Organometallic Approach for the Preparation of Zinc Oxide Nanostructured Gas Sensitive Layers

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Abstract. A reproducible organometallic approach was used in order to prepare zinc oxide gas sensitive layers. Various ZnO nanostructures with well-defined morphology were prepared by controlled hydrolysis of suitable organometallic precursor. These nanomaterials were deposited on miniaturized gas sensors substrates by an ink-jet method. The as prepared devices were tested towards different reducing gases, namely: CO, C_3H_8, and NH_3. We showed that the morphology of these nanostructures significantly influences the sensor response level to the reducing gases.

Introduction

The achievement of highly sensitive sensors can be accomplished by using materials with very small grains thanks to thier high surface-to-volume ratio [1, 2]. Therefore, the controlled synthesis of nano- or microsized particles with different morphology has attracted considerable interest [3]. It is well known that the successful control of these parameters depends strongly on the synthetic method used for the nanostructures preparation. Compared with high temperature vapor phase method, solution based synthesis methods can be conducted at low temperatures and offer additional advantages such as straightforward processing, low cost, and eases of scale up [4]. Among them, the organometallic approach presents several advantages to get well-controlled nanostructures in terms of size dispersion, chemical composition, surface properties, shape or organization. Few metal oxides (ZnO, SnO_2, In_2O_3, and RuO_2) were obtained in our laboratory by oxidation of metal NPs prepared from organometallic precursors [5, 6]. Moreover, the extension of this method, based on the controlled hydrolysis of metal precursors in the presence of alkylamines ligands, allowed a direct access to well defined nanostructures of magnetic metal oxides (NiO, γ-Fe_2O_3, FeO) [7-9] and semi-conducting oxides (ZnO) [10-12] by a one-step procedure. Drawing from this research, ZnO nanostructures were synthetized and used as gas sensitive layers. The results suggest that the morphology of zinc oxide nanostructures can influence the sensor performance.

Materials and Methods

Organometallic precursor ($Zn(c\text{-}C_6H_{11})_2$, NanoMePS) and octylamine (Sigma Aldrich) were stored in the glovebox. THF was collected after going through drying columns (MB-SPS-800 solvent purification system) prior to use. Distilled water was degassed with argon during 30 min prior to use. All reactions were performed at room temperature and under argon atmosphere in standard Schlenk tubes except for ZnO nanorods which were prepared in a flat-bottomed reactor.

ZnO cloudy-like nanoparticles were obtained from a THF (4 mL) solution of $Zn(c\text{-}C_6H_{11})_2$ (0.25 mmol, 57.9 mg). The hydrolysis was performed by addition of THF (2 mL) containing water (1 mmol, 18 µL) to this solution. After 16 h, the nanoparticles and solvent were separated by centrifugation (5 min, 5000 rpm, 20°C, here and after).

ZnO isotropic nanoparticles were obtained from a THF (4 mL) solution of $Zn(c\text{-}C_6H_{11})_2$ (0.25 mmol, 57.9 mg). Octylamine (0.25 mmol, 32.5 mg) was used as growth orienting ligand. The hydrolysis was performed by addition of THF (2 mL) containing water (1 mmol, 18 µL) to this solution. After 16 h the nanoparticles and solvent were separated by centrifugation and the nanoparticles were washed 3 times with 5 mL of acetone (Sigma Aldrich).

ZnO nanorods were obtained from a mixture of $Zn(c\text{-}C_6H_{11})_2$ (0.25 mmol, 57.9 mg) and octylamine (0.5 mmol, 65 mg). The hydrolysis was performed by addition of water to the reactor (1 mmol, 18 µL). The reaction system was left for 4 days. Then the nanorods were dispersed in THF (6 mL). Afterwards, the nanorods and the solvent were separated by centrifugation. Finally, the nanorods were washed 3 times with 5 mL of acetone.

TEM specimens were prepared on carbon-supported copper grids. TEM images were obtained using a Hitachi 7700 microscope operating at 80 kV.

Sensors preparation: All freshly prepared and washed nanostructures were dispersed in ethanol (Sigma Aldrich). The concentration of the nanostructures in the solution was 5 mg mL^{-1}. The solutions were then deposited on miniaturized gas sensors substrates [13] by an ink-jet method (Microdrop AG) [14] (Fig. 1).

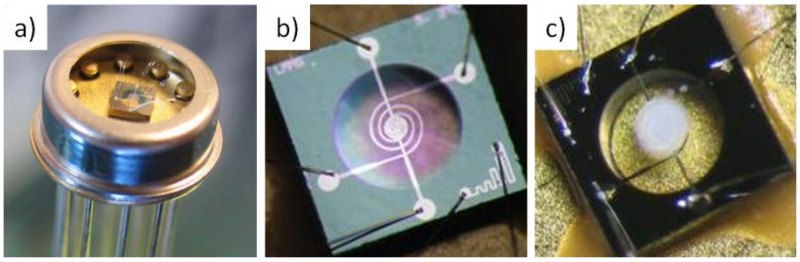

Fig. 1. Gas sensor substrate (a), silicon platform before (b) and after (c) sensitive layer deposition.

Gas tests were performed using a PC controlled setup composed of different gas bottles connected to adequate mass flow controllers (QualiFlow) commanded by Data Acquisition/Switch Unit 34970A. Sensors were placed in a specially designed measurement cell containing also the humidity and temperature sensors commanded by another Data Acquisition/Switch Unit 34970A. The heater was commanded by HP6642A tension controller. The NI 6035E electronic card established the connection between computer and measurements. Freshly prepared sensors were conditioned by successive *in situ* heating of the sensitive layers up to 500°C in synthetic air and at humidity up to 50%. The total gas flow rate was 1L/min. All tests were also performed at these conditions. Firstly, sensors were stabilized in synthetic air for 2h. Then, all sensors were exposed for 15 min to reducing gas mixture containing synthetic air and one of reducing gases, namely: CO, C_3H_8, or NH_3. Resistance was measured before and after sensors exposure to reducing gas mixture and the sensitivity (%) to each gas was calculated as $S = (R_{air} - R_{gas})/R_{air}*100$, where R_{air} – sensor resistance in synthetic air, R_{gas} – sensor resistance in reducing gas mixture.

Results and discussion

TEM images of the nanostructures (Fig. 2) showed that under various reaction conditions it is possible to master the morphology of the ZnO particles prepared by the organometallic approach. The hydrolysis of zinc precursor, $[Zn(c\text{-}C_6H_{11})_2]$, led to the formation of either cloudy-like nanoparticles, isotropic nanoparticles (diameter of *ca.* 5 ± 1 nm), or nanorods (diameter of *ca.* 5 ± 0.8 nm and length of *ca.* 20 nm ± 6) made of ZnO. The synthesis and mechanism of the ZnO particles growth and stabilization have been previously described [12, 15]. The alkylamine ligands play a fundamental role all along the synthesis process and remain coordinated to the particles

preventing them from aggregation. That is why, the synthesis in the absence of alkylamine led to the formation of agglomerated structures – cloud-like nanoparticles (Fig 2a). The presence of organic solvent (THF) plays also an important role in the nanoparticles growth process (Fig. 2b). Indeed, isotropic nanoparticles are obtained when the synthesis is performed in THF in the presence of alkylamine ligands while the formation of ZnO nanorods is directly obtained when the synthesis is performed in pure alkylamine. In these conditions, the nanocrystals grow along the *c* crystallographic axis of the hexagonal ZnO structure (Fig. 2c).

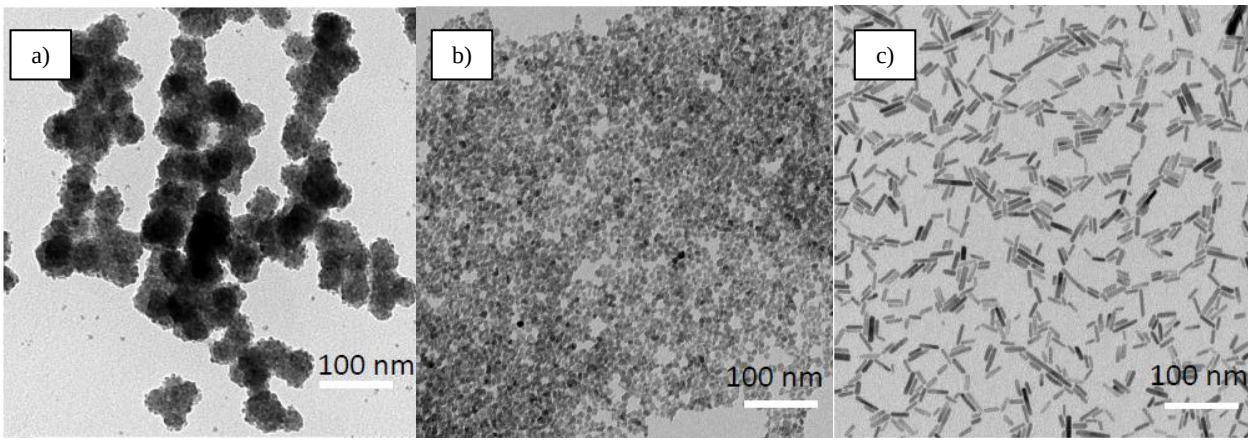

Figure 2. TEM images of various ZnO nanostructures: cloud-like nanoparticles (a), isotropic nanoparticles (b) and nanorods (c).

After the removal of ligands, all prepared ZnO nanostructures were ink-jet deposited on a miniaturized gas sensors substrates to be used as gas sensitive layers. Sensors were exposed to different reducing gases in humid air conditions (RH 50%) at 500°C, namely: 100 ppm of CO, 100 ppm of C_3H_8, and 5 ppm of NH_3. The sensors response towards propane is presented on Fig. 3 and the sensitivities for all the gases are presented in Table 1. In air, the sensitive layers exhibit a resistance of few MOhm. In the presence of reducing gases, the resistance decreased significantly which is characteristic for sensors based on n type semiconductors.

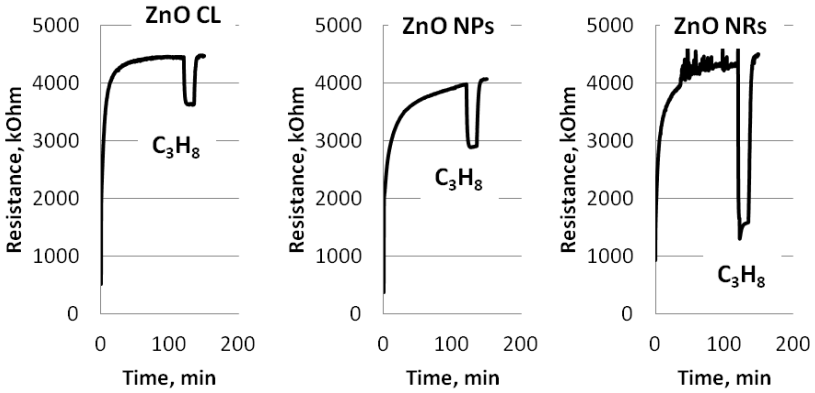

Fig. 3. Example of sensor responses towards propane (ZnO CL – cloud-like nanoparticles, ZnO NPs – isotropic nanoparticles, ZnO NRs – nanorods).

The highest sensitivity towards CO and C_3H_8 was obtained for ZnO nanorods with S = 70% and 63%, respectively. Cloud-like nanoparticles and isotropic nanoparticles exhibit quite similar sensitivity when exposed to CO (*ca.* 40 %), but ZnO cloud-like sensors showed the weakest sensitivity towards propane (S = 10%). Regardless of the ZnO sensors, a quite similar sensitivity to NH_3 (*ca.* S = 5-8%) is obtained. These gas-sensing performances highlight the leading role of the nanoparticle's shape on the CO and especially C_3H_8 detections, whereas it is of little importance for

NH_3. These results demonstrate that sensitivity and selectivity can be improved using the same material but modifying only its shape paving the way for new powerful arrays of selective gas sensors.

Table 1. Sensitivity (%) of ZnO based sensors toward different reducing gases (ZnO CL – cloud-like nanoparticles, ZnO NPs – isotropic nanoparticles, ZnO NRs – nanorods) with RH = 50 %.

	ZnO CL	ZnO NPs	ZnO NRs
100 ppm CO	42	39	63
100 ppm C_3H_8	10	29	70
5 ppm NH_3	8	5	7

Summary

Sensors based on different ZnO nanostructures, prepared following a one-pot organometallic method, were exposed to different reducing gases. The results highlight the influence of the nanostructure's morphology on both the gas sensor sensitivity and selectivity.

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