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Humidity response property of $Ba_{0.8}Sr_{0.2}TiO_3$ ordered nanofiber arrays synthetized via electrospinning

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ABSTRACT

Uniaxially aligned $Ba_{0.8}Sr_{0.2}TiO_3$ (BST) nanofiber arrays were fabricated via electrospinning combined with annealing. A specially designed collector composed of two paralleled aluminum electrodes and an insulative substrate were used in the electrospinning process. The morphology and structure of the resultant arrays were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The SEM shows well uniaxial arrangement and the diameters before (300–500 nm) and after (100 nm) calcination. XRD shows well-defined perovskite crystal structure of the as-synthesized arrays. The humidity sensor based on the as-synthesized arrays exhibited a rapid response-recovery property at room temperature. The possible sensing mechanism was proposed.

1. Introduction

Over the past decade, one-dimensional (1D) nanomaterials including nanotubes, nanowires, nanobelts, and nanofibers have attracted a lot of attention owing to their potential applications in a broad range of areas such as electronics, optoelectronics, sensors, and composites [1–4]. Taking effective electronic transimission ability results from the large draw ratio, the applications of 1D nanomaterial have brought many improved properties to the field of chemical sensor [5,6]. Recently, uniaxially aligned nanofibers array, whose anisotropic properties can be used in a variety of electrical, optical, mechanical and biomedical [7,8] applications, has also caused a lot of interests of people. And because of strong capacity of axial transmission for electron [9], the 1D aligned array materials also bring an opportunity to improve the sensing properties of chemical sensor deeply, such as gas [10] and humidity [11] sensors. Meanwhile, relevant reports of the synthesis for this material via electrospinning have appeared constantly [12,13].

$Ba_xSr_{1-x}TiO_3$ (BST) with the structure of perovskite (ABO_3) is a kind of dielectric material develops from $BaTiO_3$ (BT). Additionally, it is also a kind of ternary material, so the own components can be easily accommodated to adjust the properties of the material. The high dielectric constant and low dielectric combined with the excellent properties of ferroelectricity, piezoelectricity and insulativity make BST material widely used in the field of button capacitor, thermistor, and pressure converter [14,15]. Recently, some researches about the fabrication of electrospun BST nanofibers [16,17], and the humidity sensing property of electrospun nanofibers had been also reported [18,19]. So in view of the above mentioned reason, we considered that the import of ordered BST nanofiber to the field of humidity sensor may bring some excellent effects. In this research work, we report the uniaxially aligned BST ($x=0.8$) nanofibers array fabricated by using a revised collector which has been demonstrated by Li and Xia [12]. And the humidity sensing properties of the sensor based on this array was investigated.

2. Experiment

2.1. Sample preparation

All the chemicals, purchased from Beijing Chemicals Co. Ltd., were analytic grade reagents and used without further purification.

In a typical procedure for electrospinning, 0.6 g of barium acetate and 0.13 g of strontium acetate were mixed with 3 mL of glacial acetic and 1 mL of tetrabutyl titanate. After stirring for 10 min, 1.2 g of poly(vinylpyrrolidone) dissolved in 4 mL of glacial acetic was added into the above solution. The mixture was held in a syringe for electrospinning after constantly stirred for 1 day at room temperature. The products were collected in every 5 min. The schematic of electrospinning was shown in Fig. 1(a). A collector shown in Fig. 1(b) was used to collect the as-spun products. The collector has two pieces of aluminum placed in parallel with a gap width of 15 mm on a PMMA

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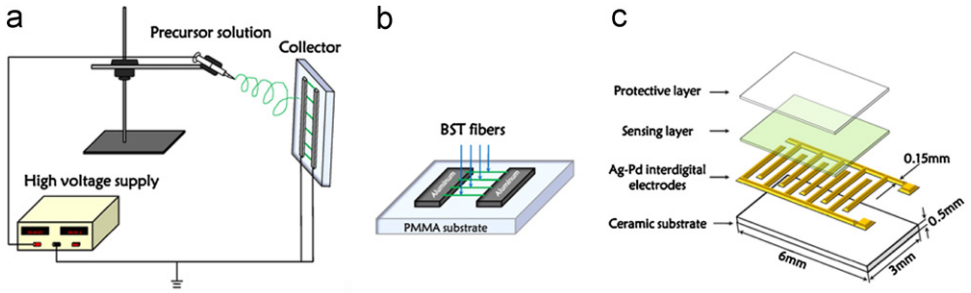

Fig. 1. (a) Schematic of electrospinning. (b) The collector setup used in electrospinning. (c) Structure of the humidity sensor applied in our measurement.

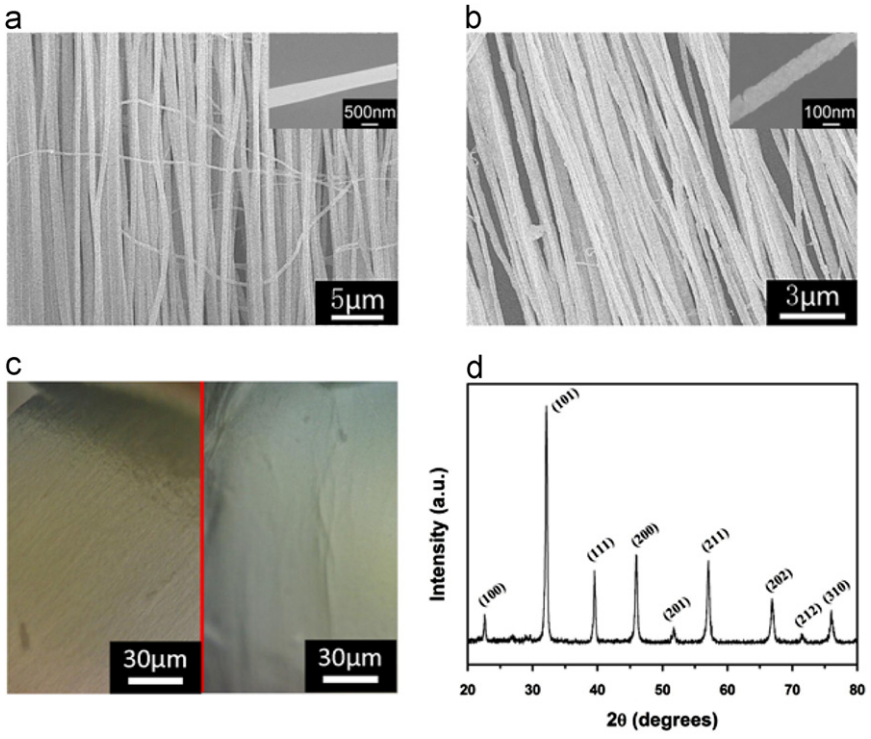

Fig. 2. SEM images of electrospun BST fiber arrays (a) before and (b) after calcination at 800 °C for 2 h. (c) Optical microscope images of BST fiber array and disordered fibrous nonwoven. (d) XRD patterns of BST fibers after calcination.

(polymethylmethacrylate) substrate. After electrospinning the samples were calcined at 800 °C for 2 h, giving the BST aligned nanofiber array.

2.2. Characterization

X-ray diffraction (XRD) analysis was conducted on a Rigaku D/max-2500 X-ray diffractometer with Cu K_α radiation ($\lambda = 1.5418$ Å). Scanning electron microscopy (SEM) images were performed on a JEOL JEM-6700 F microscope operating at 5 kV. The humidity sensitivity test was carried out by a ZL-5 intelligent LCR analyzer (made in Shanghai China) at room temperature.

2.3. Fabrication and measurement of sensors

In order to study the humidity sensing properties, the above obtained material was transported onto a ceramic substrate (6×3 mm, 0.5 mm in thick) with five pairs of Ag–Pd interdigitated electrodes and dipcoated with deionized water to form a sensitive film with a thickness of about 10 μm. And it was dried in air at room temperature for 12 h. Then a protective film of ethyl cellulose was spin coated on the surface of the sensitive film to avoid pollution. The top view and photograph of the humidity sensor are shown in Fig. 1(c). Finally, the humidity sensor was obtained after aging at 95% relative humidity (RH) with a voltage of 1 V, 100 Hz for 24 h to improve stability and durability. The response-recovery property measurement was also taken by an auto test system for humidity sensors established by our lab [20].

3. Result and discussion

Fig. 2(a) shows the SEM images of the composite fiber array with high order degree before calcination. The surface of the fibers before calcination is smooth and uniform, and the diameter ranges from 300 to 500 nm. After calcination as shown in Fig. 2(b), the surface turns rougher and the average diameters decreased to about 100 nm. This contraction is caused by the volatilization of organic compounds in the formation of BST fibers at high temperature. The optical microscope images of the fibers after calcination are shown in Fig. 2(c), it can be seen that the array material (left) shows a surface with metallic luster which is different from the rough surface of disordered material (right). Fig. 2(d) shows the XRD pattern of as-synthesized BST fibers. These diffraction peaks and their relative intensities match very well with JCPDS card no. 44-0093.