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Ethanol sensing characteristics of $BaTiO_3/LaFeO_3$ nanocomposite

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ABSTRACT

$BaTiO_3/LaFeO_3$ nanocomposite with $BaTiO_3$ and $LaFeO_3$ nanoparticles in the mole ratio of 1:2 was prepared by a citric sol-gel method and used as sensing materials to fabricate nanoparticle-based sensors. TEM, BET and XPS results suggested that the capability of absorbing oxygen species from air played the more important role than the grain size or specific surface area in the determination of gas sensing performance for nanoparticles. $BaTiO_3/LaFeO_3$ sensor showed improved gas response towards ethanol with respect to the $LaFeO_3$ sensor at the expense of deteriorated dynamic response. Owing to the higher content of adsorbed oxygen species and ratio of Fe^{4+}/Fe on the surface of the sensing material, better and stable sensing performance to ethanol was achieved by the $BaTiO_3/LaFeO_3$ sensor at the prime working temperature of 128 °C, with a high gas response (102.7) to 100 ppm ethanol.

1. Introduction

Nowadays, perovskite oxide $LaFeO_3$ (LFO) has become one of the most important materials for its intriguing physical properties and potential applications in the fields of monitoring and remediation of environmental pollutants [1–3]. In order to improve the gas sensing performance of sensing material, the introduction of various dopants or nanostructure engineering has been frequently adopted [4–10]. Besides, the formation of nanocomposite materials by the filling of another material into the host matrix can improve the specific property of the host material according to the feature of the filler, and the formation of hybrid materials which consist of two different materials can take advantage of the properties of both. Recently, the construction of p-n heterostructures by composing the p-type LFO with n-type semiconductors, such as SnO_2 [11] and α-Fe_2O_3 [12], in the form of nanocomposite or hybrid material, has been demonstrated to be able to decrease the base electrical resistance and improve the gas sensing performance efficiently due to enhanced charge transfer efficiency.

In the present work, an efficient way to improve the gas sensing performance of the LFO nanoparticle-based sensors was provided by the introduction of another insulating perovskite oxide $BaTiO_3$ (BTO). The formation of BTO/LFO nanocomposite in the appropriate mole ratio of 1:2 resulted in a better ethanol sensing performance than the LFO nanoparticle, the origin of which was ascribed to the higher content of adsorbed oxygen species and ratio of Fe^{4+}/Fe on the surface of the sensing material.

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2. Experimental details

LFO nanoparticles were prepared by a citric sol-gel method as described in our previous work [4], where $La(NO_3)_3{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$ were used as the source of La and Fe, and the final powders were calcined at 600 °C for 2 h. BTO nanoparticles were prepared by the same method, where $Ba(NO_3)_2$ and $[CH_3(CH_2)_3O]_4$-Ti were used as the source of Ba and Ti, respectively, while the final calcination took place at 900 °C for 3 h. The obtained BTO and LFO nanoparticles were then mixed and ground in the mole ratio of 1:2, and calcined at 200 °C for 2 h to form the BTO/LFO nanocomposite. The mole ratio was chosen as 1:2 because of the better ethanol sensing performance than other ratios of 1:1, 1:3 and 1:4. Thereafter, LFO nanoparticle and BTO/LFO nanocomposite were used separately as sensing material to fabricate sensors with three layers of sensing material [13], which were calcined in air at 200 °C for 2 h to achieve stable sensor configuration. The information about the ceramic tube was described in our previous work [4]. The gas response was defined as the ratio of the resistance of the sensor in target gas (Rg) and that in dry air (Ra), and the response and recovery time were defined as the time taken by the sensor to achieve 90% of the total resistance change in the case of adsorption and desorption, respectively [8].

3. Results and discussion

The XRD patterns of LFO and BTO powders in Fig. 1 are in accordance with orthorhombic $LaFeO_3$ (PDF#37-1493) and cubic $BaTiO_3$ (PDF#31-0174), and the corresponding average grain sizes were

estimated by TEM to be 30.56 and 86.38 nm, respectively. The BTO/LFO composite showed the mixed phases of LFO and BTO, and the average grain size was 33.71 nm, indicating that extra grinding with LFO small grains greatly prohibited the presence of large BTO grains and led to the reduced average grain size of BTO in the nanocomposite.

The temperature dependence of resistance for LFO and BTO/LFO sensors is displayed in Fig. 2a. At each fixed operating temperature, the BTO/LFO sensor showed higher resistance than that of LFO sensor due to the insulating nature of the BTO filler. The intrinsic resistance of both sensors fits best to Holsteins model of small polaron hopping (SPH) conduction at relatively higher temperature [14,15]:

$$R(T) = R_0 T exp(E_a/k_B T)$$

where k_B is the Boltzmann constant. The activation energy E_a was estimated to be 0.58 and 0.66 eV respectively for LFO and BTO/LFO based on the ln[R/T] vs. 1000/T curves in the inset, indicating that the insulating BTO in LFO matrix resulted in increased Ea for SPH in LFO. Fig. 2b presents the operating temperature dependence of the gas response to 100 ppm ethanol. The prime working temperature (T_p) was 128 °C for both sensors, at which the BTO/LFO sensor exhibited much higher gas response (102.9) than the LFO sensor (40.7). As shown in the inset of Fig. 2b, the BTO/LFO sensor showed a better selectivity towards other 100 ppm target gases, such as acetone, DMF, dichloromethane, N-hexane, carbon dioxide, and hydrogen. Fig. 2c displays the gas responses to different concentration of ethanol at 128 °C. Both sensors showed good gas response even to the low concentration of 20 ppm, with the higher gas response of 31.2 obtained by the BTO/LFO sensor. Both sensors can be called stable according to the results in Fig. 2d, although the gas responses have some fluctuations due to the variation of the surrounding atmosphere such as temperature and humidity.

The dynamic responses of resistance to 100 ppm ethanol at 128 °C are displayed in Fig. 3. For the LFO sensor, good recovery of resistance to the state before gas was set in could be apparently observed after gas was taken out at 128 °C, and the corresponding response and recovery time were 13 s and 11 s respectively. As for

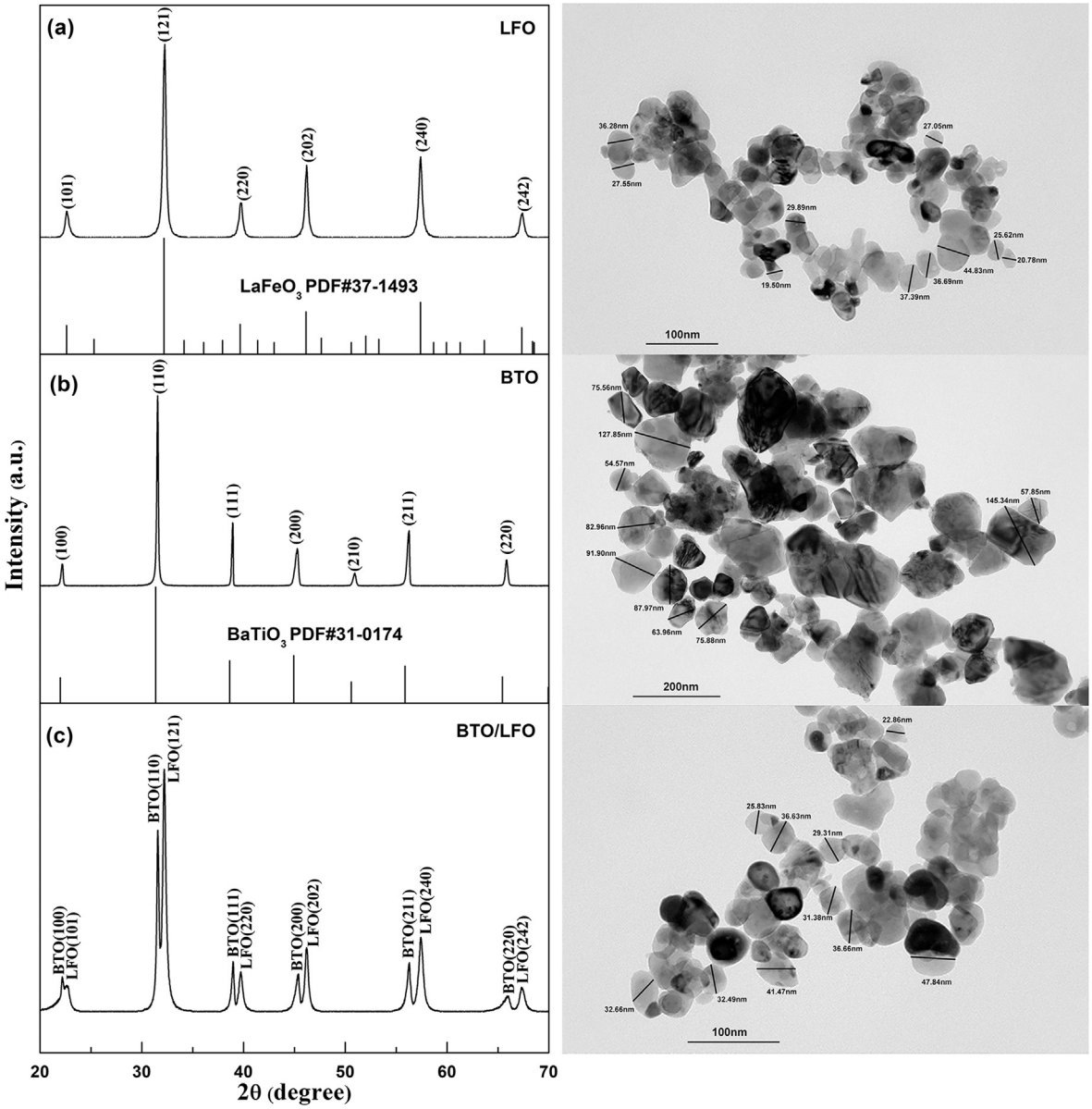

Fig. 1. XRD patterns (left) and TEM images (right) of (a) LFO; (b) BTO and (c) BTO/LFO powders.