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Humidity sensing mechanism of mesoporous MgO/KCl–SiO_2 composites analyzed by complex impedance spectra and bode diagrams

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ABSTRACT

Composites of mesoporous silica SBA-15 and MgO/KCl were prepared by a simple grind method following a heat-treatment process. Their structures were characterized by X-ray diffraction (XRD). Humidity sensing properties were studied and the results indicated that, under the same preparation condition, KCl–SBA-15 composite was more suitable to be a promising humidity sensing material than MgO–SBA-15 composite. The impedance of KCl–SBA-15 composite changed more than four orders of magnitude when relative humidity changed from 11% to 95%. The response and recovery time were about 6 s and 26 s, respectively. High stability and low hysteresis were also observed. Complex impedance spectra, the corresponding equivalent circuit, and bode diagrams under different relative humidity was analyzed to explore the humidity sensing mechanism of this material.

1. Introduction

Humidity sensor, which is a device used for measuring the relative humidity or moisture content in environmental air, has attracted more and more attention from researchers because it has gained increasing applications in many fields such as libraries, museums, industries, medicine, agriculture, and so on. Its basic work principle is that some physical quantities such as impedance, current, capacitance or volume of the sensing material will change as moisture is adsorbed. So, relative humidity can be measured by measuring the value of these physical quantities. The performance of a humidity sensor is mainly depended on its sensing material, so we can say that sensing material is the heart of a good humidity sensor. In the past decades, many kinds of materials including polymer [1–4], electrolytes [5–7], organic–inorganic hybrid composites [8–11], photonic crystal [12–14] and metal oxides or ceramic [15–20] have been explored as humidity sensing materials. However, one material does not always completely meet all requirements desired for an excellent sensor such as high sensitivity, good linearity, quick response–recovery, and long-term stability. So, various ways have been developed to improve the performance of a humidity senor. One method which is widely used is the addition of additives or doping in a controlled quantity [21–23]. Feng and his co-worker [23] found that the humidity sensitivity of $HZr_2P_3O_{12}$ can be improved by increasing its palletizing pressure or adding an ionically insulating compound ZrP_2O_7 to form a composite. Another way used to improve the humidity performance is that taking porous materials as the candidate sensing materials, such as zeolites or mesoporous materials [24–27]. This is because that these porous materials have controlled pore size, connected channel and large surface area, which are beneficial to the adsorption and transfer of water molecules. Among these porous materials, mesoporous silica, which was first synthesized by the researchers in Mobil company [28] and was proved having better humidity response than non-porous silica [29], have became a popular humidity sensing material in recent years [30,31]. However, from the viewpoint of design of humidity-sensing materials, investigation of the humidity sensing mechanism is of more great importance. The design of high-performance sensors can be more efficient only the sensing mechanism is clear. Generally, complex impedance spectra technique played an important role in analyzing the sensing mechanism of a humidity sensing material [32,33]. However, to our best know, few works have been reported to analyze the humidity sensing mechanism using bode diagrams. In the present work, the advantages of both mesoporous structure and

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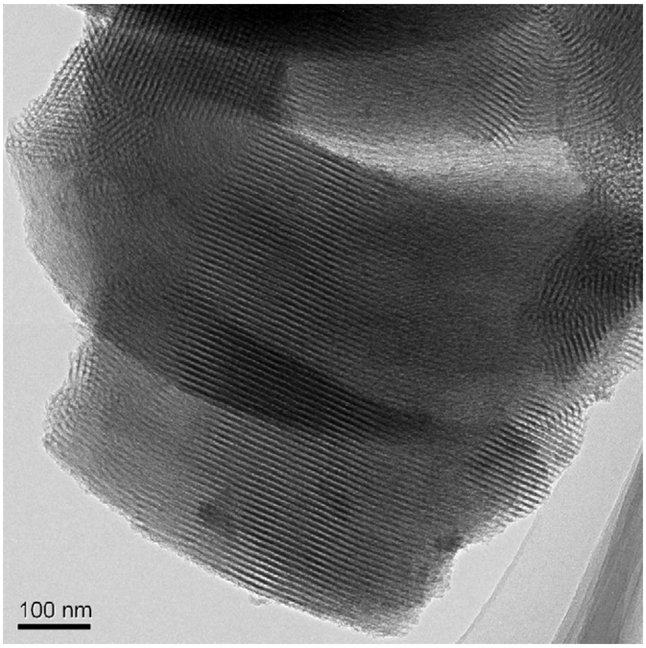

Fig. 1. TEM image of mesoporous silica SBA15.

composites are combined to synthesize composites of mesoporous silica SBA-15 and MgO/KCl. The investigation of humidity sensing property indicated that KCl–SBA-15 was more ideal as a humidity sensing material than MgO–SBA-15. Its impedance changed more than four orders of magnitude when relative humidity changed from 11% to 95%. Complex impedance spectra and the corresponding bode diagrams of this sensing material were carefully analyzed. Equivalent circuits under different relative humidity were also built up to help to understand the humidity sensing mechanism. And finally, the correlation between the shape of bode diagrams and the equivalent circuits was discussed.

2. Experimental

2.1. Preparation of mesoporous silica SBA-15

Mesoporous silica SBA-15 was synthesized using a similar method reported by Zhao [34]. The detailed procedure was as follows: 2.0 g non-ionic surfactant poly (ethylene oxide)–poly (propylene oxide)–poly (ethylene oxide) (EO_{20}–PO_{70}–EO_{20}, P123) was dissolved in 60 ml HCl solution (2 M) at room temperature (25 °C). Then 4.4 g tetraethyl orthosilicate (TEOS) was added dropwise under stirring at 40 °C for 24 h. Subsequently the resultant mixture was aged at 60 °C for 24 h without stirring. The product was filtered and washed with distilled water, then dried at 100 °C over night. The surfactant template was removed at 550 °C for 8 h to obtain the pure mesoporous silica SBA-15. The average pore size of SBA-15 was about 6.2 nm obtained from the transmission electron microscopy (TEM) image as shown in Fig. 1. The non-porous silica sample was prepared with the similar steps described above without the addition of P123 and the heat-treatment under 550 °C, the resulted sample was marked as NP-silica (non-porous silica).

2.2. Preparation of humidity sensing materials and humidity sensors

Composites of mesoporous silica SBA-15 and MgO/KCl were prepared as follows: the mixture of 2.5×10^{-3} mol of magnesium chloride or 2.5×10^{-3} mol of potassium chloride and 1.0 g (1.67×10^{-2} mol) of mesoporous silica SBA-15 was ground for 0.5 h in an agate mortar. The as-ground sample was transferred into a quartz boat and subsequently heated at 550 °C (heating rate: 2 °C/min) for 10 h in a tube furnace under air atmosphere. The resulting samples were marked as MgO–SBA-15 and KCl–SBA-15, respectively. The KCl–non-porous silica composite was prepared using the similar method with KCl–SBA-15, the resulted sample was marked as KCl–NP-silica (abbreviation of KCl–non-porous silica composite). In order to form a humidity sensor, the prepared powder sample was ground with distilled water in a weight ratio of 1:4 (0.15 g of powder sample and 0.6 g of distilled water) to form 0.75 g of paste. Then about 0.15 g of paste was screen-printed on a ceramic plate (0.7 cm × 0.5 cm) on which interdigital gold electrodes were printed (electrodes width and distance: 0.3 mm).

2.3. Measurements

The XRD patterns were measured on D8 Tools X-ray diffraction instrument using the CuKα radiation at 40 kV and 30 mA. Transmission electron microscopy (TEM) experiments were performed on a FEI-Tecnai 30-G2 electron microscope with an acceleration voltage of 300 kV. Energy dispersive X-ray spectra (EDX) were carried out on a scanning electronic microscope of JSM-6700F. Humidity sensing property was measured on a TH2817A model LCR meter (Changzhou, China) at room temperature (28 °C) in a frequency range from 50 Hz to 100 kHz under different relative humidity (RH). The controlled RH was achieved using saturated aqueous solutions of different salts: LiCl, $MgCl_2$, $Mg(NO_3)_2$, NaCl, KCl, and KNO_3 in closed glass chambers at ambient temperature (28 °C), which yielded 11%, 33%, 54%, 75%, 85% and 95% RH, respectively. The Schematic figure of humidity sensing measurement system was shown in Fig. 2.

3. Results and discussion

Fig. 3 shows the low-angle XRD patterns of pure SBA-15, MgO–SBA-15 and KCl–SBA-15. As can be seen, both of MgO–SBA-15 and KCl–SBA-15 samples possess an ordered mesoporous structure with three well-resolved diffraction peaks, indicating that the

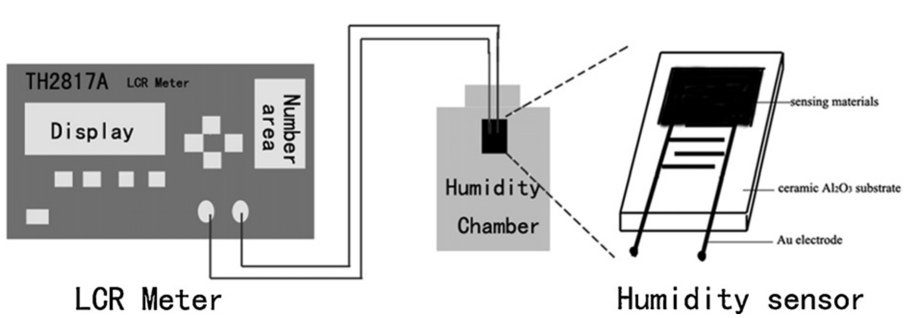

Fig. 2. Schematic figure of humidity sensing measurement system.