NO_2 Gas Sensing Characteristics of SnO_2 Nanofiber-Based Sensors

Phan Hong Phuoc, Chu Manh Hung*, Nguyen Van Duy
Hanoi University of Science and Technology – No. 1, Dai Co Viet Str., Hai Ba Trung, Ha Noi, Viet Nam
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Abstract

In this work, the SnO_2 nanofibers (NFs) were directly synthesized through a electrospinning method following the annealing treatment process at 600°C for 3h. The morphological, compositional, crystal properties of material were characterized using field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), respectively. The FESEM images of SnO_2 NFs shows the typical spider-net like morphology with ~ 150 nm in diameter. Besides, the EDX spectrum reveals the presence of Sn and O atoms in the synthesized nanofibers. The XRD exhibited the formation of crystalline phases of tetragonal SnO_2. The gas sensing properties of fibers were tested towards NO_2 gas as a function concentration within a temperature range of 250 to 450°C. Under the optimal operating temperature of 350°C, the SnO_2 NF sensors can be detected NO_2 gas at low concentration down to 0.015 ppm. These results show its ability for NO_2 gas detection in gas sensor application.

Keywords: SnO_2, metal oxide, nanofibers, gas sensors, NO_2

1. Introduction

Nitrogen dioxide (NO_2) is a pungent red-brown oxidizing gas, which comes from the combustion of the automobile engines when fuel is burned at high temperatures [1]. NO_2 is one of the most harmful gases, which negatively impacts on human health, irritating the eyes, nose, throat and lung irritant. In addition, the emission of NO_2 gas in the air can cause acid rain, which affects human life and plant development [2]. Furthermore, it can be reacted and destructed the ozone layer [2]. Therefore, it is important to detect and monitor the NO_2 gas emitted into the air. One-dimensional (1D) nanostructures, including nanowires, nanorods, nanotubes, nanobelts, and NFs were widely used as a gas sensing element. Among them, the NFs was exhibited its outstanding advantages. Fig.1 presents a typical resistive sensor configuration.

Electrospinning is a facile, versatile, inexpensive method to directly produce NFs with highly porous structure, specific surface area ratio [3]. These properties show high potential for gas sensing applications.

Tin dioxide (SnO_2) is an *n*-type semiconductor with a rutile structure has a large bandgap of 3.6 eV [4], which is one of the most promising materials for gas sensing application due to their high carrier concentration, high chemical, and thermal stability [5]. The gas sensors based on SnO_2 NFs have also been intensively developed for many reducing gases such as ethanol [6], H_2 [7]. In our previous work, the gas sensors based on SnO_2 NFs have shown its ability for H_2S reducing gas [8]. However, the gas sensors based on SnO_2 NFs for oxidizing NO_2 gas are rarely reported.

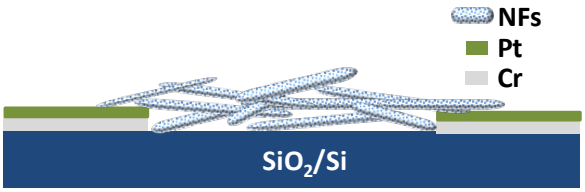

Fig.1. The scheme of a typical resistive sensor system.

In the present work, sensors based on SnO_2 NFs synthesized through electrospinning method, were tested gas sensing characteristics towards NO_2 gas with various concentrations from 1 - 10 ppm at different temperatures. The results exhibit the SnO_2 NF sensors have high sensitivity to oxidizing NO_2 gas.

2. Experiments

The electrospinning solutions were prepared following by the procedure shown in Fig.2(a).

Firstly, 1.5g Tin (II) chloride dehydrate was dissolved in the ethanol (EOH)/dimethylformamide (DMF) solvent (1:1 ratio). Then, 1g polyvinylpyrrolidone polymer (PVP, Mw=360.000, Sigma-Aldrich Corp.) was added into the above-solution and was continued stirring at room

* Corresponding author: Tel.: (+84) 988.138.085
Email: mhchu@itims.edu.vn/ hung.chumanh@hust.edu.vn

temperature for 24h to obtain the desired viscous solvent. The solution was loaded into a plastic syringe, equipped a stainless needle. In electrospinning process, the high voltage of 17 kV was generated between the needle and the collector. The jet ejected from the needle tip has undergone evaporation and whipping instability, finally deposited on the collector, which attached to the Si/SiO_2 substrate. The real electrospinning system used in the present work was shown in Fig.2(b). The as-spun fibers were undergone a heat treatment process at 600°C for 3h to remove polymer and to form crystalline SnO_2 NFs. Details of the synthesis process can be found elsewhere [8], [9].

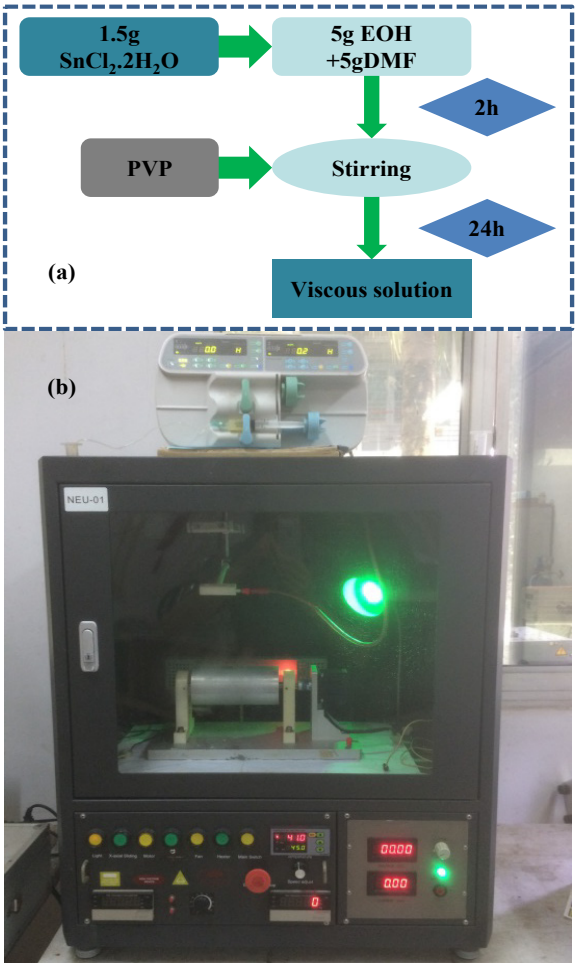

Fig.2. (a) The procedure of preparation of the electrospinning solution. (b) real electrospinning system for the NF synthesis

The morphology and composition, and crystal properties of fibers were characterized using FESEM (Hitachi S-4800), EDX attached to FESEM (Hitachi S-4800), XRD (D8 Advance, Bruker), respectively. The gas sensing characteristic of fibers was tested using a home-made gas sensing system [10]. The oxidizing gas response (R) of sensors was typically defined as $R = R_g/R_a$ where R_g and R_a were the resistance in the test gas and air environment, respectively. The response and recovery times were defined as the time to reach 90% change in resistance upon the supply and removal of the target gas, respectively.

3. Results and discussion

The SEM image (Fig.3) were showed the typical morphology of the NFs. It can be seen the nanofibers were randomly deposited on the substrate. The average diameter of fibers was approximately about 150 nm.

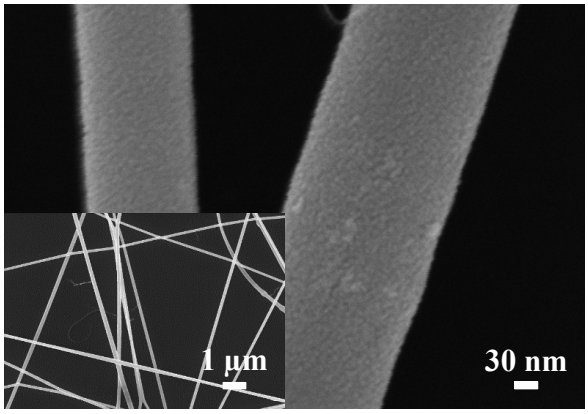

Fig. 3. SEM images of the SnO_2 NFs.

The high-magnification SEM image showed the NFs were composed of many nanograins. Fig.4(a) reveals the EDX spectrum, indicating the presence of Sn and O which belong to SnO_2 NF component. The Si composition in the spectrum is due to the fibers were directly deposited on Si/SiO_2 substrate [8].

The XRD results of SnO_2 NFs (Fig.4(b)) indicated that all diffraction peaks at 2θ values of 26.611°, 33.893°, 37.95°, 51.781°, 54.759°, 57.820°, 61.872°, corresponding to (110), (101), (200), (211), (220), (002), (310) planes of tetragonal SnO_2 (JCPDS 41-1445), respectively [8]. The average grain sizes of SnO_2 NFs were calculated using the Scherrer formula: $D=0.9\lambda/\beta\cos\theta$, where D is the average crystalline size, λ is the X-ray wavelength (0.154 nm), β and θ are the line broadening at half the maximum intensity (FWHM) and the Bragg angle of the diffraction peak, respectively. Herein, the highest peaks of (110) crystal planes of the tetragonal-SnO_2 were used to determine the average grain size of the fibers. It could be found that the average grains size of SnO_2 NFs was about 13 nm.

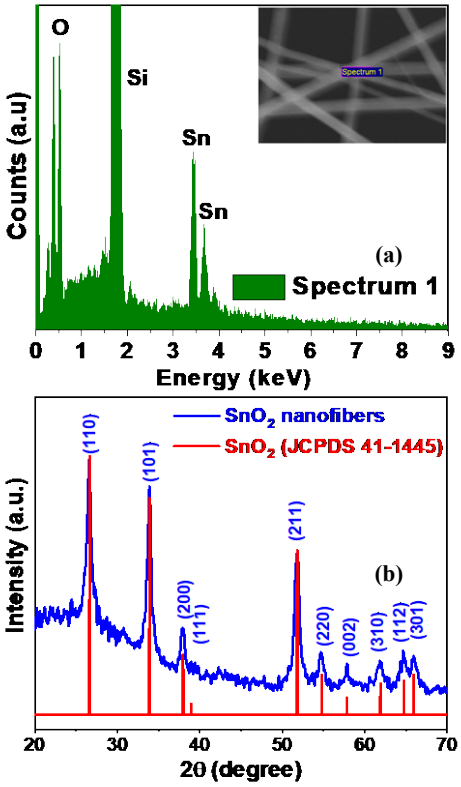

Fig 4. (a) The EDX spectrum and (b) XRD pattern of the SnO_2 NFs.

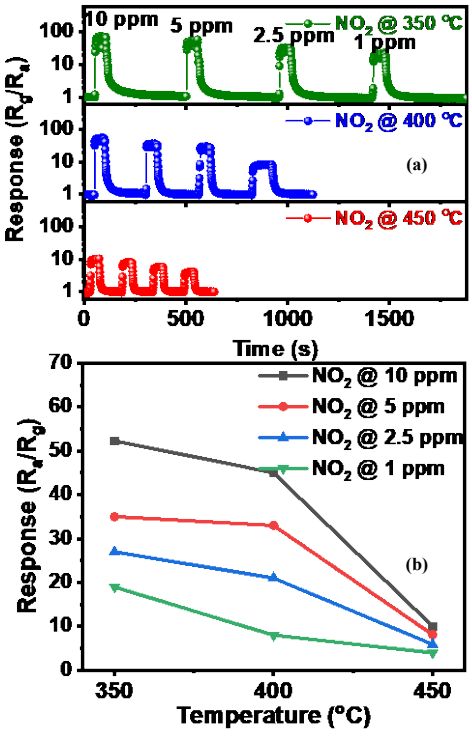

Fig. 5. (a) NO_2 sensing transients of the SnO_2 NFs at various operating temperatures and (b) Gas responses as a function of the NO_2 concentration at different temperatures.

Fig.5(a) shows the transient response of SnO_2 NFs towards NO_2 gas as a function of concentration from 1 - 10 ppm within a temperature range of 350-450°C. As can be seen in Fig.5(b), the response of sensors was varied with gas concentration. At high concentration, more NO_2 molecules absorbed on the oxide surface, consequently, the gas response of sensors was higher compared to low concentration. It can be visualized when the temperature decreased from 450 to 350°C, the response of fibers was increased. At the temperature of 350°C, the response of sensors was 53 times.

The detection limit (*DL*) is one of the key parameters of sensors. The *DL* value can be calculated as *DL* (ppm) = $3(rms_{noise}/S)$ [11], [12], where rms_{noise} is the root-mean-square standard deviation and *S* is the slope value of the linear fit of the gas response versus gas concentration. The *DL* of the SnO_2 NF sensors was found to be 0.015 ppm. This value is much lower compared to the threshold limit value of American health safety standards (3ppm) [13].

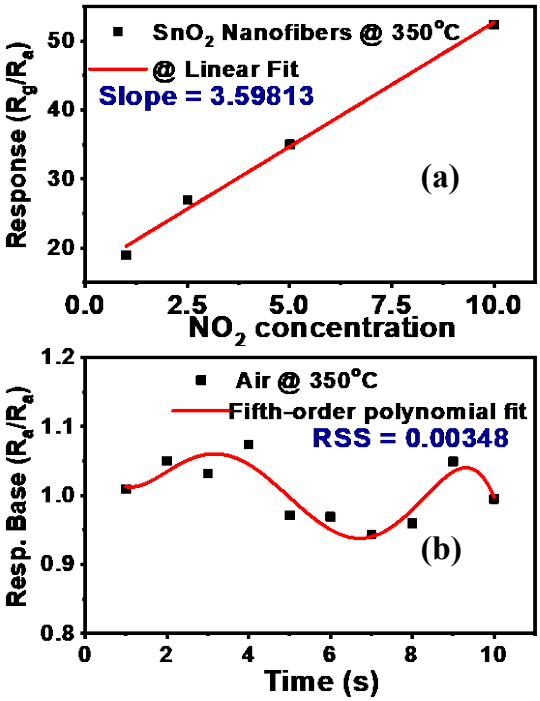

Fig. 6. (a) Slope for *DL* calculation of the SnO_2 NFs sensors. (b) fitted values of residual sum of square (*RSS*).

It has been known that when SnO_2 NFs were placed in the air, the oxygen will capture electrons from SnO_2, which generates ionosorption species of O_2^-, O^-, and O^{2-} on the surface [14], leading to form the depletion layer at the surface of the material. When SnO_2 NF sensors exposed to oxidizing NO_2 gas, it can be reacted with oxygen pre-adsorbed on

the surface of the material or directly trapping electrons from the conduction band. The competition absorbed reaction can take place between oxygen and oxidizing gas as anionic ions. The adsorption of NO_2 gas is considerably stronger compared to oxygen [15], [16]. In this case, the adsorbed reaction of NO_2 gas on the surface of *n*-type semiconductor may be dominated, which can be described in the following equation [17], [18]:

$$NO_{2(gas)} + e^- \leftrightarrow NO_2^-{}_{(ads)}$$

$$NO_{2(gas)} + 2O^-{}_{(ads)} \leftrightarrow NO_2^-{}_{(ads)} + O_{2(gas)} + e^-$$

$$2NO_{2(gas)} + O_2^-{}_{(ads)} + 2e^- \leftrightarrow 2NO_2^-{}_{(ads)} + 2O^-{}_{(ads)}$$

$$NO_2^-{}_{(ads)} + 2O^-{}_{(ads)} + e^- \leftrightarrow NO_{(gas)} + \tfrac{1}{2}\, O_{2(gas)} + 2O^{2-}{}_{(ads)}$$

The adsorption of oxidizing gas on the *n*-type semiconductor takes electrons away SnO_2 NFs, which provides more charge density on the surface of material. Thus, the electron depletion layer further extended leading to increase the potential barrier at the surface of material as well as the grains boundaries created by nanograins in NFs (Fig. 7). Therefore, the sensor resistance increases upon exposure to the oxidizing gas [16], [19].

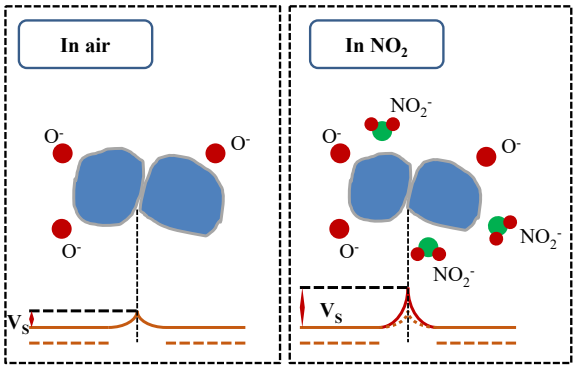

Fig.7. Schematic illustration the NO_2 sensing mechanism of the SnO_2 NFs.

The response of the sensors decreased with a further decrease in the temperature as shown in Fig.8(a). Furthermore, the response-recovery times were long (Fig.8(b)). This phenomenon can be explained by the activation energy for the reaction between the NO_2 gas and the surface of the sensors. At lower temperature, the activation energy for the adsorption of NO_2 is insufficient for physical absorbed while at higher temperatures, the NO_2 molecular tend to escape before absorbed on the surface of the material due to their high activation.

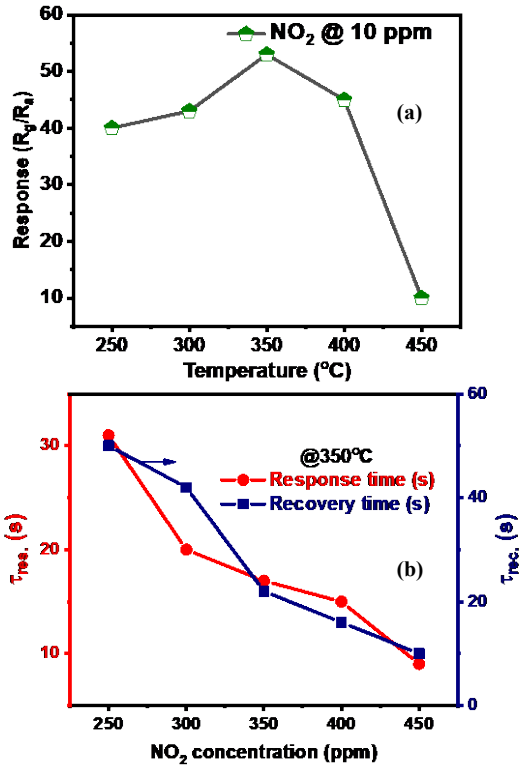

Fig.8. (a) Gas response and (b) response-recovery time at different temperatures.

4. Conclusion

In the present work, we have fabricated the SnO_2 NF based sensors for effective detection of NO_2 oxidizing gas. The gas sensing properties of the SnO_2 NF sensors were tested to 1-10 ppm NO_2 gas in the temperature range from 250 °C to 450 °C. The results showed highest response of 53 times to 10 ppm NO_2 at optimal operating temperature. The obtained high sensitivity was explained by the surface depletion and grain boundary in NFs.

Acknowledgments

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