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Formaldehyde gas sensor based on nanostructured nickel oxide and the microstructure effects on its response

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Abstract. NiO nanostructures can be used as a promising material for semiconductor gas sensor to detect formaldehyde at low concentrations (< 1 ppm). Here, the effect of the morphology of the synthesized NiO nanostructures on gas sensing properties is studied and discussed. NiO nanostructures have been synthesized by thermal decomposition of precursors obtained by two different chemical precipitation methods and a sol-gel technique. Thick films of the synthesized NiO nanostructures were deposited by spray coating on alumina substrates fitted with gold interdigitated electrodes and a platinum heater. The gas sensing properties of those NiO films were studied for low concentrations of formaldehyde gas at different working temperatures. A clear difference in response characteristics was observed between the samples prepared by different synthesis routes.

1. Introduction

In Europe, formaldehyde is now considered by the authorities as one of the priority pollutants in indoor air because of its carcinogenic character and because of the many sources in our closed environment: paper products, stiffeners, wrinkle resisters and water repellents, insulation, combustion devices, pressed-wood products, etc. The WHO guideline for indoor air formaldehyde concentration is 0.08 ppm (0.1 mg/m^3) [1].

It seems therefore necessary to measure the concentration of formaldehyde in closed environments because this data is essential for preventive actions (choice of the materials/furniture treatment, ventilation or indoor air purification). There exist many chemical and biochemical sensors (indicator tubes, electrochemical cells...) that are the subject of numerous works [2]. However, these inexpensive and miniature sensors lack in selectivity and possess relatively high detection limits which are not compatible for "indoor" detection for which the useful range is typically 10 ppb to 1 ppm. NiO was already pointed as a sensitive material for formaldehyde at low concentrations [3, 4]. Because of its applications in various fields (smart windows, supercapacitors, catalysis), a lot of synthesis routes for NiO nanopowders or films were proposed [5].



We present in this paper the characteristics of NiO layers synthesized by three different methods and compare the performances towards formaldehyde detection.

2. Experimental

2.1. Synthesis of the Nickel Oxide powders

NiO powders were synthesized by three different methods, sol-gel from nickel chloride and two precipitation methods from nickel malonate and nickel sulfate precursors.

2.1.1. By Sol-gel method [6]. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (1.5 g, 0.0063 mol) was dissolved in 70 ml of absolute ethanol at room temperature, leading to a clear green coloured solution. In another beaker, NaOH (0.5g, 0.0125 mol) was dissolved in 100 ml absolute ethanol and the NaOH solution was added to the nickel chloride solution dropwise. The mixture was stirred at room temperature for 2 h. During this time, the reaction mixture was found to form light green coloured gel. After 2 h, the gel was filtered, washed thoroughly with distilled water and then finally with ethanol. The precipitate was air dried, yielding a light green coloured powder. The TGA data showed that this green powder decomposes at $\sim 294^\circ\text{C}$.

2.1.2. By precipitation from nickel sulfate [6]. 0.083 mol of urea was added to 5.2 mmol of nickel sulphate dissolved in 80 ml of distilled water. The mixture was heated to 80°C for 4 h. The green precipitate formed was filtered, washed with distilled water several times to remove the unreacted nickel salt and urea and finally with absolute ethanol, and dried at room temperature. The TGA data showed that the green powder decomposes at $\sim 369^\circ\text{C}$.

2.1.3. By precipitation from nickel malonate [7]. The NiO here was obtained via two experimental steps: the synthesis of the precursor by precipitation in aqueous solution containing nickel ions using the malonate ligand as precipitating agent and its subsequent decomposition. Using nickel malonate precursor, lithium malonate was first prepared in aqueous solution by adding lithium hydroxide (10 mmol) to malonic acid (5 mmol) and the pH adjusted to 7. After 5 min, an aqueous solution containing nickel chloride was poured drop by drop into the previously prepared solution of lithium malonate with continuous stirring. The resulting green solution was then stirred for 3h at 90°C under reflux. The obtained precipitate was filtered, washed successively with distilled water, isopropanol and acetone to ensure the total removal of impurities and dried in an oven at $70\text{--}80^\circ\text{C}$ to obtain a light green powder. The as-prepared precursor powder was calcined in a ceramic crucible at 500°C in a muffle oven ($10^\circ\text{C}/\text{min}$) for 1 h under air flow. The TGA data showed that green powder decomposes at $\sim 343^\circ\text{C}$.

2.2. Sensor preparation

For measuring gas sensing, synthesized NiO powders were subjected to calcination at 400°C for 1 h and each coated on alumina substrates fitted with interdigitated gold electrodes and platinum heating element (Fig. 1) by simple spray-coating of the corresponding ink. The ink was prepared by mixing the metal oxide powder with distilled water and the resulting solution (charged with 10 % of metal oxide) was placed for 24 h in a TURBULA Shaker-Mixer to separate all the agglomerate particles. The thickness of the sensitive layers is $\sim 8\text{--}10\ \mu\text{m}$ (checked with an optical profiler). Finally the NiO coating was annealed at 400°C for 1h in air before their exposure to the gases in a Teflon chamber.

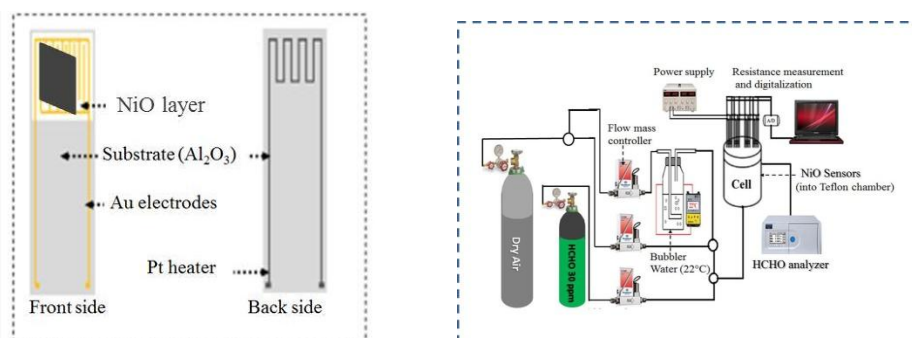


Fig.1. Substrate used for sensing measurement and setup used for formaldehyde sensing measurements

3. Results and discussion

In order to obtain the insight information about the surface morphology and particle size of the samples, FE-SEM analysis was performed. Fig.2 shows the FE-SEM images of three synthesized NiO.

It can be observed that the film obtained from sol-gel method had a uniform distribution of small size particles approximately 15-20 nm on the surface (Fig.2A). In the sample obtained with precipitation from nickel malonate (Fig.2C), the film is composed of particles with various sizes between 20 and 100 nm. Whereas in the case of the sulfate precursor (Fig.2B), the particles possess an agglomerated hexagonal sheet-like morphology.

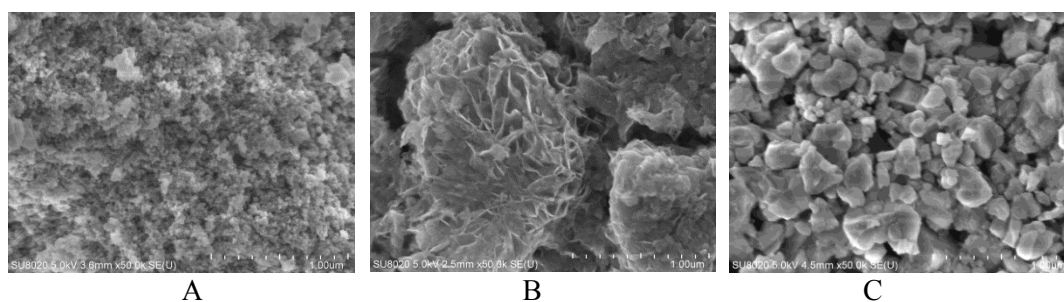


Fig.2. FE-SEM image showing nanostructures NiO obtained from precursor prepared by (A) sol-gel from nickel chloride, (B) precipitation from nickel sulfate and (C) precipitation from nickel malonate

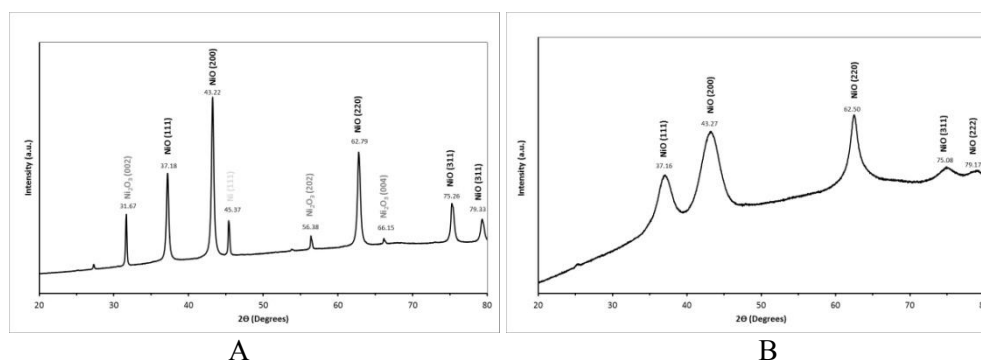


Fig.3. XRD patterns of NiO nanoparticles synthesized by sol-gel method from nickel chloride (A) and by precipitation from nickel sulfate (B).

The XRD patterns of calcined samples are shown in Fig.3. XRD pattern of powder prepared by precipitations from nickel malonate and nickel sulfate (Fig.3B) revealed the formation of face-centered-cubic structured NiO (JCPDS file N°. 78-0428). Whereas the XRD pattern of calcined sample prepared by sol-gel method from nickel chloride shows in addition other peaks (Fig.3A) which were identified as Ni₂O₃ [8].

In order to compare the effect of synthesized NiO method on formaldehyde response of sensors, electrical resistances of sensing layers were recorded with formaldehyde diluted in humid clean air (RH=50 %) at concentrations under 1 ppm at different operating temperatures (between 150 and 280 °C). The setup for the exposure tests of sensors to formaldehyde is shown in Fig. 1.

Since NiO is a p-type semiconductor, the electric resistance of NiO sensor increases when formaldehyde gas is introduced to testing chamber. The sensitivity, *S*, described in this paper was defined, according to the following formula:

$$S = \frac{R_{\text{gas}} - R_{\text{air}}}{R_{\text{air}}} \times 100$$

Where, *R_{gas}* and *R_{air}* are the resistance of sensor after exposure to formaldehyde and clean air, respectively.

The Fig. 4 and Fig. 5 show the dynamic response of different NiO-based sensors operated at 280 and 220 °C. It can be seen that at higher temperature, the NiO sample prepared by precipitation from malonate shows the better sensitivity to formaldehyde. At lower temperature, the sample fabricated by sol-gel method from nickel chloride shows a better response. Whereas the formaldehyde response of NiO sample prepared by precipitation from nickel sulfate is very slow in the studied temperature range. It can be observed that for all temperatures the response and recovery times of the sensors based on the chloride route are shorter.

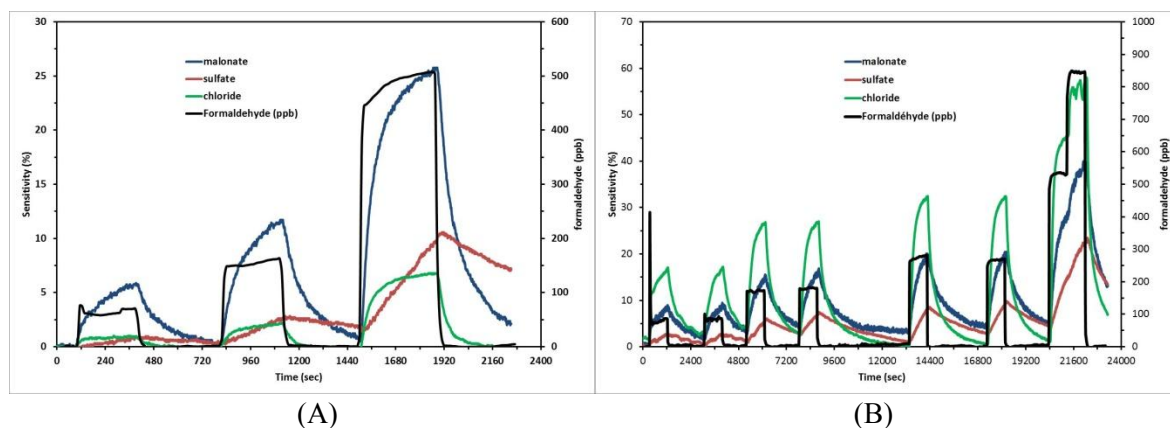


Fig.4. Dynamic response of different type of NiO sensors at different operating temperatures (A) 280 °C and (B) 220 °C.

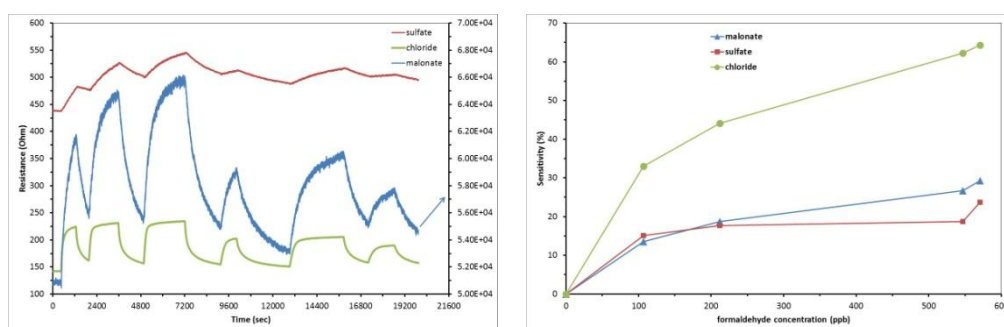


Fig. 5. Dynamic response of different NiO sensor exposed to 532, 547, 571, 197, 212 and 107 ppb of formaldehyde at 200 °C.

The formaldehyde sensing characteristics of these NiO-films are strongly influenced by the surface microstructure and the synthesis method. The more favourable microstructure corresponds to that of NiO sample obtained by sol-gel method from nickel chloride. A possible reason is the morphology of the layers showing very fine particles in a porous stacking. XPS analyses are underway to complete understanding.

Fig. 6 shows the variation of sensitivities against formaldehyde in NiO sensor based on this sample, which was measured at different operating temperatures. The sensor exhibits a maximum sensitivity at a temperature of 200 °C.

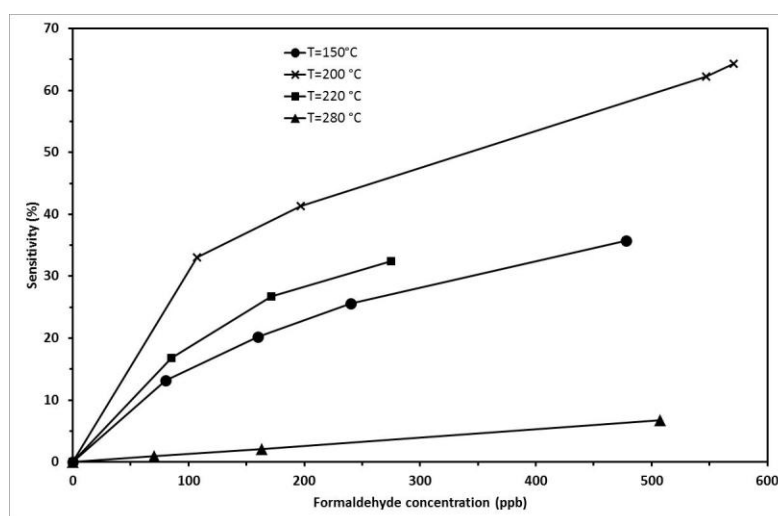


Fig.6. Variation of sensitivity of NiO sensor prepared by precipitation from nickel chloride with formaldehyde concentration at different operating temperature.

4. Conclusion

This study has demonstrated that chemical sensors based on nanostructures NiO are able to detect very low concentration of formaldehyde (<1 ppm) with good performance at working temperature around 200 °C. The effect of the synthesis routes was clearly put in evidence. These results are promising for development of simple and inexpensive devices allowing the analysis of formaldehyde in parts per billion (ppb) in indoor air.

Acknowledgment

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