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# Nanostructured zinc and tin oxides for gas sensors

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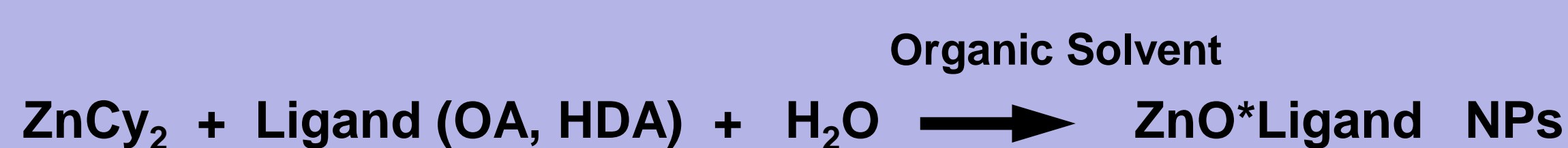
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<sup>4</sup> Alpha MOS, 20 avenue Didier Daurat, 31400 Toulouse, France

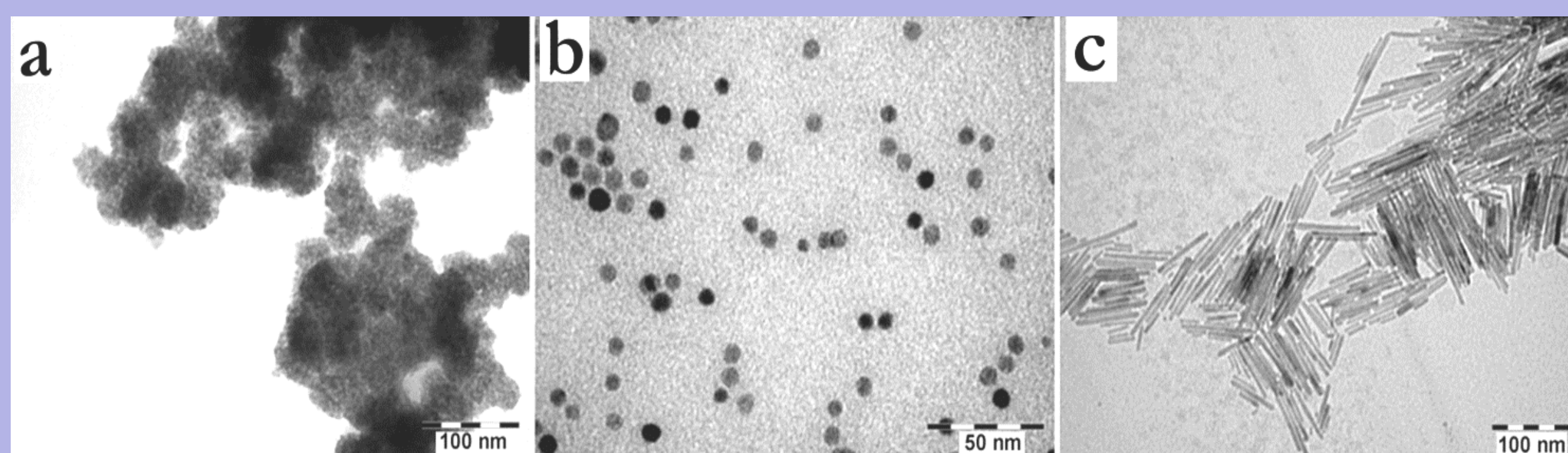
## Aim of the project

The development of high sensitivity and selectivity MOS (metal oxide semiconductor) gas sensors with SnO<sub>2</sub> and ZnO nanoparticles layers based on micromachined silicon substrate for the detection of CO, C<sub>3</sub>H<sub>8</sub>, NH<sub>3</sub>, NO<sub>2</sub>, ...

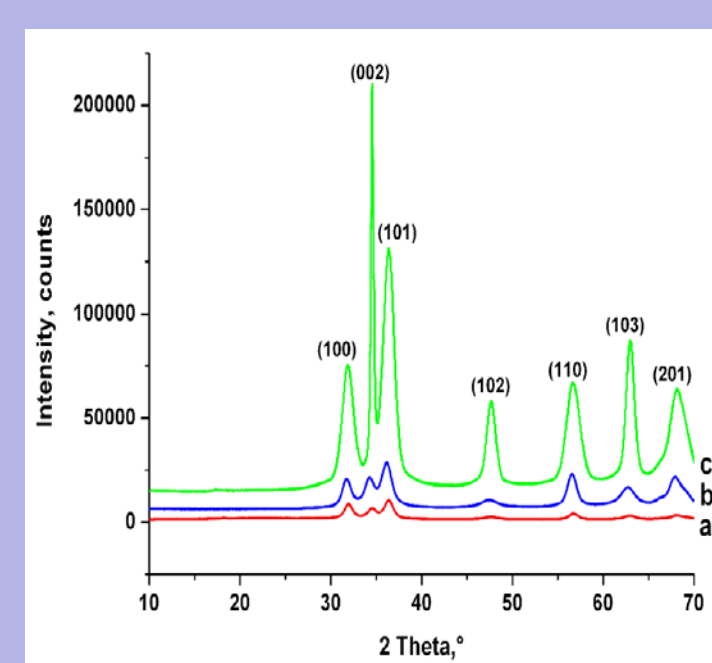
### ZnO Nanoparticles synthesis<sup>1,2</sup>



(ZnCy<sub>2</sub> – dicyclohexylzinc, OA – octylamine, HDA – hexadecylamine)  
CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>NH<sub>2</sub> CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>NH<sub>2</sub>



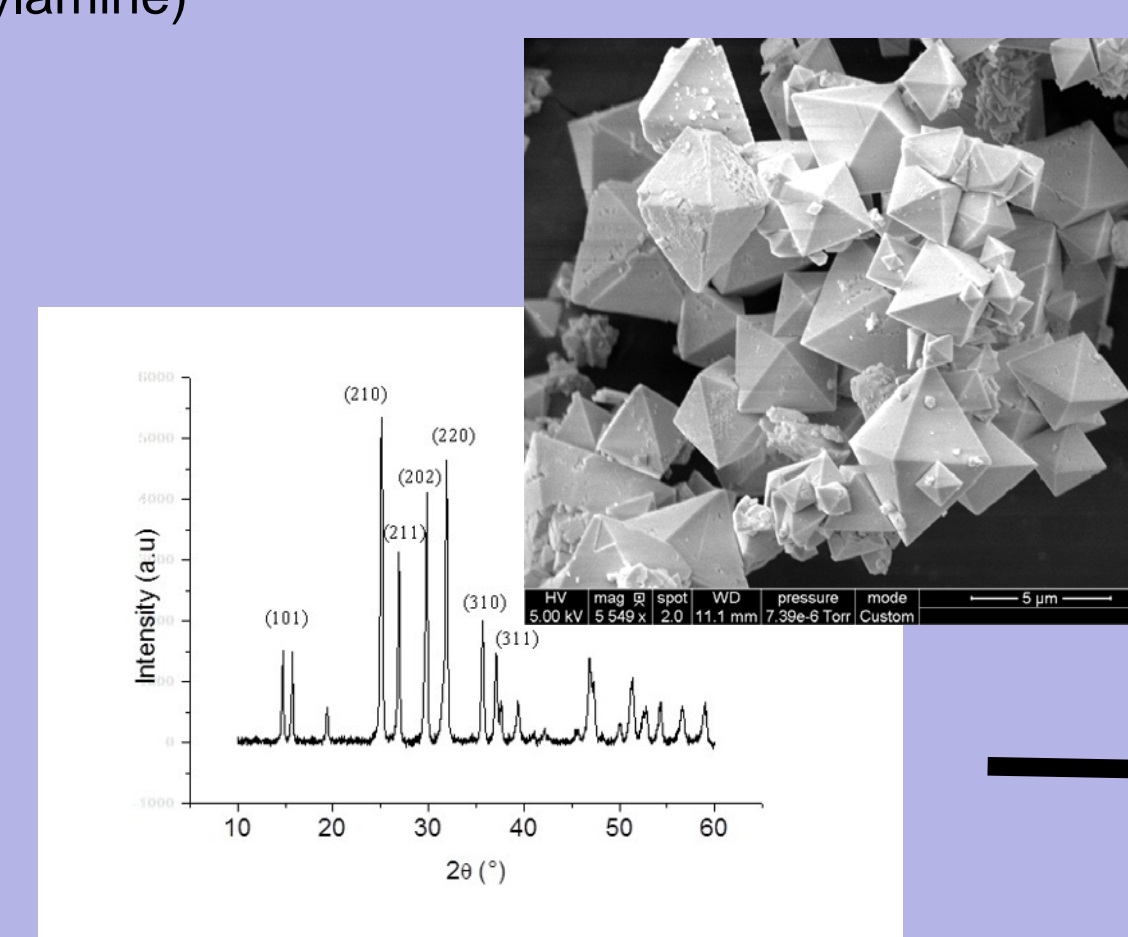
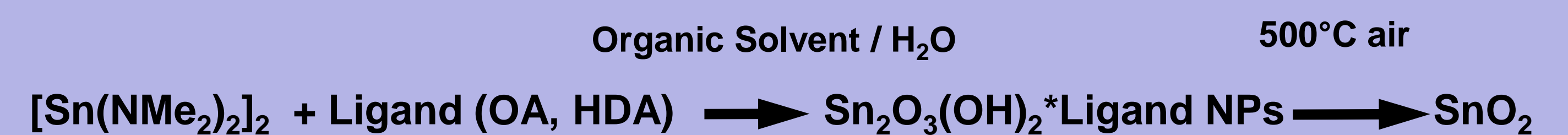
TEM images of ZnO nanoparticles with various morphology: a. ZnO CL, b. ZnO NPs (NP1), c. ZnO NRs (NR1)



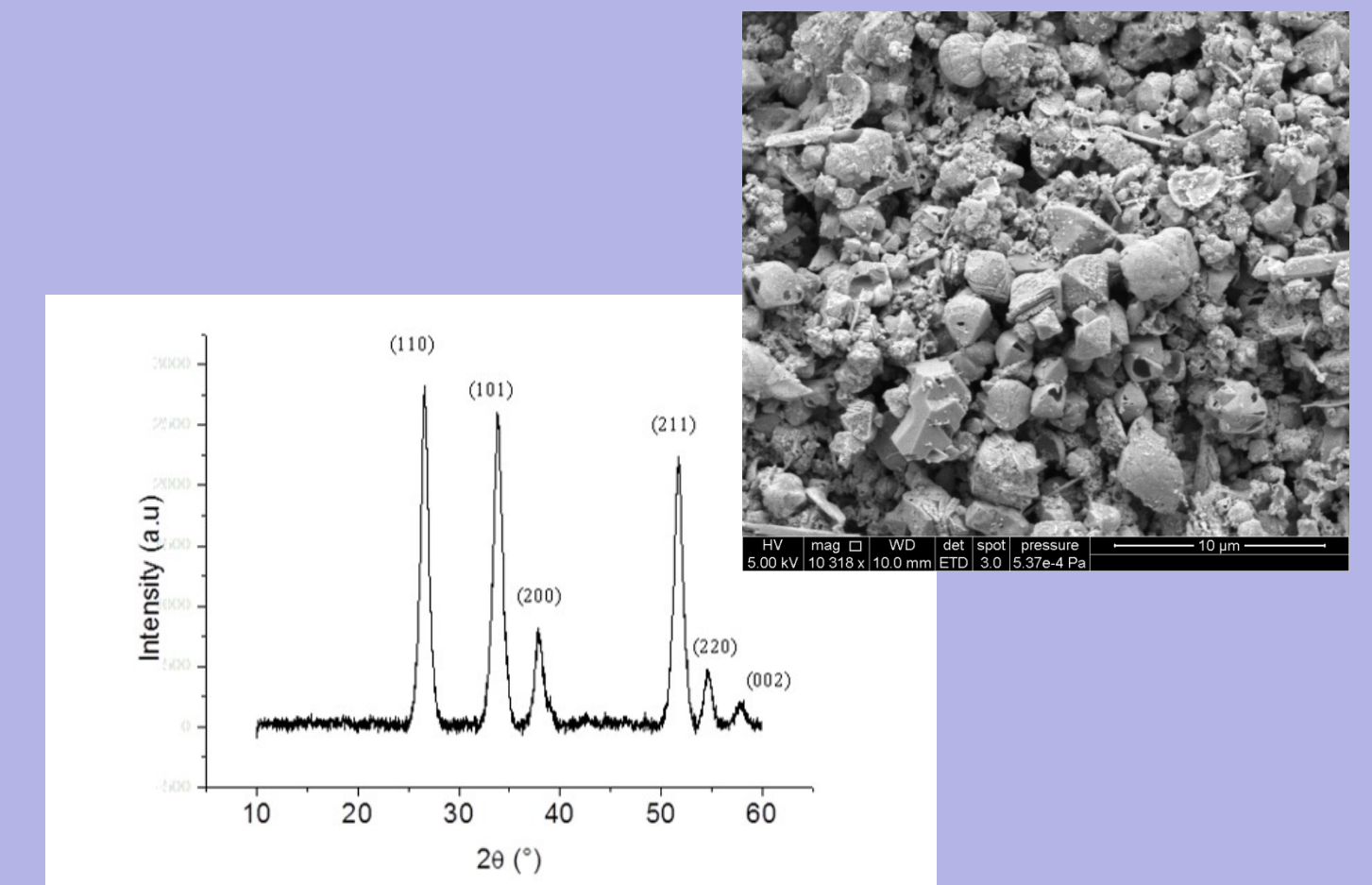
XRD diagrams of ZnO nanoparticle a. cloudy-like structures, b. isotropic nanoparticles, c. nanorods

## Results

### SnO<sub>2</sub> Nanoparticles synthesis



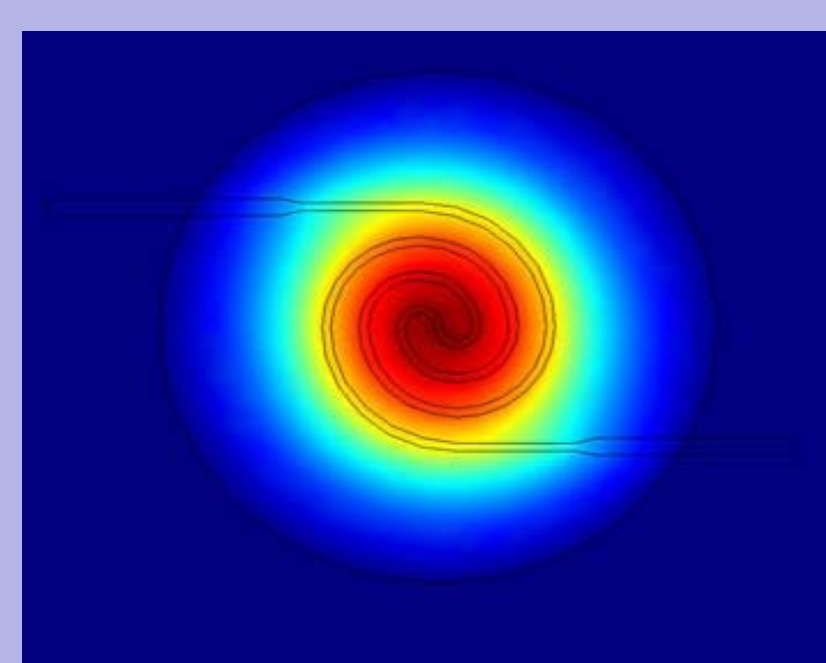
XRD diagram of Sn<sub>2</sub>O<sub>3</sub>(OH)<sub>2</sub>



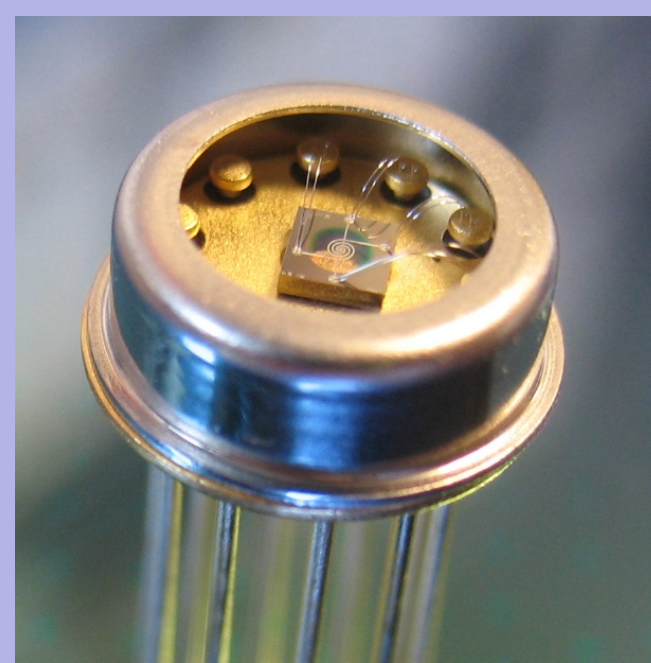
XRD diagram of SnO<sub>2</sub>

### Micromachined silicon platform<sup>3</sup> and sensitive layer deposition

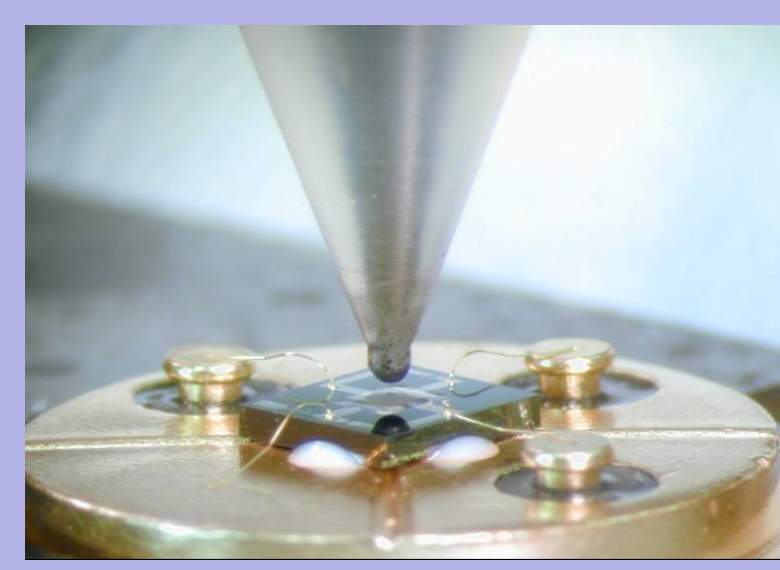
Design of the round shaped platinum heater and interdigitated electrodes for the sensitive layer contact



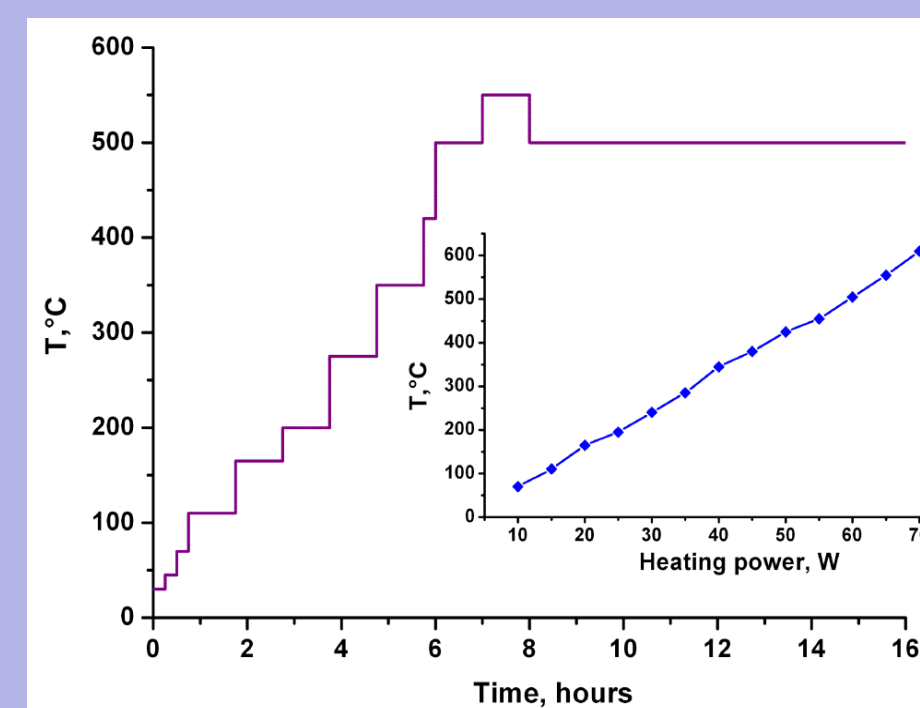
Thermal homogeneity of the heater operating at 400°C



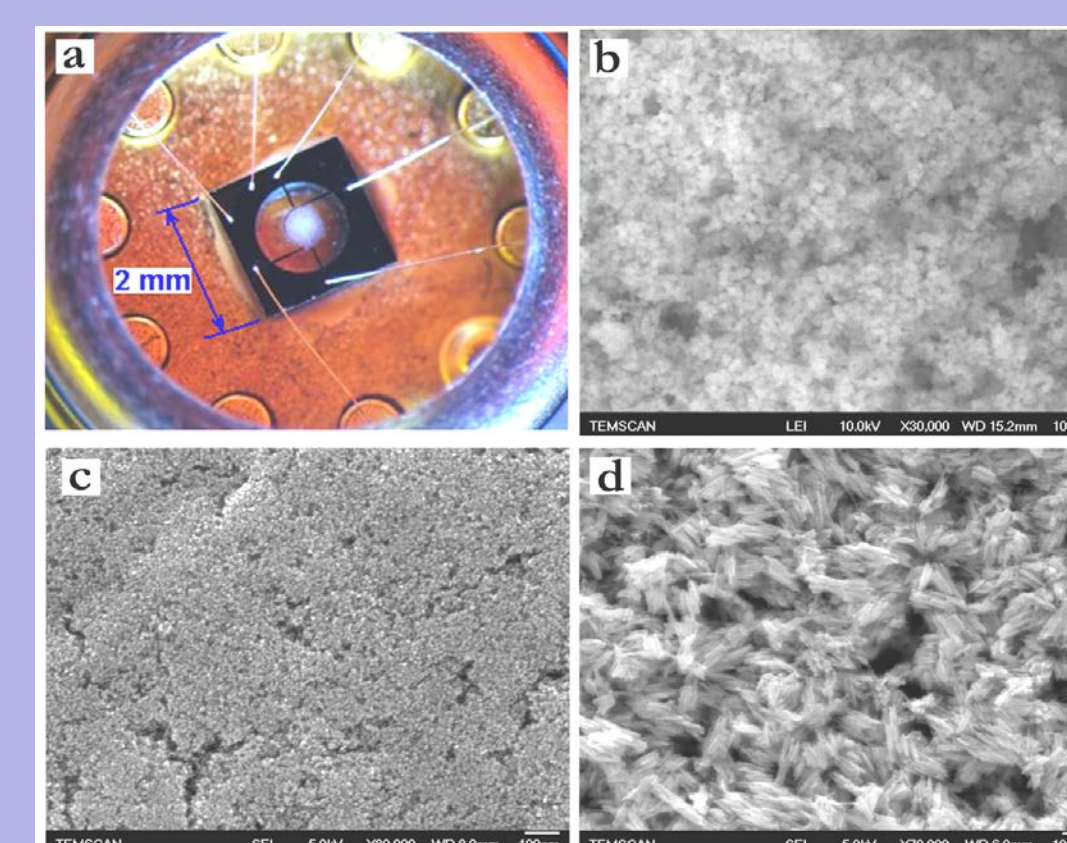
Gas sensor silicon platform on TO5 package.



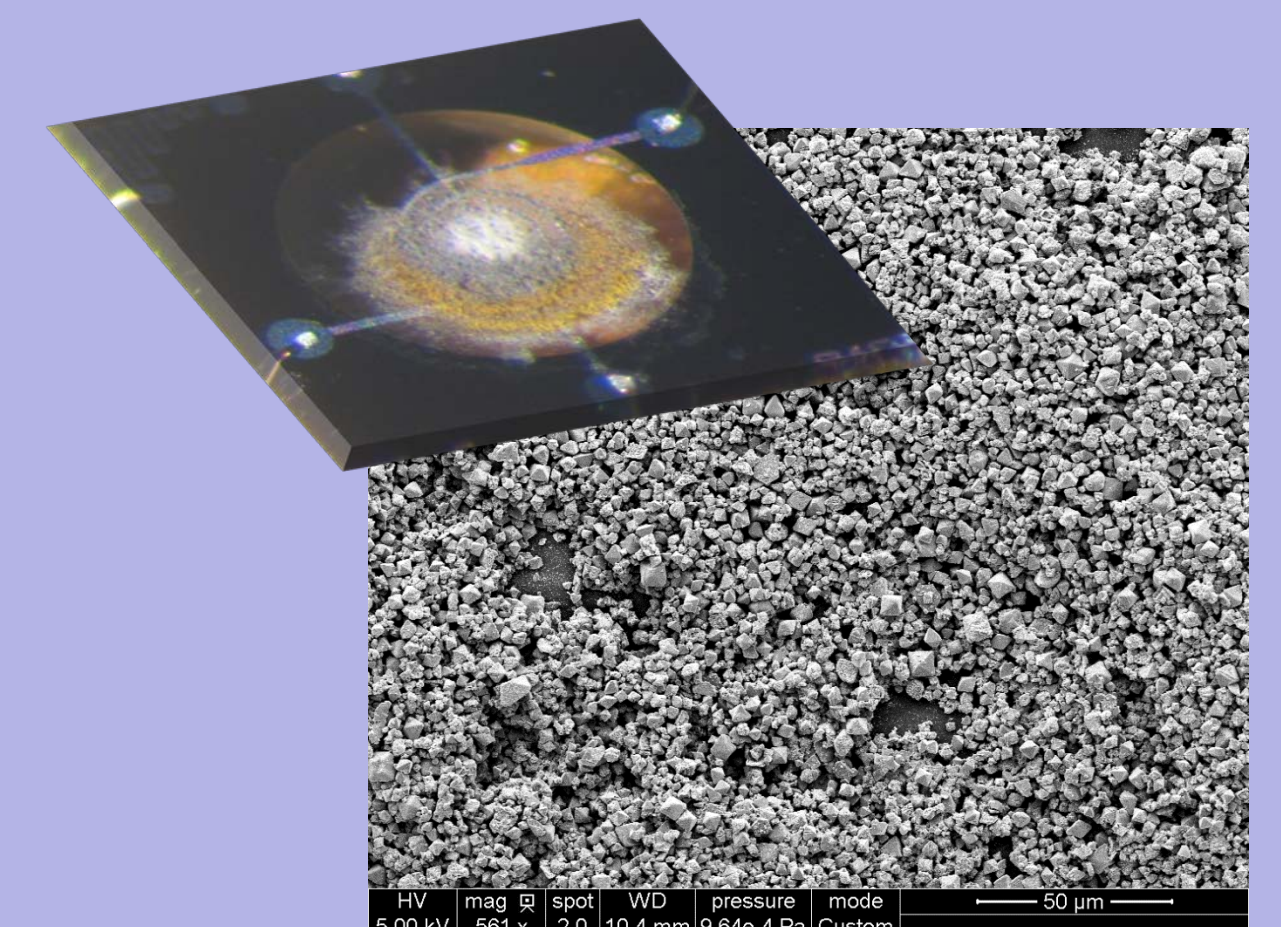
Drop deposition of the metal oxide nanoparticles on the silicon platform



Temperature profile of annealing and stabilization procedure of sensing layers

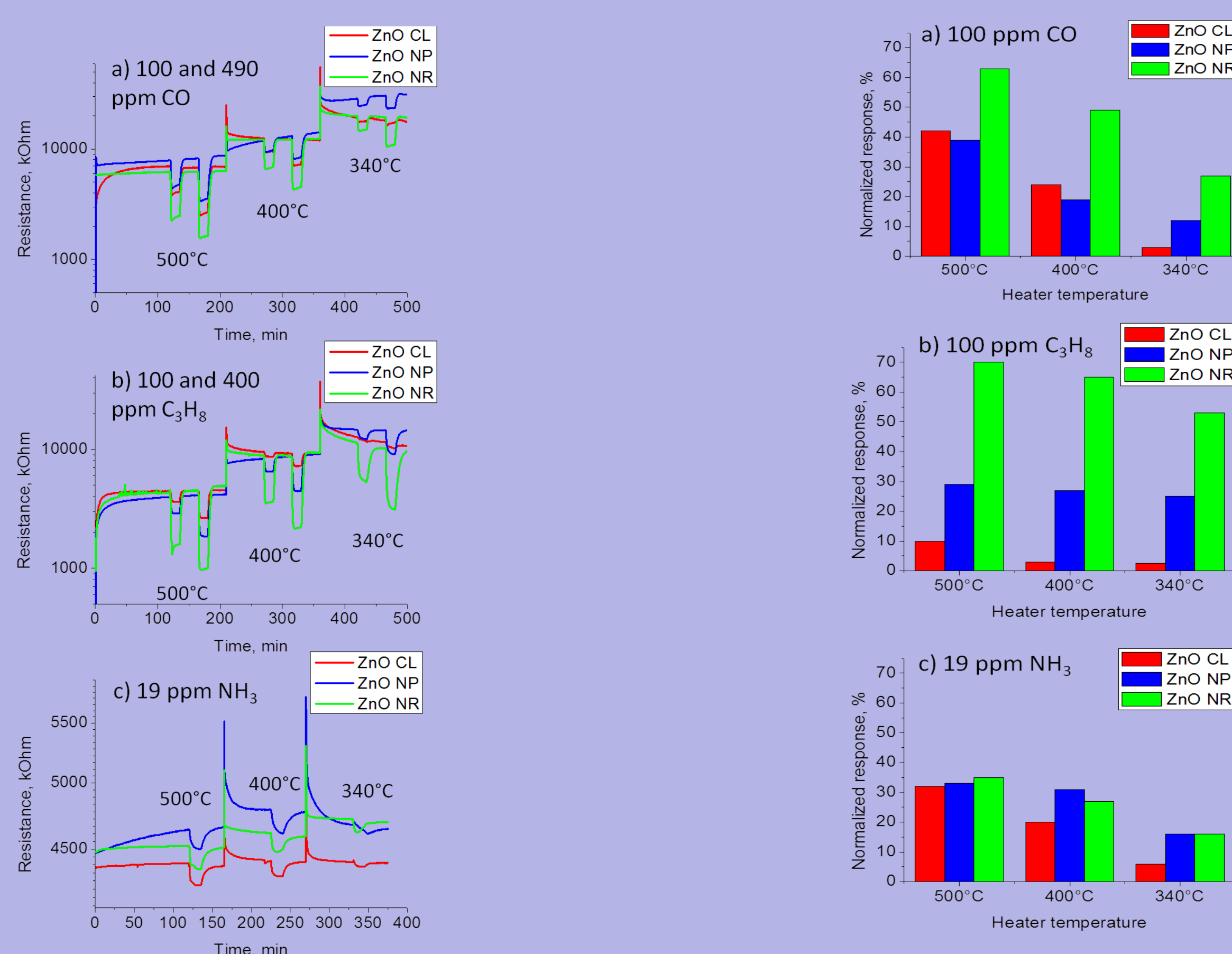


Optical image of sensor with ZnO sensitive layer and SEM-FEG images of b. ZnO CL, c. ZnO NPs, d. ZnO NRs



Optical image of sensor with SnO<sub>2</sub> sensitive layer and SEM-FEG characterization

### ZnO Nanoparticles gas sensors

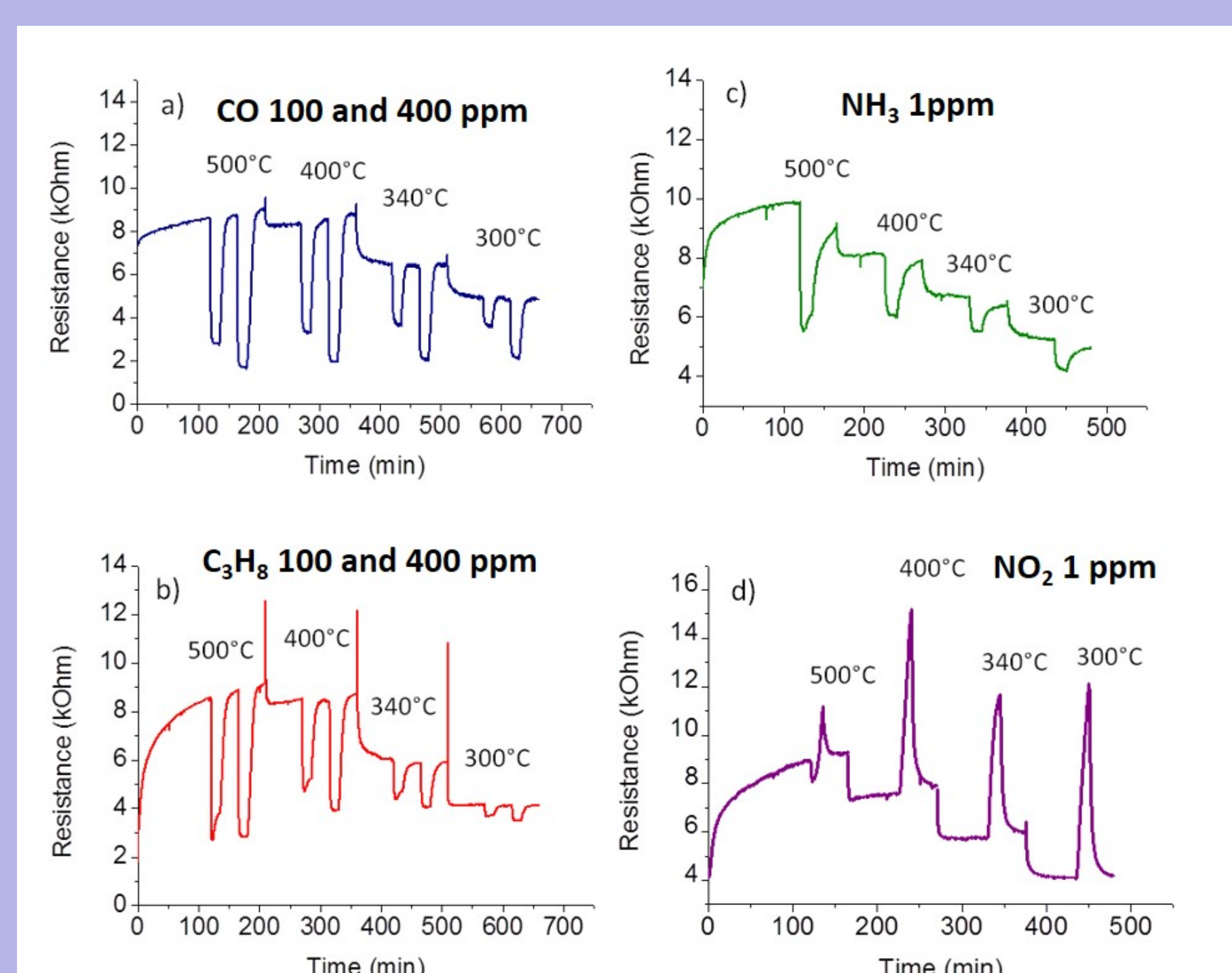


Sensors responses obtained with ZnO CL, NP, and NR at different operating temperatures (500, 400 and 340°C) and relative humidity 50% (Y scale in log plot). (a) 100 and 490 ppm CO, (b) 100 and 400 ppm C<sub>3</sub>H<sub>8</sub>, (c) 19 ppm NH<sub>3</sub>.

Normalized responses obtained with ZnO CL, NP and NR at different operating temperatures (500, 400 and 340°C) and relative humidity 50%. (a) 100 ppm CO, (b) 100 ppm C<sub>3</sub>H<sub>8</sub>, (c) 19 ppm NH<sub>3</sub>

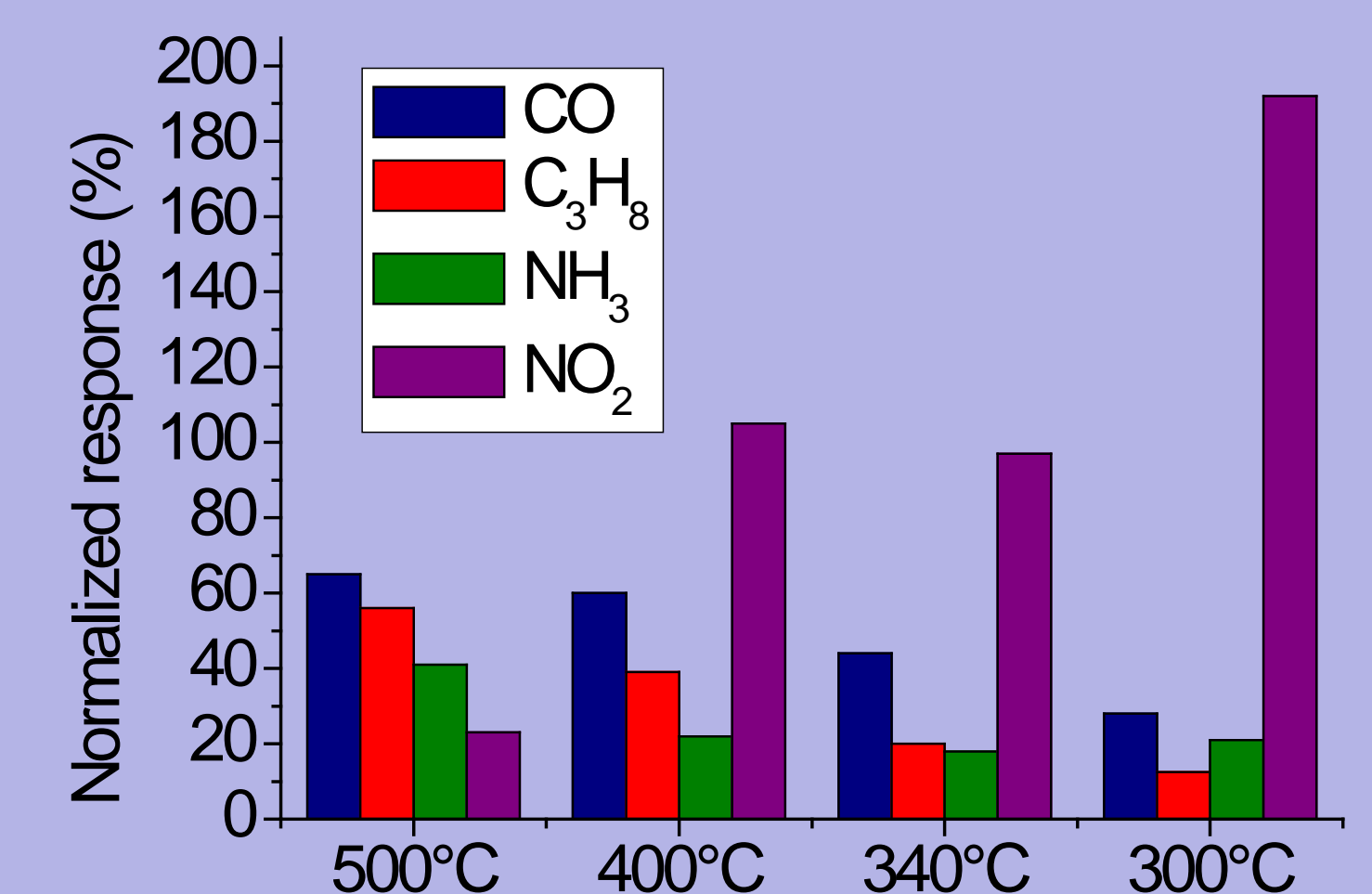
### gas responses

$$S = (R_{air} - R_{gas}) / R_{gas}$$



SnO<sub>2</sub> sensors responses to a) 100 and 490 ppm CO, b) 100 and 400 ppm C<sub>3</sub>H<sub>8</sub>, c) 5 ppm NH<sub>3</sub>, d) 1 ppm NO<sub>2</sub> at different temperatures (RH 50%).

### SnO<sub>2</sub> Nanoparticles gas sensors



SnO<sub>2</sub> sensors' normalized responses to 100 ppm CO, 100 ppm C<sub>3</sub>H<sub>8</sub>, 5 ppm NH<sub>3</sub> and 1 ppm NO<sub>2</sub> at different temperatures and RH 50%

## Conclusions

The morphology of ZnO nanostructures significantly influences the sensors gases responses and therefore offers a possible selectivity improvement way for gas sensing device. The sensors based on ZnO CL structures present the highest selectivity for CO or NH<sub>3</sub> relatively to C<sub>3</sub>H<sub>8</sub> when operating at 400°C. ZnO NR sensors display a high response to all tested gases with an optimum selectivity for C<sub>3</sub>H<sub>8</sub> comparatively to CO and NH<sub>3</sub> when operating at 340°C. ZnO NP layers present the best stability of the response for C<sub>3</sub>H<sub>8</sub> between 340 to 500°C. Sn<sub>2</sub>O<sub>3</sub>(OH)<sub>2</sub> octahedra have been prepared from tin amidure precursor in mild conditions, and transforms into SnO<sub>2</sub> at 500°C. Gas sensing properties of SnO<sub>2</sub> sensor to CO, C<sub>3</sub>H<sub>8</sub>, NH<sub>3</sub>, and NO<sub>2</sub> gases have been investigated. At 340°C, the sensors present the best selectivity between CO and other reducing gases (C<sub>3</sub>H<sub>8</sub> and NH<sub>3</sub>). At 300°C, the sensors are extremely sensitive and sensitive to 1 ppm of NO<sub>2</sub> (R<sub>n</sub> = 196%). This study is the first step dedicated to the preparation of a multisensor system based on chemoresistive layers with specific morphologies and different operating temperatures.

[1] M. Monge, M. L. Kahn, A. Maisonnat and B. Chaudret, Angew. Chem. Int. Ed., 2003, 42, 5321-5324.

[2] A. Ryzhikov, J. Jonca, M.L. Kahn, K. Fajerwerg, B. Chaudret, A. Chapelle, P. Ménini, C.H.H. Shim, A. Gaudon, P. Fau J. Nanopart. Res., 2015, Volume 17, Issue 7 (DOI 10.1007/s11051-015-3086-2)

[3] Ph. Menini et al., Eurosensors XXII proceedings, (2008) 342.

### ACKNOWLEDGMENTS:

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