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Short Communication

Novel acetone sensing performance of La$_{1\text{-}x}$Sr $_x$CoO$_3$ nanoparticles at room temperature

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ABSTRACT

La$_{1\text{-}x}$Sr $_x$CoO$_3$ (x = 0, 0.1) nanoparticles were synthesized by the simple sol-gel technique. Based on characteristics by scanning electron microscope, transmission electron microscope and X-ray diffractometer, the nanoparticles with the size distributed ranging from 40 to 80 nm all show a single phase with rhombohedral distortion perovskite structure. The sensors exhibit excellent acetone sensing performance at room temperature (~25 °C), especially showing a nearly linear relation with the acetone concentration between 10 and 100 ppm. Sr^{2+} doping can bring holes in the *p*-type semiconductor, thus increasing the resistance variation range of LaCoO$_3$ and enhancing the sensing performance. It suggests that the La$_{1\text{-}x}$Sr $_x$CoO$_3$ nanoparticles can be considered as a potential candidate for acetone detecting at room temperature.

1. Introduction

Transition metal oxide materials with perovskite structure show a rich variety of physical properties and have attracted much attention in recent decades [1–3]. Among them, LaCoO$_3$ (LCO) is an excellent candidate for various devices with applications in electronics and sensors [4,5]. Furthermore, the substitution of alkaline-earths such as Ca^{2+} or Sr^{2+} can strongly affect its physical properties [6,7]. LCO has characteristic gas responses to NH$_3$ [8], CO [9], CO$_2$ [10], and so on. But there are few reports on the gas sensing properties of LCO or doped LCO to other gases. On the other hand, acetone is a colorless, high-volatile and flammable gas, widely used as raw material for organic synthesis, solvent, cleaning age etc. Though acetone is considered to be nontoxic when at a low concentration, it may cause irritation to eyes and throat and also cause nausea when its concentration above 10,000 ppm [11,12]. More interestingly, recent investigation suggests that acetone is found in the breath of diabetic patients and the change in its concentration can be taken as an indication of diabetes [13]. Nowadays, SnO$_2$ [14], In$_2$O$_3$ [15], and ZnO [16] have been investigated as acetone sensing materials. However, the working temperatures are especially high (about 200–300 °C), which results in higher power consumption and may even cause an explosion. Unfortunately, there are only few reports about acetone detecting at room temperature [11]. As we know, there is no relevant report on the acetone sensing properties of LCO or doped LCO at room temperature.

Thus, in the present work, La$_{1\text{-}x}$Sr $_x$CoO$_3$ (x = 0, 0.1) nanoparticles were synthesized by the sol-gel technique. Based on characteristics for the morphology and crystal structure, the effects of doped Sr^{2+} on crystal structure distortion were investigated. The acetone sensing properties of the La$_{1\text{-}x}$Sr $_x$CoO$_3$ nanoparticles were then performed. As expected, La$_{1\text{-}x}$Sr $_x$CoO$_3$ exhibits excellent performance to acetone at room temperature.

2. Experimental

La$_{1\text{-}x}$Sr $_x$CoO$_3$ nanoparticles were prepared by a sol-gel method. A stoichiometric amount of La(NO$_3$)$_3$·nH$_2$O, Co(NO$_3$)$_2$·6H$_2$O and Sr(NO$_3$)$_2$ were dissolved in deionizer water, then citric acid was added. After 1 h stirring, an amount of acrylamide was added. The solution was stirred for ~30 min and then heated up to ~120 °C to form a gel. The gel was dehydrated at ~150 °C for 24 h, decomposed at ~400 °C for 12 h. Each precursor powder was further annealed at 700 °C for 2 h, to obtain the La$_{1\text{-}x}$Sr $_x$CoO$_3$ nanoparticles. Each La$_{1\text{-x}}$Sr$_{\text{x}}$CoO$_3$ powder was mixed with deionized water to form a slurry and coated on a ceramic tube to form a gas sensor, as shown in Fig. 1(a).

The morphology of La$_{1\text{-}x}$Sr $_x$CoO$_3$ nanoparticles was observed with an FEI Sirion 200 field emission scanning electron microscope (SEM) and an FEI Tecnai G2 F20 field emission transmission electron

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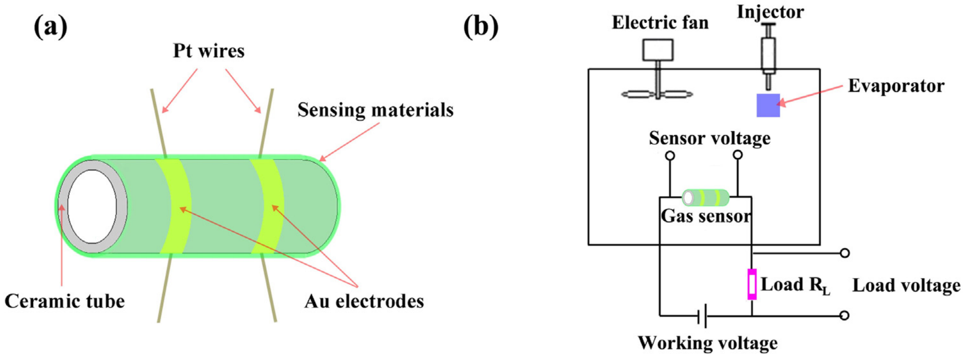

Fig. 1. Schematic diagrams of (a) the $La_{1-x}Sr_xCoO_3$ gas sensor and (b) equipment for gas sensing measurement.

microscope (TEM). The structural characterization was characterized via a Rigaku D/max TTRШ X-ray diffractometer (XRD) with Cu K_α radiation. The changes of chemical bonds of $La_{1-x}Sr_xCoO_3$ nanoparticles in the acetone sensing process were investigated by a Renishaw inVia confocal microprobe Raman spectroscopy at room temperature. The gas sensing properties of the sensors were investigated by the WS-30A gas sensing measurement system (Zhengzhou Winsen Electronic Technology Co., Ltd., China), the schematic diagram is shown in Fig. 1(b). The response of sensor was defined as $S = (Rg - Ra)/Ra$, where Rg and Ra were the resistance of sensor in the target gas and in air, respectively. Ra and Rg can be obtained by measuring the voltage on the load resistance R_L.

3. Results and discussion

3.1. Morphological and structural characteristics

Fig. 2(a) and (b) show the SEM images of undoped LCO and $La_{0.9}Sr_{0.1}CoO_3$ samples, respectively. It can be seen that each sample is composed of irregular nanoparticles, and the size is distributed in the range from 40 to 80 nm. However, there is no obvious difference in particle size between the undoped LCO and $La_{0.9}Sr_{0.1}CoO_3$ samples, demonstrating the comparable specific surface area. Thus the influence of particle size to the quantity of gas adsorption may be ignored when discussing the acetone sensing performance. Furthermore, the size and shape of the products are also confirmed by the TEM images given in Fig. 2(c) and (d).

The XRD patterns of the $La_{1-x}Sr_xCoO_3$ nanoparticles are shown in Fig. 3. For undoped LCO, observed from Fig. 3(a), all diffraction peaks can be well indexed by a single phase with rhombohedral distortion perovskite structure, consistent with the standard data file (PDF # 001-1053). For the $La_{0.9}Sr_{0.1}CoO_3$ sample, no other obvious trace of impurity phase especially strontium oxide is detected. This indicates that the added Sr^{2+} could be doped into the crystal structure of LCO, remaining the rhombohedral distortion perovskite structure. Furthermore, as seen in Fig. 3(b), the (110), (104) and (024) diffraction peaks of the $La_{0.9}Sr_{0.1}CoO_3$ sample all shift to lower 2θ degrees compared with those of undoped LCO. This can be attributed to the substitutions of La^{3+} by Sr^{2+}, where the ionic radius of La^{3+} and Sr^{2+} are 1.36 Å and 1.44 Å [17], respectively. Though the doping of Sr^{2+} dose not change the crystal phase of LCO, it converts Co^{3+} to Co^{4+}, which can also be considered as the hole-doping. This may strongly affect the physical properties of this system.

3.2. Acetone sensing properties

Fig. 4(a) displays the response of the sensors based on undoped LCO and $La_{0.9}Sr_{0.1}CoO_3$ nanoparticles versus acetone concentration at 25 °C and ~45% relative humidity (RH). Each curve ascends or descends when acetone turns on or turns off. It is exciting that both LCO and $La_{0.9}Sr_{0.1}CoO_3$ nanoparticles are sensitive to acetone at room temperature, and the response increases with increasing acetone concentration ranging from 10 to 500 ppm. The sensor based on $La_{0.9}Sr_{0.1}CoO_3$ nanoparticles shows higher response. The response, shown in Fig. 4(b), exhibits a nearly linear relation with the acetone concentration between 10 and 100 ppm. It is advantageous for the sensor calibration. As depicted in Fig. 4(c), the cycle curves indicate that the acetone sensing behavior of the $La_{1-x}Sr_xCoO_3$ nanoparticles are fully reversible. Moreover, in Fig. 4(d), the selectivity was tested by exposing the sensors to 50 ppm potential interference gases (ethanol, ammonia and methane) at 25 °C and ~45% RH. Compared with other gases, the response of sensors to acetone is the highest, indicating that the sensor of $La_{1-x}Sr_xCoO_3$ has an excellent selectivity for acetone. Additionally, the effect of relative humidity was also assessed (see Fig. 4e). It reveals that the response to acetone exhibits a little higher in dryer air. However, by comparison, the magnitude of response in dry air and wet air (~68%RH) are probably at the same level, and the sensors show lower response to a large change in relative humidity, about 1% of the change in acetone response per 10% of the change in relative humidity. Therefore, despite the effect of humidity, the good selectivity coupled with high response at 25 °C makes the sensor based on LCO especially $La_{0.9}Sr_{0.1}CoO_3$ nanoparticles promising for room temperature acetone detecting.

During the sensing process, in consideration of that the scission and changes of the C—O, C—C or C—H bonds may occur if acetone reacts with the absorbed oxygen, Raman spectrometer was used to characterize these changes. Firstly $La_{0.9}Sr_{0.1}CoO_3$ nanoparticles were selected, and the corresponding Raman spectra was obtained at room temperature. Then the powder was put in a sealed box where ~1 mL acetone had been placed in a beaker. The volatile acetone might react with the absorbed oxygen on the surface of $La_{0.9}Sr_{0.1}CoO_3$. After ~3 min, the powder was taken out and tested by Raman spectrometer immediately. From the Raman spectra of $La_{0.9}Sr_{0.1}CoO_3$ after adsorption reaction (see Fig. 4f), two weak Raman modes locating at ~1260 cm^{-1} and 1380 cm^{-1} are observed, which may be correspond to the Raman vibration modes of C═O of CO_2, while the stretching vibrations of C═O of acetone is located at ~1700 cm^{-1} [18]. However, the two weak peaks are not observed in the Raman spectra of $La_{0.9}Sr_{0.1}CoO_3$ before adsorption reaction. This indicates that acetone may be oxidized after the surface reaction and formed CO_2. Therefore, the acetone sensing mechanism of $La_{1-x}Sr_xCoO_3$ nanoparticles can be explained as follows (depicted in Fig. 5). LCO is a *p*-type semiconductor with holes as majority carriers [9]. Due to the large specific surface area and higher surface energy of nanostructures, oxygen in air can be adsorbed on the surface mainly in the form of O_2^- by taking electrons near the surface even at lower temperatures [19]. It is worth noting that LCO is a traditional active catalyst depending on the B site Co^{3+}, which can absorb the organic compounds and reduce the reaction barrier