NaCl, KCl, and KNO_3, and their corresponding RH values were 11, 33, 54, 75, 85 and 95% RH, respectively [38]. The saturated salt solutions were placed in the chambers for 10 h to ensure the humidity levels in the air had reached equilibrium. An automatic drier was used in our laboratory to maintain the laboratory atmosphere at 25% RH. The selectivity properties of the sensor were measured by comparing the impedance of sensor in air (RH is about 25%) with that in a mixture of target gas and air. The whole procedure of the sensor fabrication and measurement is shown in Fig. 1.

X-ray powder diffraction (XRD) data were collected on an X'Pert MPD Philips diffractometer (Cu Kα X-radiation at 40 kV and 50 mA). Scanning electron microscopy (SEM) images were recorded on a SHIMADZU SSX-550 (Japan) instrument.

3. Results and discussion

Fig. 2 shows the XRD patterns of the ZnO nanofiber after calcination. All the diffraction peaks can be indexed as a Wurtzite structure with lattice constants of $a = 3.24$ Å and $c = 5.19$ Å, which together with the intensity distribution are consistent with those