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Low temperature selective NO_2 sensors by nanostructured fibres of ZnO

C. Baratto [a,*], G. Sberveglieri [a], A. Onischuk [c], B. Caruso [b], S. di Stasio [b]

[a] Department of Chemistry and Physics and INFM, University of Brescia, via Valotti 9, Brescia 25133, Italy
[b] Istituto Motori C.N.R., Aerosol and Nanostructures Laboratory, via Marconi 8, 80125 Napoli, Italy
[c] Institute of Chemical Kinetics and Combustion, 630090 Novosibirsk, Russia

Abstract

We studied the gas sensing properties of Zn nanopowders synthesised by an aerosol route. Two different powder morphologies were obtained: fibre-mats and cauliflower structure. Both sensors showed a great sensitivity against sub-ppm concentration of NO_2 at low working temperature. The fibre powders relative response towards 0.4 ppm of NO_2 is 50, while relative response of the cauliflower structure is 8 at 100 °C. Both sensors were also selective, since no resistance variation was observed for CO, and ethanol. On the contrary resistance variations were observed with relative humidity changes. Sensors behaviour was studied at different working temperatures in the range 20–150 °C.

Keywords: Zinc oxide; Gas sensor; NO_2 detection; Low working temperature

1. Introduction

Zinc oxide is one of the oxides that were applied earlier in gas sensing for many gases. It is known in literature as a sensor for ethanol (0.01%), H_2 (0.2%) [1], humidity in the range 2–85% [2], NH_3 (30 ppm) [3], NO_2 (10–50 ppm) and CO [4].

It shows good stability and its selectivity can be improved by mean of catalysts, but the detection limit is quite high for developing environmental pollutant sensors. For example, for NO_2 detection in outdoor urban environment, Italian legislation fixed alarm level at 0.1 ppm and attention level at 0.2 ppm.

Moreover zinc oxide working temperature is higher than 300 °C. The decrease of the working temperature is desirable to lower power consumption and to use the sensor in explosive environment.

We prepared zinc oxide powders by mean of an aerosol route: the nanometer-size of the powders obtained and the peculiar morphology improved sensing performances towards sub-ppm NO_2 concentration at very low working temperature.

2. Experimental

The zinc/zinc oxide nanostructured powders were synthesised by an evaporation/condensation scheme, which is described in detail elsewhere [5–7]. Briefly, the experimental set-up is constituted by a quartz reactor equipped with a furnace. A flux of nitrogen (0.5–1 l min^{-1}) is used to work as carrier gas.

Quality certified bottled N_2 is filtered by hydrophobic EPA filters to remove all the impurities from the carrier gas. Zn grains (Aldrich, 20 mesh, purity better than 99.8%) are used as feedstock matter to fill a small quartz boat, positioned inside the reactor in correspondence of the heated zone. The evaporation temperature is varied within 500–750 °C. At the outlet of the hot zone, zinc vapours undergo a fast expansion through a nozzle and contemporary a further cooling by a co-annular flux of nitrogen at ambient temperature. Both these treatments produce the supersaturation condition, which starts the homogeneous nucleation process. The aerosol nanoparticles properties (size, crystal structure, clustering degree and morphology) do depend on the synthesis parameters, primarily on the temperature inside the reactor. Zinc fibres are collected as mats formed at the exit of the expansion nozzle after run times typically of 1 h. This fibre shaped material will be hereinafter called type A. Otherwise, zinc powders with a compact cauliflower

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[*] Corresponding author. Tel.: +39-030-209-1271; fax: +39-030-209-1271.
E-mail address: baratto@tflab.ing.unibs.it (C. Baratto).

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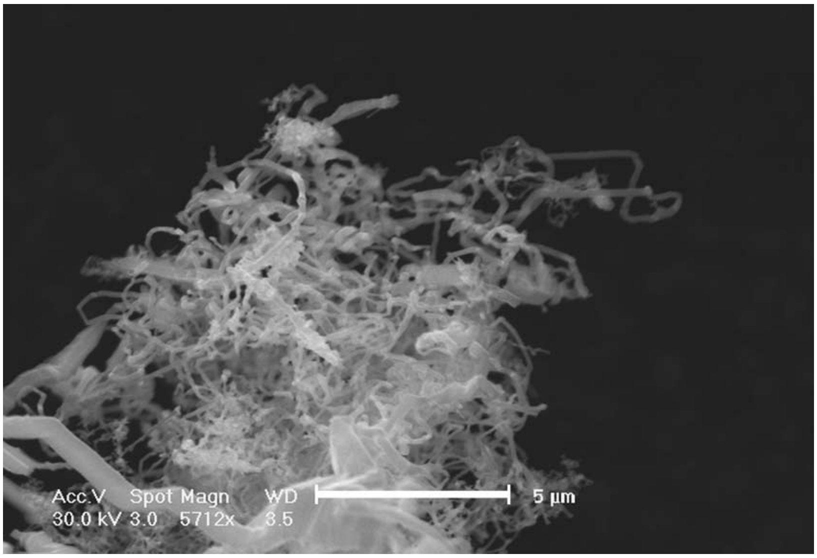

Fig. 1. SEM micrograph of powder type A showing fibre-mats obtained as deposit from the aerosol deposition experiment. Scale bar 5 µm.

structure are obtained by scratching directly the reactor walls. Hereinafter this material will be called type B.

Morphology and structure of the prepared powders were investigated by TEM, SEM and XRD [6,7]. Fig. 1 reports SEM micrograph of the powder type A: it is composed of mats of sponge-like material, in which we can distinguish nanofibres, nanowires and nanotubes with external size in the range 100–300 nm. XRD analysis proved that powder type A is formed by metallic Zn (wurtzite structure) with 15% relative percentage of ZnO, before oxidation treatment. The powder type B is composed by aggregation of particles that constitute a cauliflower structure (see SEM micrograph in Fig. 2). The dimension of the smaller particles is about 20–30 nm. XRD analysis showed that is mainly composed of metallic Zn. A commercial Zn powder manufactured by Aldrich was used as standard material for comparison.

A partial surface oxidation treatment was performed by keeping powders type A, B plus the commercial one in a oven under a flux of humid synthetic air at 200 °C for 24 h.

XRD analyses after annealing treatment are underway.

2.1. Functional characterisation

We developed a special container to measure the change in resistance of nanosized powders. The powders were positioned in a quartz container with two Pt contacts and rear Pt heater deposited by sputtering. We were able to vary the working temperature of the powders in the range 20–150 °C. The value of the working temperature was estimated by placing a thermocouple near to the powders.

We used a volt-amperometric technique at constant bias (10 V) to test sensor response in controlled environment. The

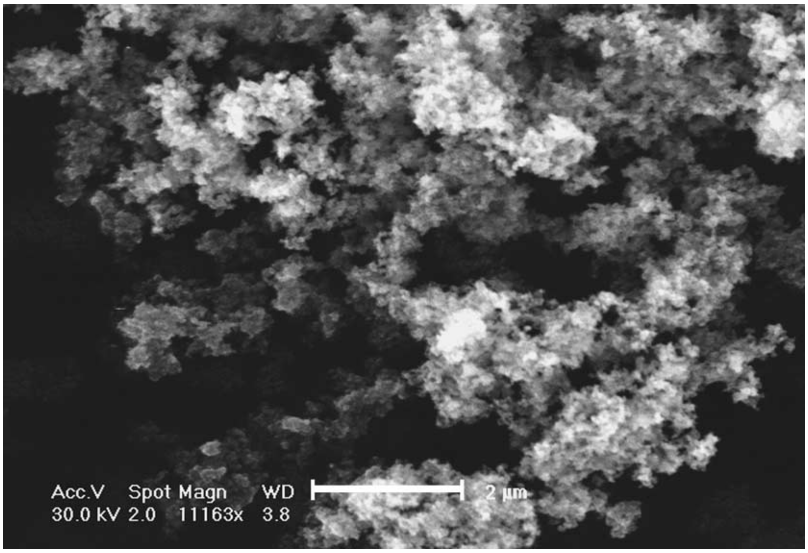

Fig. 2. SEM micrograph of powder type B showing stratification of aggregates with cauliflower morphology. Scale bar 2 µm.

test chamber was kept at constant temperature (20 °C) in a climatic chamber. The system used to reproduce in a controlled and repeatable way environmental conditions in the test chamber is a dynamic one based on volumetric mixing through mass flow controllers (MKS) and certified bottles. Since our interest was to monitor pollutant gases in environmental condition, we used synthetic air as a gas carrier. All measurements were performed at constant relative humidity (RH = 50%).

The gas tested were NO_2 (in the range 0.1–0.5 ppm), ethanol (500 ppm) and CO (400 ppm). Relative humidity was tested in the range of 60% (dry air). The tests were performed at RT, 100 and 150 °C working temperatures.

To compare sensors response to oxidising species, we define the relative response as $\Delta R/R = (R_f - R_0)/R_0$, where R_0 is the sensor resistance in air, while R_f is the sensor resistance in equilibrium with gas.

3. Results and discussion

Fig. 3 shows the dynamic electric response of ZnO type A, ZnO type B and commercial powders at 100 °C working temperature and 50%RH towards low concentrations of NO_2, ethanol and CO. The current of each sensor was normalised to its baseline value to compare their performances on the same plot. Nanosized powders show typical metal oxide semiconductor n-type behaviour: resistance increases with oxidising gases and decreases with reducing gases.

Powder type A can sense concentration as low as 0.1 ppm of NO_2 at low working temperature with relative response of 3. Response and recovery times are of the order of minutes. High ethanol concentration induces very small current variation, while high CO concentration does not induce any variation. NO_2 detection limit of powder type B is 0.2 ppm. Also in this case very small current change is associated to ethanol presence into the test chamber, while no variation is observed in the case of CO.

Commercial powder performances with NO_2 at 100 °C are smaller than that observed with nanosized powders, since it cannot reveal 0.2 ppm. Relative response at 0.4 ppm is 1.8, smaller than that of nanosized powders. The behaviour with CO and ethanol is comparable with other powders.

We studied the influence of the working temperature on NO_2 detection. The results are summarised in Fig. 4. We plotted sensor response at 0.4 ppm of NO_2 as a function of the working temperature for ZnO type A, type B and commercial powder.

The performances of powder type A are superior to that of powder type B at every working temperature. Relative response is higher than 100 at RT and decreases at about 2 for 150 °C. In the case of powder type B the higher relative response towards NO_2 was observed at 100 °C, and it decreases to zero for higher working temperatures. Performances of nanosized powders are higher than that of commercial powder. The differences between the sensing properties of the two powders can be ascribed to differences in their morphologies, since the surface available for reaction with the gas is higher for sponge-like material than for compact cauliflower structure.

Fig. 5 shows powders behaviour towards changes of RH from dry air up to 60%. At 100 °C working temperature, commercial powder is a good humidity sensor while powder type A and type B are not. This result is confirmed at room

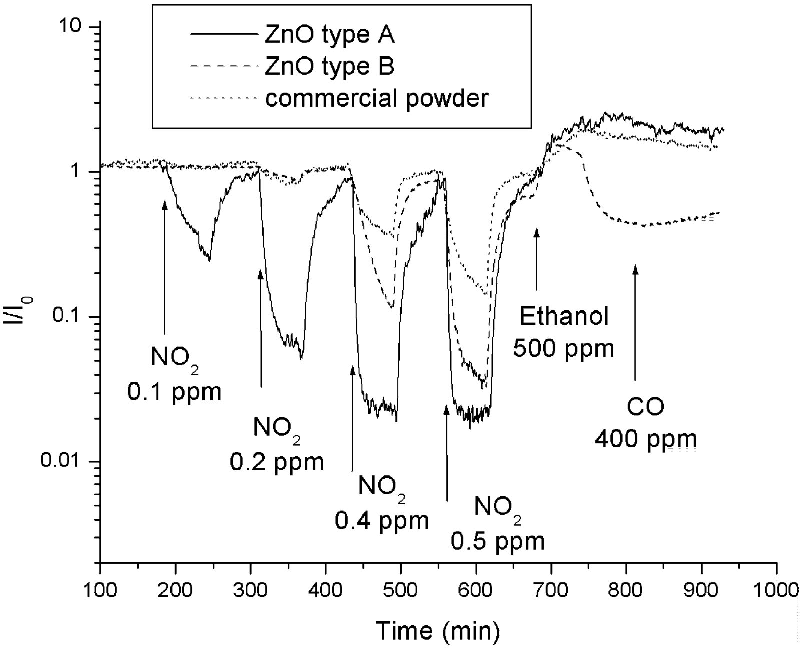

Fig. 3. Dynamic electric response of sensor type A, B and commercial powders towards NO_2, ethanol and CO at 50%RH and 100 °C working temperature. Five-point adjacent averaging was used to smooth the experimental data.

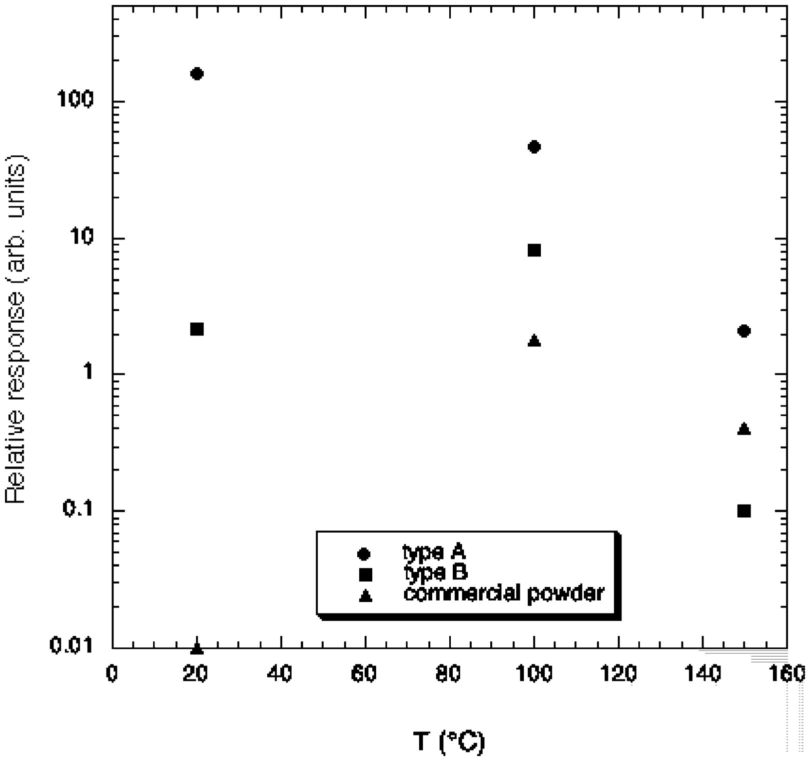

Fig. 4. Sensor relative response towards 0.4 ppm of NO_2 at 50%RH as a function of working temperature.

temperature. We can conclude that powder prepared by an aerosol route show better rejection of humidity variation; particularly, for sensor type A the use at RT is recommended, featuring higher selectivity towards NO_2.

The mechanism of NO_2 interaction with zinc oxide surface should follow conventional metal oxide semiconductor sensor theory [8,9]. When NO_2 adsorbs on the zinc oxide surface creates acceptor surface states, thus increasing the band bending at the grain surface; this results in an increase of the resistance.

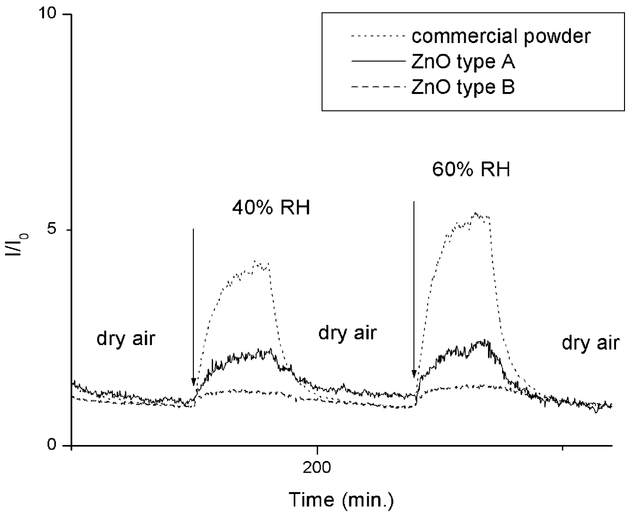

Fig. 5. Dynamic electric response of sensor type A, B and commercial powders towards relative humidity at 100 °C working temperature.

Recently, Malagù et al. [10] extended this theory to the case of nanometric dimension of the grains. They demonstrated that an enhancement in sensitivity is expected in the case of grains size below 10 nm. In our case we have bigger structures for both type A and type B, but we think that oxidation of Zn after annealing is not complete and a core of metallic zinc remains.

In this case, the thin shell rules the electrical behaviour of the material, giving a ‘nanometric material behaviour’ even if the structure are sometimes higher than 100 nm. Further investigations on the structure and morphology of the powders after oxidation are due to verify this hypothesis.

The selectivity towards CO and ethanol can be explained in terms of working temperatures. It is known from literature that CO and ethanol interactions with metal oxide surface are favoured in the temperature range 300–500 °C, while sensor response at lower working temperature tends to zero, thus explaining the selectivity obtained at $T \leq 150$ °C.

Tests at higher working temperature are planned to study sensor behaviour in larger temperature range.

4. Conclusions

The sensor response of powders fabricated via aerosol route is both size and morphology depending. Nanostructured samples with shape of fibre-mats and stratified aggregates with cauliflower morphology do show a significantly enhanced NO_2 response at low working temperatures (RT,

−100 °C) towards sub-ppm concentrations and a relative insensitivity to the humidity with respect to a standard powder available in commerce.

The fibre-mats structure produces an increase of relative response towards NO_2 of about one order of magnitude with respect to cauliflower structure. Fibre-mats powder sensor can reach alarm level (0.1 ppm) for NO_2 detection in urban environment with relative response of 3 at 100 °C and good rejection of CO and ethanol interference. In all cases, we observe no interference from CO and ethanol, due to low working temperature.

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