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Super-fast response humidity sensor based on $La_{0.7}Sr_{0.3}MnO_3$ nanocrystals prepared by PVP-assisted sol-gel method

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ABSTRACT

$La_{0.7}Sr_{0.3}MnO_3$ (LSMO) nanocrystals were prepared by polyvinylpyrrolidone (PVP)-assisted sol-gel method and characterized by a variety of characterization techniques. The humidity sensor based on LSMO nanocrystals was fabricated and its humidity sensing properties were investigated at room temperature (25 °C) within the relative humidity (RH) range of 11–95%. The optimum working frequency of the LSMO humidity sensor was 10 Hz and the impedance variation was about four orders of magnitude within the whole humidity range from 11% to 95% RH. The LSMO humidity sensor was of super-fast response speed, which was only about 0.8 s from 11% to 95% RH at 10 Hz. The super-fast response property may be ascribed to the strong hydrophilicity of LSMO nanocrystals. In addition, the LSMO humidity sensor was of good reproducibility, stability, small humidity hysteresis (4% RH at 75% RH) and a fast recovery speed (~4.9 s). These results indicate the LSMO nanocrystals can be used as a novel humidity sensing material to fabricate high performances humidity sensors.

1. Introduction

Relative humidity (RH) is an important environment parameter and the high performances humidity sensors are used in diverse areas of human activity such as industry processing, agriculture, weather forecasting, food storage and so on [1–4]. The humidity sensors usually require more than several seconds to reach a stable water adsorption state and the slow response speed restricts the applications of the humidity sensors in many fields of transient humidity changes, such as meteorology applications, medical diagnostics of exhaled air and aerospace applications on board of space vehicles [5,6]. The sensing materials with large specific surface area and nanoporous features are important for improving the sensing performance of various sensors [7–9]. Recently, many especial preparation methods have been utilized for improving the unique crystal structure and morphology of sensing functional materials [10,11]. Jiang et al. reported an excellent humidity sensor based on LiCl loaded hierarchically porous polymeric microspheres (HPPMs) with the rapid response time (2 s), and the fast response property is attributed to the stable cross-linked porous framework and a large numbers of reactive −OH groups of HPPMs [12]. Zhang et al. reported a fast and highly sensitive humidity sensor based on $NaNbO_3$ nanofibers, which response time was less than 3 s and its highly sensitive humidity sensing performance may be ascribed to ultrahigh specific surface area of the $NaNbO_3$ nanofiber networks [13]. Wang et al. synthesized urchinlike CuO modified by reduced grapheme oxide (rGO) by a one-pot microwave-assisted hydrothermal method, and the humidity sensor based on CuO/rGO composites exhibited a fast response time of 1 s [14].

The response process of the humidity sensor mainly consists of two parts: 1. The adsorption process of water molecules onto the materials surface; 2. The process for water dissociation and carrier transport. Compare with the former, the time required for the latter can be almost neglected, resulting in the response time of the humidity sensor mainly depends on the adsorption speed of water molecules onto the material surface. The humidity sensing materials with strong hydrophilicity capacity can adsorb water molecules quickly [15–17], and may contribute to improve the response speed of the humidity sensor. $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) has been widely used in solid oxide fuel cells [18,19], gas sensors [20], magnetic sensors [21], and information storage devices [22,23] due to its various distinct properties, and its super-hydrophilicity [24], as another important parameter, may result in its outstanding wettability, which may make LSMO have potential applications in the fabrication of fast response humidity sensors. However, as far as we know, few reports focus on the humidity sensing properties of LSMO.

In this paper, promoted by both the excellent performance of nanocrystal materials in humidity sensors [25,26], and the distinct super-hydrophilicity property of LSMO nanocrystals [24], the

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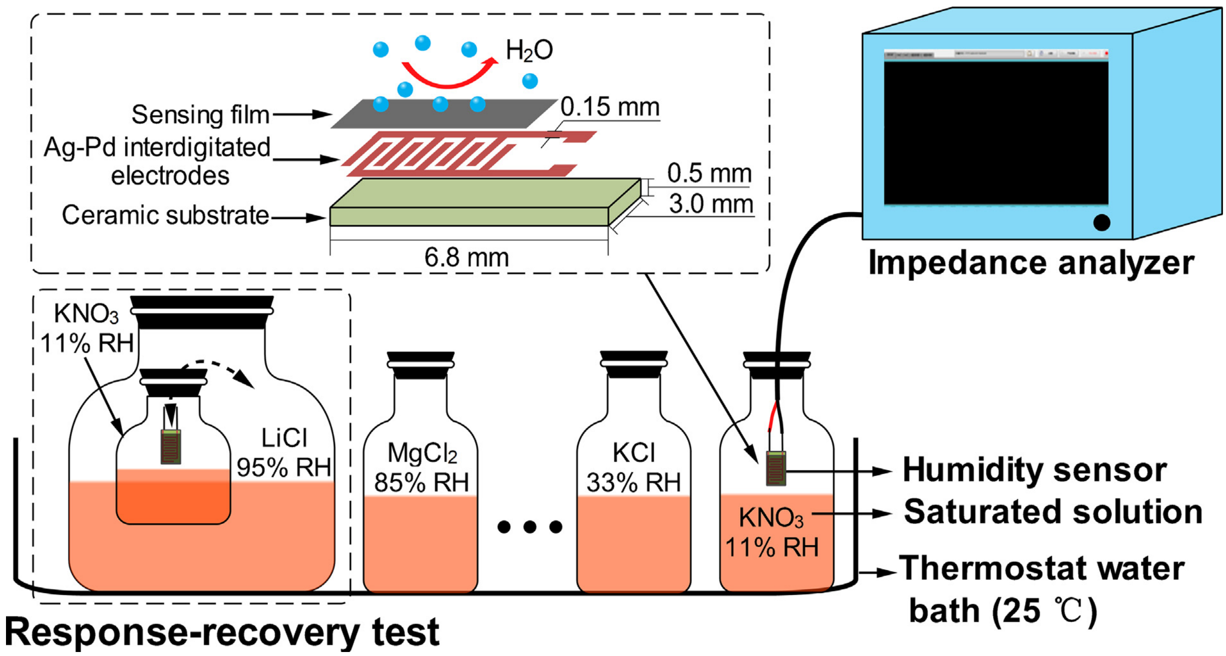

Fig. 1. The schematic diagram of the measurement system and humidity sensor.

LSMO nanocrystals were prepared via a facile polyvinylpyrrolidone (PVP)-assisted sol-gel method and characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), energy dispersive spectrometer (EDS), X-ray photoelectron spectroscopy (XPS), water contact angle measurement and specific surface and pore size analysis instrument. The humidity sensor based on LSMO nanocrystals was fabricated for investigating its humidity sensing properties at different RH and frequency, and expected to be of fast response speed due to its super-hydrophilicity characterization.

2. Experimental details

2.1. Preparation and characterization of LSMO nanocrystals

$La(NO_3)_3{\cdot}H_2O$, $Sr(NO_3)_2$, $C_4H_6MnO_4{\cdot}4H_2O$ and N,N-dimethylformamide (DMF) were purchased from Chengdu Kolong Chemical Reagent Co., Ltd (Chengdu, China). Polyvinylpyrrolidone (PVP, K-90) was purchased from Aladdin Industrial Co., Ltd (Shanghai, China). All the reagents were analytical grade and used as received without further purification. LSMO nanocrystals were prepared by PVP-assisted sol-gel method [27,28]. First, $La(NO_3)_3{\cdot}H_2O$, $Sr(NO_3)_2$ and $C_4H_6MnO_4{\cdot}4H_2O$ with molar ratio of 0.7: 0.3: 1 were dissolved in DMF and the total concentration of metal ions was 0.5 mol/L. Then, 8 wt% PVP (MW = 1,300,000) was added to the above mixed solution, which was helpful to form a uniform sol. After that, the mixed solution was stirred at 80 °C for 4 h until a homogeneous sol precursor solution was formed and the sol precursor solution was dried at 120 °C for 24 h to acquire gel precursor. And the gel precursor was first sintered at 300 °C for 1 h and then sintered at 800 °C for 2 h with a moderate heating ratio 2 °C/min. Finally, LSMO nanocrystals were obtained. The crystallization, morphologies, elemental composition, chemical valence states, water contact angle, and specific surface area and pore size were characterized using various techniques including XRD (Liuzhou Zinc Products Co., Ltd., DX-1000) with Cu Kα radiation source (λ = 0.15418 nm) at a step of 0.01° in the range of 2θ from 10° to 90°, FE-SEM (FEI, Inspect F50), TEM (JEOL, JEM-2100), XPS (Thermo Scientific, ESCALAB 250Xi), water contact angle analyzer (Kino China, SL200B), and specific surface and pore size analysis instrument (Beishide, 3H-2000PS).

2.2. Fabrication and measurement of the humidity sensor

To investigate the humidity sensing properties of synthesized LSMO nanocrystals, LSMO nanocrystals mixed with appropriate deionized water were coated onto an Al_2O_3 ceramic substrate (6.8 mm × 3 mm, 0.5 mm in thick) with five pairs of Ag-Pd interdigitated electrodes (electrodes width and distance: 0.15 mm) to form a humidity sensing film, and then the film was dried in air at 60 °C for 2 h. Finally, the LSMO humidity sensor was obtained after aging at 95% RH with the AC voltage of 1 V, 100 Hz for 24 h to improve its stability and durability [29,30]. The RH environments were achieved with the different saturated salt solutions in closed glass vessels at a constant temperature of 25 °C controlled by a thermostat water bath. The different saturated salt solutions were LiCl, $MgCl_2$, $Mg(NO_3)_2$, NaCl, KCl, and KNO_3, and their corresponding RH values are 11, 33, 54, 75, 85 and 95% RH, respectively [31]. The schematic diagram of measuring setup and humidity sensor is depicted in Fig. 1. To ensure the reliability of the humidity environment, there is a standard humidity instrument (Testo, 605H1) in our system to monitor the RH values. For avoiding the disturbance of the laboratory atmosphere during the switching process, the response and recovery curves were measured by the two nested vessels (11% and 95% RH) [32,33]. The impedance-type humidity sensor is of many advantages like high sensitivity, good linearity and no polarization effects of the adsorbed water [1]. So the complex impedance is used to evaluate the humidity sensitive properties of the LSMO humidity sensor. The humidity sensing properties of the LSMO humidity sensor were measured by an impedance analyzer (Beijing Zhongke Micro-Nano Networking Technology Co., Ltd., 1S-6000). The testing voltage was AC voltage of 1 V and the frequency varied from 10 Hz to 100 kHz. The time taken by the sensor to achieve 90% of the total complex impedance change from 11% to 95% RH was defined as the response time in the case of adsorption or the recovery time in the case of desorption from 95% to 11% RH [14].