Synthesis and No_x Gas Sensing Properties of $In_{1.82}$ $ni_{0.18}o_3$ Electrospun Nanofibers

Jinxing Wang, Kejin Zhang, Dan Wang, Dechao Xu, Bin Zhang and Zhongling Zhao

Abstract The detection and control of nitrogen oxides (NOX) in exhaust gases emitted by combustion engines has been an important subject in the last decades. Regulations of vehicle emissions focus on the minimization of NOX in automotive exhaust gases, particularly in lean combustion exhaust gases. Fast response times and high sensitivity of NOX sensor in lean combustion environments are necessary to meet those regulations. In this paper a new sensing material ($In_{1.82}Ni_{0.18}O_3$ nanofibers) was synthesized via a simple and effective electrospinning method. The morphology and crystal structure of the as-prepared samples were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectra (XPS). Potentiometric-type NOX sensor based on yttria-stabilized zirconia (YSZ) with $In_{1.82}Ni_{0.18}O_3$ nanofibers sensing electrode was prepared and its gas sensing properties were also tested. The results show that large-scale $In_{1.82}Ni_{0.18}O_3$ nanofibers with diameters ranging from 40 to 80 nm and lengths of several tens of micrometers were successfully synthesized by this technique. A loose reticular porous non-woven lap structure was formed by many fibers. The results of sensing tests show that the sensitivity ΔEMF of sensor prepared can reach 85 mV for 500 ppm NO, and the ΔEMF is stable. Moreover, the sensor also exhibited fast response time and good selectivity.

Keywords NOX · Gas sensor · Electrospinning · $In_{1.82}Ni_{0.18}O_3$ nanofibers · Sensitivity

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1 Introduction

Lean-burn gasoline and direct-injection diesel engines offer the possibility of significant improvements in automotive fuel efficiency. Their developments, however, also induce high NOX emissions [1, 2]. NOX gas has caused serious damage to human health and the surrounding environment. In order to reduce the emission of nitrogen oxide and implementation of stringent regulations of NOX emission require the development of new technologies for NOX gas sensor which can work steady in cruel combustion gas environment. Several publications have described a method of NOX sensing based on the electrochemical oxygen pump cell using yttria-stabilized zirconia (YSZ). According to the introduction of Patent EP1942338A1, the NOX sensor consists of two internal cavities and three oxygen pumping cells [3]. Its measuring concept consists of lowing an oxygen concentration of a measuring gas to a predetermined level in the first internal cavity, in which NOX does not decompose, and further lowing the oxygen concentration of the measuring gas to a predetermined level in the second internal cavity. The second cavity also contains a NOX detection cell (the third oxygen pumping cells) with a rhodium catalytic electrode which has NOX reduction catalytic activity. Therefore, NOX decomposes on the measuring electrode and the oxygen generated is detected as an oxygen pumping current which is in proportion to NOX concentrations.

Patent 97117135.1[4] has also reported a new method by measuring the electromotive force (EMF) between measuring electrode and reference electrode. This new method works as potentiometric sensor. It should be noted that, regardless of the pump current or electromotive force (EMF), the catalytic electrode materials was very critical, because it direct effects the sensitivity and response time of the NOX sensor.

At present, the catalytic electrode usually using noble metals, such as Pt, Rh et al., as Patent US2010/0243447 A1, EP 2107366A2, US 2008/0156644 A1 reported[5–7]. However, the noble metal will lose its catalytic activity after undergoing long-term high temperature aging and exposure to toxic gases (such as SO_2 and Pb). The failure of noble metal seriously affects the life and sensitivity of gas sensor.

Therefore, it is urgent to develop non noble metal catalyst electrode materials. In_2O_3 with wide band-gap, good catalysis and high electric conductance has aroused significant interests in recent years. It has been proven to be an excellent sensing material for detection of many toxic and combustible gases after doped with metal ions in its crystal lattice. Because the dopant metal ions could be introduced into the structure of host material to change its lattice parameters, leading to a larger lattice distortion. The larger lattice distortion is beneficial for interaction between gas and material surface.

In addition, as a result of indium oxide gas-sensitive mechanism is based on the tested gas adsorption and surface reaction, therefore, higher specific surface area of gas sensitive material is beneficial for gas sensing performance improvement.

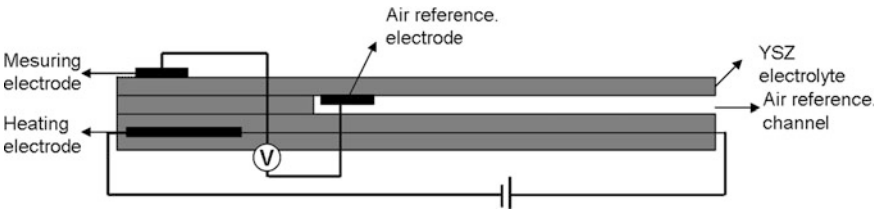

Fig. 1 Schematic image of the sensor

Recently, interest in one-dimensional (1D) has been greatly stimulated because of its increased surface-to-volume ratio and high density of surface sites. Considerable efforts have been made to fabricate 1D sensing nanomaterials via thermal oxidation, thermal evaporation, self-catalytic growth, molten salt synthesis, and electrospinning [8]. Electrosping, as a simple and versatile method, has gained great interest because it can produce 1D nanofibers with high long-diameter ratio, which makes the electron transport more effective and improves the performance of gas sensors [9].

In this paper, a new type gas sensitive material ($In_{1.82}Ni_{0.18}O_3$ nanofiber material) was prepared by a relatively simple electrospinning technique at the first time. Potentiometric-type NOx sensor based on yttria-stabilized zirconia (YSZ) with $In_{1.82}Ni_{0.18}O_3$ nanofibers sensing electrode was prepared and its gas sensing properties were also tested.

2 Experimental

To prepare $In_{1.82}Ni_{0.18}O_3$ solid solution nanofibers, 0.38 g $In(NO_3)_3{\cdot}4.5H_2O$ and 0.025 g $Ni(CH_3COO)_2{\cdot}4H_2O$ powders were added to 8.8 g mixed solvent contained DMF/EtOH with the weight ratio of 1:1 and stirred for 2 h. Then 0.8 g PVP was added to the above solution with stirring for 6 h. The obtained solution was then loaded into a plastic syringe and connected to a high-voltage power supply. 20 kV was provided between the cathode (a flat aluminum foil) and the anode (syringe) at a distance of 25 cm. In order to remove PVP completely, the composite nanofibers were calcined in air at 600 °C for 4 h. Then, 10 at. % $In_{1.82}Ni_{0.18}O_3$ nanofibers were obtained.

Details of the design and fabrication of the potentiometric gas sensors are given in [10]. Figure 1 shows a schematic image of the as-fabricated sensor. Figure 2 shows an image of a real sensor.

Gas sensing properties were measured using a dynamic test system. The sensors were tested in a Micro reactor which was connected to several gas reservoirs. Gas mixtures were regulated by mass flow controllers and computer control. Available gases were NO, NO_2, CO_2, CO. A temperature sensor was installed near the gas sensor. Temperature in the gas chamber was stabilized at 600 C. The sensitivity

Fig. 2 An image of a real sensor

of the sensor is defined as the ΔEMF. The time taken by the sensor to achieve 90 % of the total EMF change was defined as the response time or the recovery time.

The samples were characterized by X-ray diffractometer (XRD) (Shimadzu XD-3AX), field emission scanning electron microscopy (FE-SEM) (JEOL JSM-6700F at 3 kV), transmission electron microscopy (TEM) (HITACHI H-8100 using an acceleration voltage of 200 keV), high–resolution transmission electron microscopy (HRTEM JEM–3010), X-ray photoelectron spectra (XPS) (ESCALAB Mark II spectrometer with Al Kα radiation).

3 Results and Discussion

3.1 Materials Characterizatics

In order to confirm that the Ni ions were incorporated into the lattice structure, XRD was performed. The crystalline structures of In_2O_3 nanofibers and $In_{1.82}Ni_{0.18}O_3$ solid solution nanofibers were characterized by X-ray diffraction (XRD) patterns, as shown in Fig. 3. It can be seen that a slight shift of XRD peak to higher angle for the $In_{1.82}Ni_{0.18}O_3$ samples (Fig. 3b) compared with that of pure In_2O_3 (Fig. 3a). For each samples, all the observed diffraction peaks can be indexed to cubic indium oxide (JCPDS file NO. 06-0416), and no additional peaks for other phases have been found. The lattice parameters of $In_{1.82}Ni_{0.18}O_3$ samples (a = 10.091 Å) is slightly less than that of pure In_2O_3 (a = 10.118 Å), which is consistent with the formation of a substitution solid solution ($In_{1.82}Ni_{0.18}O_3$) [11]. It should be noted that although the ionic radius of Ni^{2+} (r = 0.78 Å) is bigger than that of In^{3+} (r = 0.72 Å), the lattice parameters decrease after substitution. This phenomenon can be explained by considering the change of Ni ions state as follow.

In order to maintain the charge neutrality, an electron exchange process takes place in $In_{1.82}Ni_{0.18}O_3$ solid solution structure. It leads to a partial transition of Ni^{2+} ions into Ni^{3+} which has smaller ionic radius (0.56 Å).

$$Ni^{2+} + In^{3+} \leftrightarrow Ni^{3+} + In^{2+} \quad (1)$$

The presence of Ni^{3+} was confirmed by the next XPS.

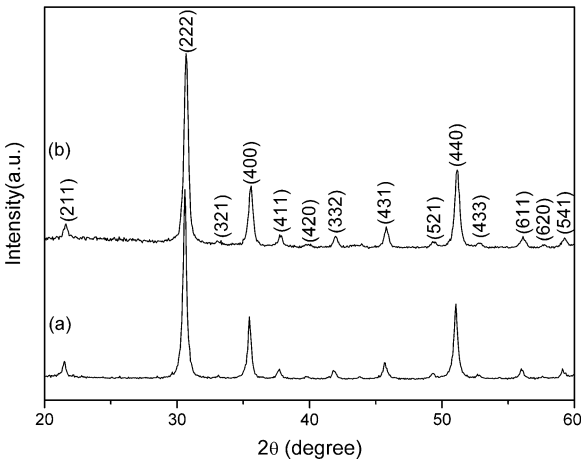

Fig. 3 XRD patterns of **a** pure In_2O_3 and **b** $In_{1.82}Ni_{0.18}O_3$ nanofibers

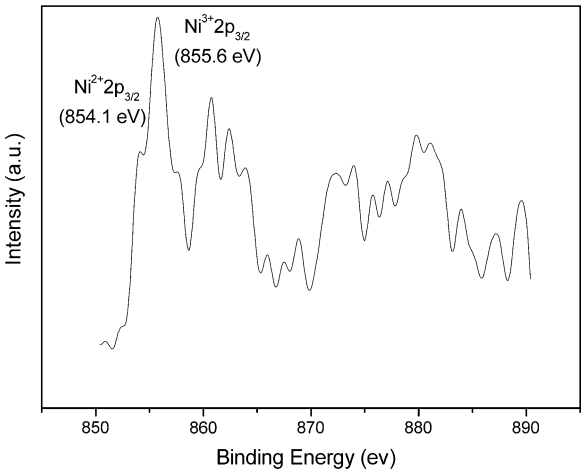

Fig. 4 XPS spectrum of Ni 2p3/2 peak of $In_{1.82}Ni_{0.18}O_3$ nanofibers

Determination of the state of the Ni ions was carried out by measuring Ni 2p3/2 binging energy (BE) with XPS and shown in Fig. 4. The BE 855.6 eV is assigned to Ni^{3+} [12] which comes from the process of an electron exchange (formula 1), and in an octahedral oxygen neighbourhood in the In_2O_3 crystal lattice [12]. The appearance of Ni^{3+} ions is further confirmed the formation of $In_{1.82}Ni_{0.18}O_3$ substitution solid solution. The BE 854.1 eV is assigned to Ni^{2+} which also in the In_2O_3 crystal lattice, and created more vacant oxygen which leading more oxygen species absorbed on the surface of $In_{1.82}Ni_{0.18}O_3$ solid solution nanofibers.

The general morphologies of the $In_{1.82}Ni_{0.18}O_3$ nanofibers were studied with field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and high–resolution transmission electron microscopy (HRTEM). Large-scale nanofibers with diameters ranging from 40 to 80 nm and lengths of several tens of micrometers can be found in the FE-SEM images

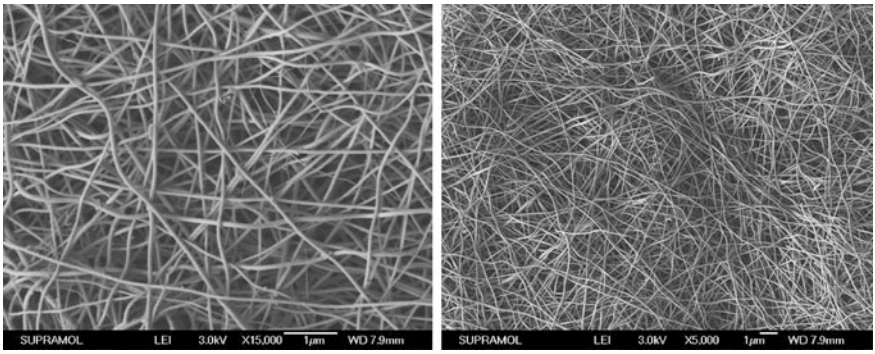

Fig. 5 FE-SEM images of $In_{1.82}Ni_{0.18}O_3$ solid solution nanofibers at different magnifications

(Fig. 5) at different magnifications. A loose reticular porous non-woven lap structure was formed by many fibers and the average diameter of these nanofibers is about 50 nm. From the TEM image (Fig. 6a), it can be seen that each nanofiber consists of many ultrafine particles with an average diameter of 20 nm. Lattice images are clearly observed from the HRTEM image (Fig. 6b), indicating the $In_{1.82}Ni_{0.18}O_3$ nanofibers are highly crystalline. The interplaner spacing of 0.41 nm are corresponds to the (211) planes of cubic In_2O_3.

4 Sensing Characteristics

Figure 7 shows the correlation between the sensitivity ΔEMF and the NO concentration for the sensor using $In_{1.82}Ni_{0.18}O_3$ nanofibers-measuring electrode. It is seen that the sensitivity ΔEMF can reach 85 mV for 500 ppm NO. The sensitivity of the sensor as a function of stepwise increasing the NO concentration from 0 to 500 ppm was shown in Fig. 8. At an NO concentration of 40 ppm, the response time was very fast (about 1 s). After purging of NH_3 from the gas phase, the sensitivity was quickly recovered to the initial level. In addition, at each NO concentration, a stable ΔEMF value was observed. The quick response and recovery characteristics of our sample are based on its structures. The large surface of the nanofibers makes the absorption of target gas molecules on the surface of the sensor easily. Simultaneously, the high long-diameter ratio of the nanofibers makes the electron transport more effective.

To further understand the practicability of our fibers, the sensor was exposed to various 400 ppm gases at 600 °C. Most of the tested gas mixtures were similar to typical exhaust gases from lean burn engines. The selectivity shown in Fig. 9 indicates that the $In_{1.82}Ni_{0.18}O_3$ nanofibers are less sensitive to NO_2, totally insensitive to CO_2, and negative sensitivity to CO. Thus the obtained nanofibers exhibit prominent and good selectivity.

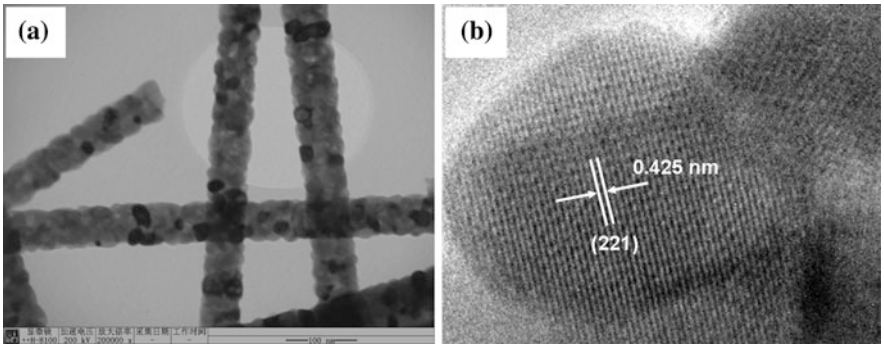

Fig. 6 **a** TEM and **b** HRTEM images of $In_{1.82}Ni_{0.18}O_3$ solid solution nanofibers

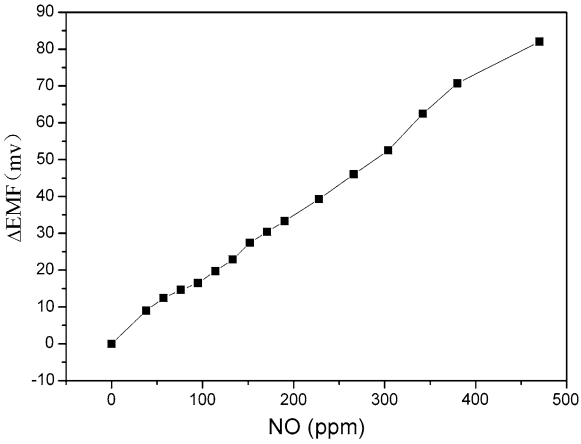

Fig. 7 Dependence of ΔEMF on the NO concentrations for the sensor

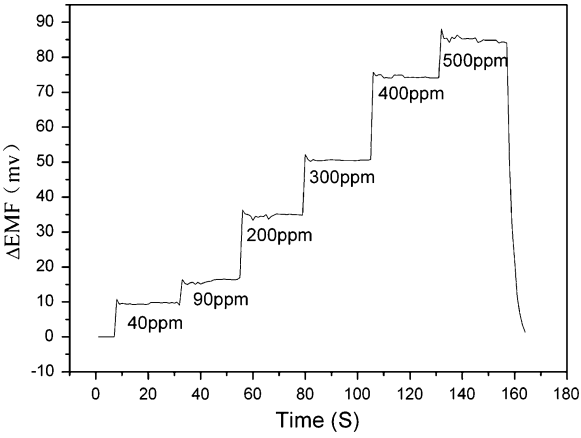

Fig. 8 The response and recovery characteristics of the sensor at different NO concentrations

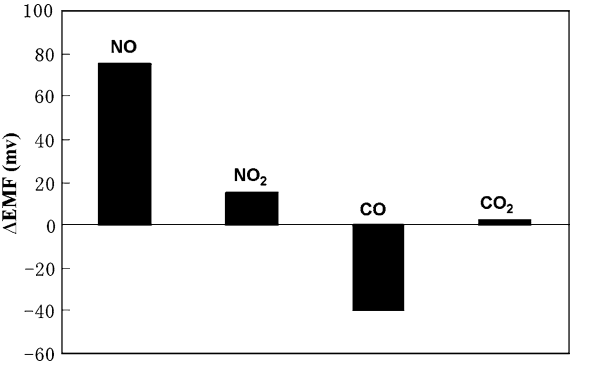

Fig. 9 The selectivity of the sensor at different gases

5 Conclusion

In summary, large-scale $In_{1.82}Ni_{0.18}O_3$ nanofibers with diameters ranging from 40 to 80 nm and lengths of several tens of micrometers were successfully synthesized through an electrospinning method. A loose reticular porous non-woven lap structure was formed by many fibers. Potentiometric-type NOx sensor based on yttria-stabilized zirconia (YSZ) with $In_{1.82}Ni_{0.18}O_3$ nanofibers sensing electrode was prepared. The results of sensing tests show that the sensor exhibited high and stable sensitivity ΔEMF, fast response time and good selectivity. The results demonstrate that $In_{1.82}Ni_{0.18}O_3$ nanofibers have excellent potential applications for fabrication high performance NO_X sensors.

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