The ZnO nanostructured hydrogen sensor fabricated by combining electrospinning technology and hydrothermal method

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Abstract

In this study, a composite structure of zinc oxide (ZnO) nanofibers and nanorods was prepared on a silicon substrate by combining electrospinning and hydrothermal methods. ZnO/PVP nanofibers are prepared by electrospinning components containing polyvinylpyrrolidone (PVP), ethanol (Ethanol) and zinc acetate, and then calcined at 500°C for 4 hours. Crystallized ZnO nanofibers are then used as the ZnO seed layer, and ZnO nanorods are grown on the nanofibers by hydrothermal method. Combining these two low-cost processes can prepare a ZnO nanostructure with a high specific surface area, which can improve the sensitivity of ZnO to hydrogen. The ZnO nanostructure was analyzed by electron microscope (SEM), and X-ray diffraction (XRD). The experimental results show that the ZnO/PVP nanofibers obtained by electrospinning for 2 hours have the best crystallinity after being calcined. ZnO nanorods are then hydrothermally grown on the surface of the nanofibers. As a component material for hydrogen sensing, the sensitivity can reach 61.7% at a hydrogen concentration of 4500 ppm.

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I. INTRODUCTION

Hydrogen will play an extremely important role in the low carbon environment of the future as it can be used as a zero carbon emission energy carrier power source, achieve a safer energy system, and reduce the dependence on fossil fuels and reduce the greenhouse effect and delay global warming. Hydrogen (H2) is an environmentally friendly, renewable and sustainable energy source. The main advantage is that it is abundant on the earth, and the final product of its oxidative combustion is water (H2O), which is also a source of H2. Although H2 has good application potential, it has a high combustion heat (142kJ/g), and the minimum ignition energy can be as low as 0.017mJ. However, the concentration of 4%–75% and the temperature of 250–400 °C belong to the flammability and autoignition temperature range of hydrogen, so it is also quite dangerous [1]. And because hydrogen is a colorless, odorless gas that cannot be detected by human senses, accidental leakage of hydrogen during storage, transportation, and use is likely to be catastrophic. As hydrogen is used in fuel cells for electric vehicles and in different industrial fields, it is becoming more and more common to use highly sensitive hydrogen sensors to detect leaked hydrogen early [2]. At the end of the 20th century, the world began to pay attention to the research and development of nanotechnology. Electrospinning technology (EP) is a technology that can easily prepare polymers into nanofibers. This process can be performed at low temperature and low cost. Polymer nanofibers with high uniformity in diameter, long length, small diameter (10-1000 nm) and large specific surface area were prepared. By mixing various materials and matching the control conditions of electrospinning, various functional nanofibers can be prepared at low temperature.

The specific surface area of nanofibers prepared by electrospinning technology is at least 10,000 times larger than that of ordinary fibers, which makes it worth looking forward to the application of nanofibers in gas sensing elements, because the large specific surface area is conducive to the sensed gas adsorption of molecules. Wang et al [3] used electrospinning (electrospinning) combined with calcination to synthesize ZnO ceramic nanofibers as humidity sensor materials. This sensor has extremely high sensing sensitivity (the maximum resistance value difference is about 105 times) and the response speed is only 6 seconds. In 2009, Wu et al. [4] synthesized ZnO nanowires by electrospinning as a resistive alcohol sensor material. It is used to sense a low alcohol concentration of 10 ppm at a temperature of 220oC, the sensitivity can reach 90%, and the sensing time is about 25 seconds. This sensor has a very high sensing sensitivity ((Ra-Rg)/Ra=90%, Ra is the resistance value of the nanowire before exposure to alcohol gas, Rg is the resistance value after exposure to alcohol gas) and The reaction time is only 25 seconds.

Metal oxide semiconductor (MOS) gas sensors have the advantages of strong responsiveness, high stability, and low cost. Among the current metal oxide gas sensors, SnO2 and ZnO are the most widely studied metal oxides because of their high sensitivity and high stability to different gases. Zinc oxide (ZnO) is an oxide semiconductor material with an energy band gap of about 3.37 eV at room temperature [5]. One-dimensional nanostructures of ZnO, such as nanofibers, nanowires, and nanorods, can be grown

using a variety of processes, including chemical vapor deposition, hydrothermal synthesis, electrochemical deposition, and electrospinning [6]. Compared with other methods, electrospinning is more economical, easy to control, versatile and a convenient process for producing composite nanofibers. Electrospun nanofibers have approximately two orders of magnitude more surface area than continuous films, and it is worth mentioning that electrospun nanofibers are continuous and easy to align, assemble, and process. When ZnO is adsorbed by an external reducing gas (H2) on the surface of the nanostructure, the resistance value will decrease, and the specific surface area of the ZnO nanofiber will increase, and it will have better gas sensing characteristics. When the H2 concentration in the environment increases, the oxygen ions (O-, O2- and O2-) adsorbed on the surface of ZnO will be desorbed, so that the originally captured electrons on the surface of ZnO will be released back to the ZnO conduction band again, increasing the carrier concentration, and reduce the thickness of the depletion region, thereby increasing the conductivity [7].

II. EXPERIENCE

The precursor solution of electrospinning is made of a mixed solution of ethanol (Ethanol), poly-vinylpyrrolidone (PVP, molecular weight is about 1,300,000) and zinc acetate (Zinc acetate). First take 7.50 grams of ethanol and 0.60 grams of ethanol to mix uniformly, and then 0.80 g of polyvinylpyrrolidine was added and stirred for 12 hours to obtain a precursor solution. The precursor solution is filled into the needle barrel of the electrospinning machine. Under the action of the electrostatic field, the ZnO/PVP composite fiber will be ejected from the tip of the barrel and then deposited on the collector of the silicon substrate. The process parameters set for the electrospinning process are: The syringe advancement speed is 0.1ml/hr.The voltage is 8kV and the distance between the needle tip and the silicon substrate collector is 12cm. The room temperature is 25°C and the humidity is about 65%. The hrdrothermal solution is made of mixture of 200g of DI water, 0.44 g of zinc acetate and 0.28 g of cyclohexamethyltetramine. Apply the substrate in the solution and perform hydrothermal growth at 90°C for 3 hours to grow zinc oxide nanorods on the surface of zinc oxide nanofibers.

The resistance value of the test piece in the air is Ra. After the hydrogen gas is introduced to balance, the resistance value of the test piece is Rg. The sensitivity is measured by the following formula.

$$\text{Sensitivity} = \frac{R_a - R_g}{R_a} \times 100\%$$

The repeatability is to repeat the measurement three times under the same conditions and observe the consistency. The recovery time is the time required for the response curve to recover from the highest value to its 10% value.

III. Results and discussion

Figure 1 shows the SEM photo of ZnO/PVP composite fiber after electrospinning and calcinating. The crystallized ZnO nanofibers were obtained with an average fiber diameter of 850 nm. After being grown by the hydrothermal method, the nanofibers are extended from the original smooth silk thread structure to have many short-column nanorods on them, which increase the specific surface area of the nanofibers as shown in Figure 2.

Figure 3 is the XRD pattern of different electrospinning time after calcinating at 500°C for 1 hour. The results show that the nanostructure has six main diffraction peaks, corresponding to the (100), (002), (101), (102), (110) and (103) of hexagonal wurtzite structure of ZnO crystal planes. No other phase impurity diffraction peaks were found, indicating that the purity of the obtained ZnO nanofibers is quite high.

Figure 4 is the XRD pattern of spinning for 2 hours and calcinating at different time after the hydrothermal growth of ZnO nanorods. The results show that under the annealed time of 1 hour, the ZnO nanofibers have an obvious preferred growth direction on the crystal plane (002), while there is not much difference in the other annealed time.

Figure 5 shows the response-recovery curve of ZnO nanofiber/nanorods composite structures for sensing different hydrogen concentrations at 350°C. The hydrogen concentrations used for sensing are 4500, 10000, 25000 ppm. The results show that the variations of sensing curve for 3 cycles at different hydrogen concentration are very similar, indicating that the ZnO nanofiber/nanorod composite structure has good reproducibility, and their recovery time are all about 113(s).

Figure 6 is a graph showing changes in hydrogen concentration versus sensitivity of ZnO nanofiber/nanorod composite structure. The results show that the sensitivity of the sensor is 61.7%, 63.3%, and 63.9% at a hydrogen concentration of 4500, 10000, and 25000 ppm respectively. In the hydrogen concentration range of 4500 to 10000 ppm, the response of the hydrogen sensor gradually increases as the hydrogen concentration increases. When the hydrogen concentration exceeds 10000 ppm, the response of the sensor approaches saturation.

Conclusions

Through simple and cheap electrospinning technology, ZnO/PVP composite nanofibers can be easily prepared. After calcining theses composite fibers at 500°C, ZnO nanofibers with good crystallinity can be obtained. Then, short column nanorods are grown on the crystallized ZnO nanofibers by hydrothermal method to further increase the hydrogen sensing area. In the hydrogen concentration range of 4500 to 25000ppm, the ZnO nanostructure exhibits good response, with a value of up to 63.9%. They also have good reproducibility and their recovery time are about 113(s). It can be expected that if the hydrothermal growth time is increased,longer nanorods will be obtained, which can provide more sensing surface area and further increase the hydrogen gas sensing ability.

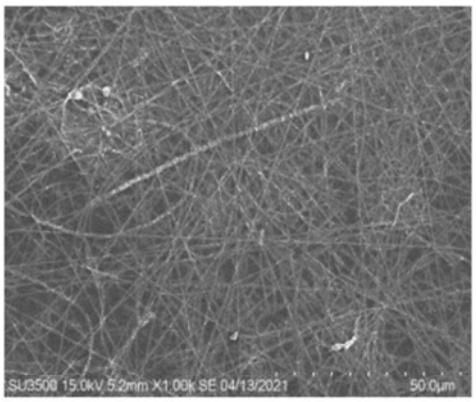

Figure 1. SEM image of ZnO nanofiber after electrospinning for 2 hours and calcinating at 500°C for 4 hours

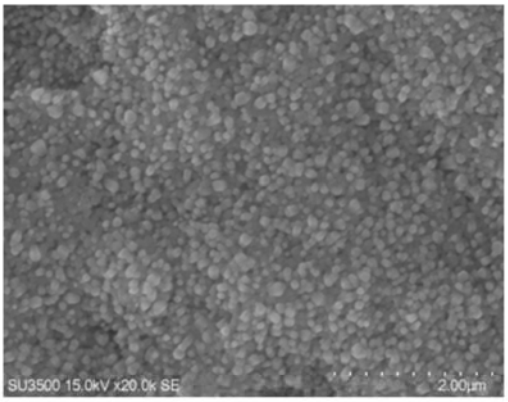

Figure 2. SEM image of ZnO short-column nanorods grown by hydrothermal and calcined at 400°C for 1 hour

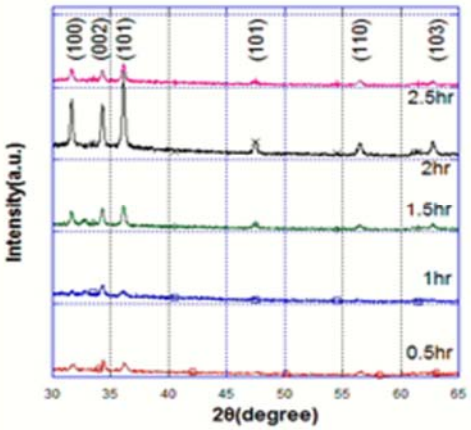

Figure 3. XRD patterns of ZnO nanofibers obtained at different electrospinning times

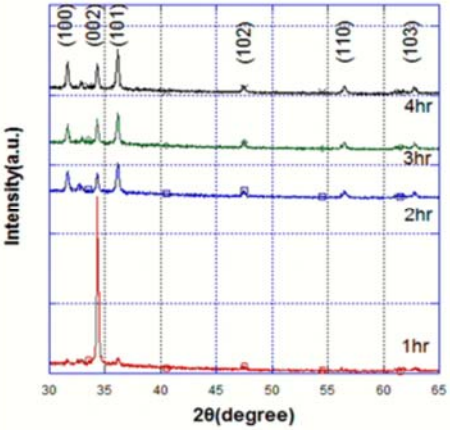

Figure 4. XRD patterns of ZnO nanofiber/nanorod calcinated at 400°C for different time after hydrothermal growth

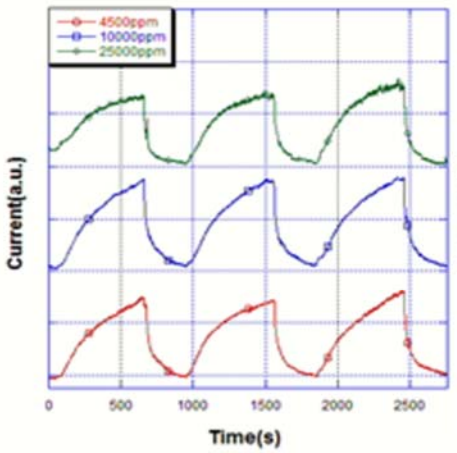

Figure5. The response-recovery curve of ZnO nanofiber/nanorod under different concentrations of hydrogen at 350°C operating temperature

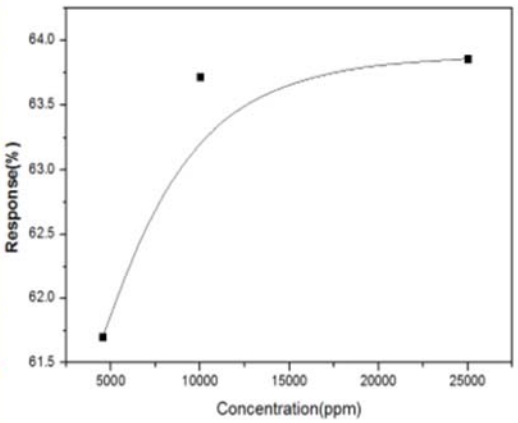

Figure 6. Changes in hydrogen concentration versus response of ZnO nanofiber/nanorod composite structure.

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IV. REFERENCES

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