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Humidity sensing and dielectric properties of mesoporous $Bi_{3.25}La_{0.75}Ti_3O_{12}$ nanorods

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ABSTRACT

$Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) nanorods are synthesized via electrospinning technique, and mesoporous structures are formed in the BLT nanorods via nanocasting method. The mesoporous BLT (M-BLT) nanorods are characterized by X-ray diffraction, field-emission scanning electron microscopy, transmission electron microscopy, and energy dispersive spectrometer, and then coated on the ceramic substrates with Ag-Pd interdigitated electrodes to form the humidity sensitive device. The humidity sensitive properties of M-BLT nanorods humidity sensitive device are investigated at room temperature within the relative humidity (RH) ranges of 11–95%. The impedance properties of M-BLT nanorods are effected by frequencies. The M-BLT nanorods have good sensing properties at low frequency. The humidity sensitive device is of high sensitivity at 100 Hz, and the impedance variations are over six orders of magnitude within the humidity ranges from 11% to 95% RH. The response time and recovery time of the M-BLT nanorods humidity sensitive device are about 8 s and 250 s, and the maximum hysteresis is about 4% RH. The results indicate that the electrospinning technique combining with nanocasting method would be one of important and effective approaches for preparing high-performance humidity-sensing material, and the M-BLT nanorods are the promising materials to fabricate high sensitivity humidity sensor.

1. Introduction

Relative humidity (RH) is an important parameter in numerous applications, including industrial process, agricultural production, weather measurement and medical monitoring [1–5]. Specific surface area of materials is an important factor influencing the humidity sensing properties of materials, because materials with large specific surface area have more active sites to the adsorbed water molecules and more defects forming on the surface [6]. One-dimensional (1D) materials, because of their large specific surface area and short electronic diffusion distance, are widely used in fabricating humidity sensitive devices. There are many preparation methods for 1D materials, such as chemical vapor deposition (CVD), electrospinning, template method etc. Due to the relatively simple and low-cost technique, the electrospinning technique has been developed to fabricate 1D nanostructures in the form of wires, belts, rods, tubes and rings from many materials [7,8]. Recent years, the mesoporous structures have been found that they not only can increase the specific surface area of materials, but also can provide abundant lattice defects which offer numerous channels and short diffusion paths for efficient transport of electrons and ions [8]. The nanocasting technique can be used to prepare mesoporous materials, which provides a porous template, and the porous template can be selectively removed after the synthesis of the material [9]. Therefore, by introducing mesoporous structures via using nanocasting method, the 1D materials can obtain large specific surface area, abundant lattice defects, resulting in further obtaining numerous channels and short diffusion paths. It is expected that the humidity sensing properties of 1D materials may be improved greatly via the introduction of mesoporous structures.

$Bi_4Ti_3O_{12}$ (BTO) is a bismuth-layered perovskite compound, which consists of $(Bi_2O_2)^{2+}$ and perovskite-like $(A_{n-1}B_nO_{3n+1})^{2-}$ layers [9–11]. The site substitution (ion substitution of A or B sites in BTO) is one of the important factors that can improve the humidity sensitive properties of the materials [12,13]. La-doped BTO can suppresses the evaporation of bismuth and the extensive grain growth [14–16], and the doping of La can cause the forming of oxygen vacancies and lattice defects, which is benefit for the adsorption of water molecules [17]. In addition, according to previous work [18–20], when the x in $Bi_{4-x}La_xTi_3O_{12}$ is around 0.75, the $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) is of good crystallinity. In this work, the mesoporous BLT (M-BLT) nanorods are synthesized by electrospin-

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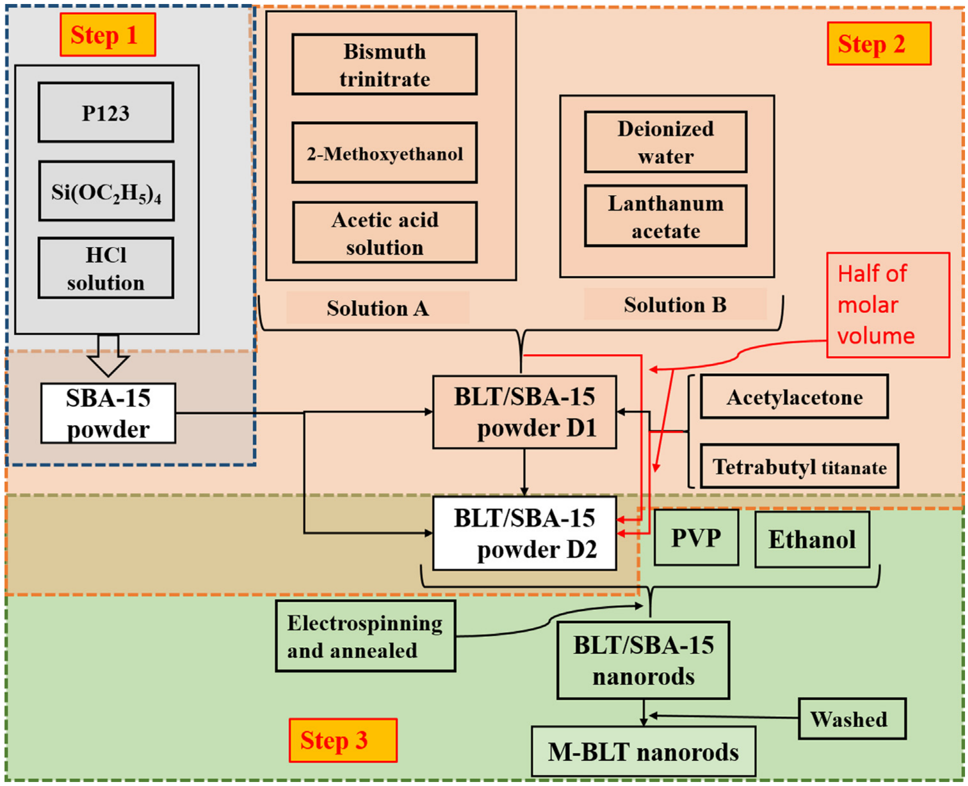

Fig. 1. The flow diagram of preparation for the M-BLT nanorods.

ning technique combining with nanocasting method. The crystal structures, morphologies and compositions of M-BLT nanorods are characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and energy dispersive spectrometer (EDS). After fabricating the M-BLT nanorods humidity sensitive device, the humidity sensing properties of M-BLT nanorods are investigated at different RH and frequency. We expect that the results may offer an effective approach to prepare high-performance humidity sensing materials.

2. Experimental details

2.1. Preparation and characterization of M-BLT nanorods

The preparation progresses of M-BLT nanorods are consisted of three steps: step 1, preparation of SBA-15; step 2, preparation of BLT/SBA-15 powders; step 3, preparation of M-BLT nanorods. The flow diagram of preparation for the M-BLT nanorods is shown in Fig. 1. The mesoporous silica SBA-15 as hard template is prepared at first. The detailed procedure is shown as follows: firstly, 2 g Pluronic P123 ($EO_{20}PO_{20}EO_{20}$, MW = 5800, Sigma-Aldrich) as a surfactant template is dissolved in 60 ml HCl solution (2 M) at room temperature. Then, 4.25 g tetraethyl orthosilicate (TEOS) is added into above solution dropwise under stirring at 40 °C for 24 h. Subsequently the mixture is transferred into a closed teflon-lined stainless steel autoclave and heated at 100 °C for 24 h under a static condition. The autoclave is cooled down naturally. Finally, the product is filtered off, washed with deionized water, dried at 80 °C for 12 h, and calcined at 550 °C for 6 h to obtain the pure mesoporous silica SBA-15.

The BLT/SBA-15 powder is synthesized via metal-organic decomposition (MOD) method combining with nanocasting method, and the preparation procedure is shown as follows: firstly, an appropriate amount of bismuth nitrate is dissolved in acetic acid and 2-methoxyethanol with a volume ratio of 1:1 (solution A). Meanwhile, lanthanum acetate is dissolved in acetic acid and deionized water with a volume ratio of 2:1 (solution B). Then, the A and B solutions are mixed and constantly stirred for about 2 h until a transparent solution (solution C1) is obtained. Secondly, 0.5 g the as-prepared silica SBA-15 is added to the solution C1. In order to prevent the hydrolysis caused by the moisture in air, acetylacetone is added into the mixture solution. Then, a stoichiometric amount of tetrabutyl titanate solution is added. The above mixture solution is stirred for 12 h at room temperature, dried at 100 °C, and calcined at 550 °C for 3 h to obtain the light yellow BLT/SBA-15 powder D1. In order to achieve high loadings, the solution C2 is prepared as the same of C1, but the molar volume of bismuth nitrate, lanthanum acetate and tetrabutyl titanate are reduced by half. 0.5 g SBA-15 and the BLT/SBA-15 powder D1 are added in solution C2. After centrifugalized, washed with water, dried at 80 °C for 12 h and calcined at 750 °C, the BLT/SBA-15 powder D2 is obtained.

The M-BLT nanorods are synthesized by electrospinning technique. Firstly, 0.6 g as-prepared M-BLT/SBA-15 powder and 4.3 g polyvinylpyrrolidone (PVP MW = 1,300,000) are added in 29 ml ethanol then thoroughly mixed with the aid of a magnetic stirrer to form a homogeneous viscous solution. Secondly, after stirred for 8 h at room temperature, the viscous solution is electrospun under 20 kV, and the distance between the needle and the collector is 15 cm. Thirdly, after the spinning is completed, the BLT/SBA-15/PVP composite nanorods are obtained, and then they are calcined at 750 °C for 3 h to obtain the BLT/SBA-15 composite nanorods. Finally, the silica template in BLT/SBA-15 composite nanorods is removed at room temperature by using 30 ml of NaOH aqueous solution (2 M) at 70 °C for 6 h. After washing with water and drying at 80 °C for 12 h, the M-BLT nanorods are obtained. The crystalline structures, morphologies and compositions of the M-BLT nanorods are characterized by XRD (Brukers, D8 Advance) with a Cu Kα