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Nanostructured zinc and tin oxides for gas sensors

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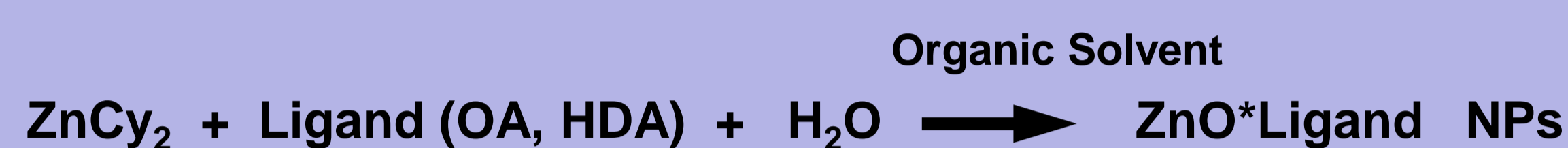
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⁴ Alpha MOS, 20 avenue Didier Daurat, 31400 Toulouse, France

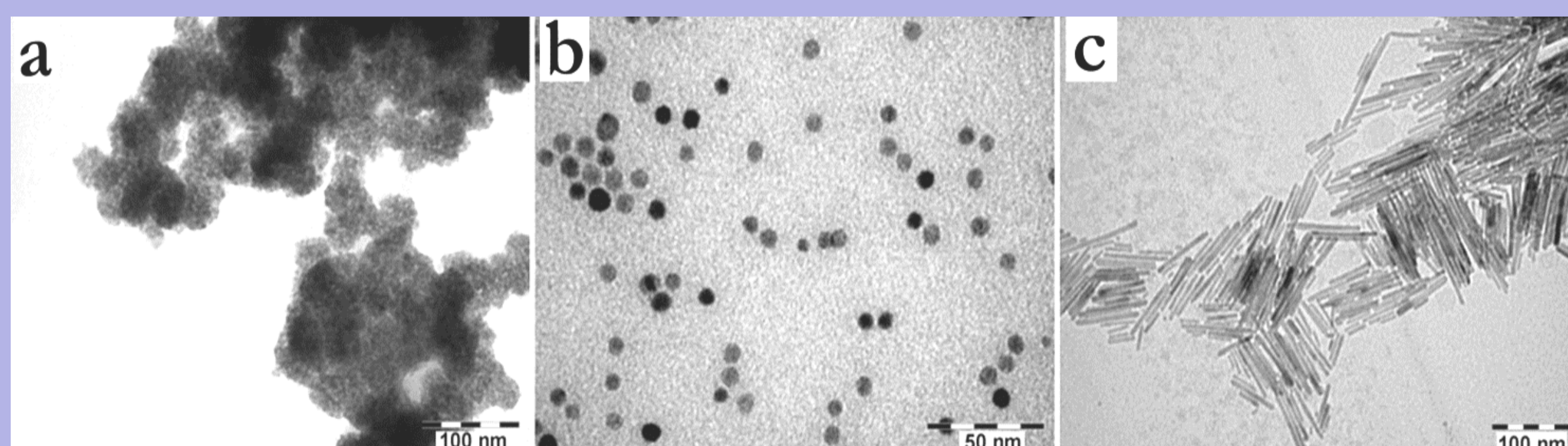
Aim of the project

The development of high sensitivity and selectivity MOS (metal oxide semiconductor) gas sensors with SnO₂ and ZnO nanoparticles layers based on micromachined silicon substrate for the detection of CO, C₃H₈, NH₃, NO₂, ...

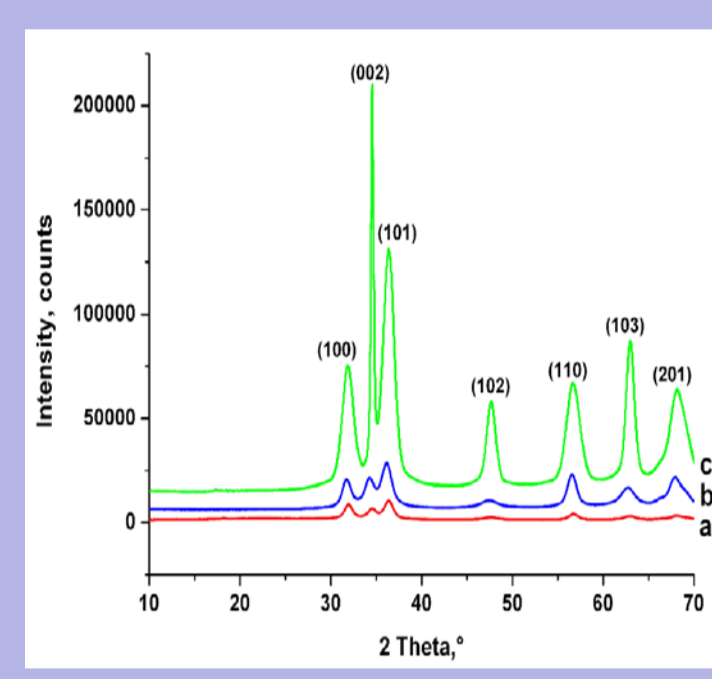
ZnO Nanoparticles synthesis^{1,2}



(ZnCy₂ – dicyclohexylzinc, OA – octylamine, HDA – hexadecylamine)
CH₃(CH₂)₇NH₂ CH₃(CH₂)₁₅NH₂



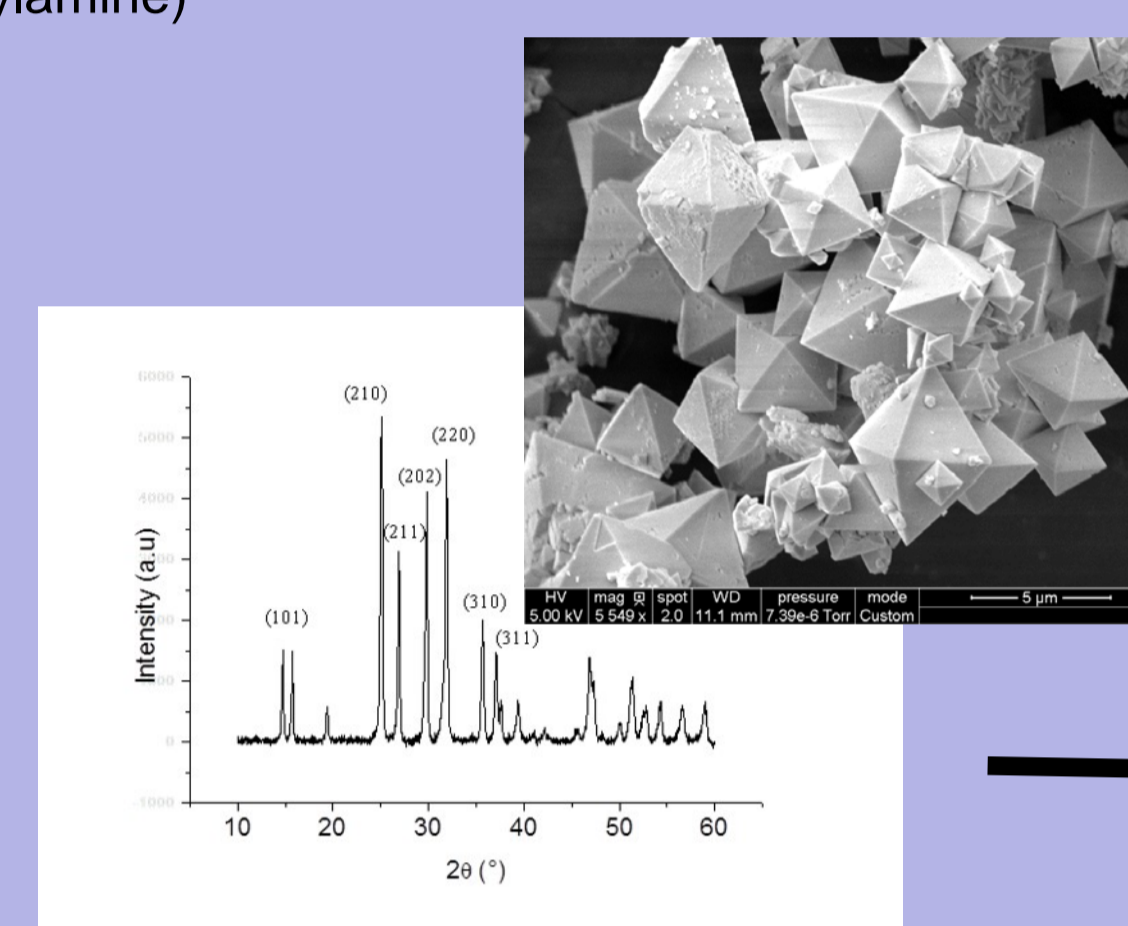
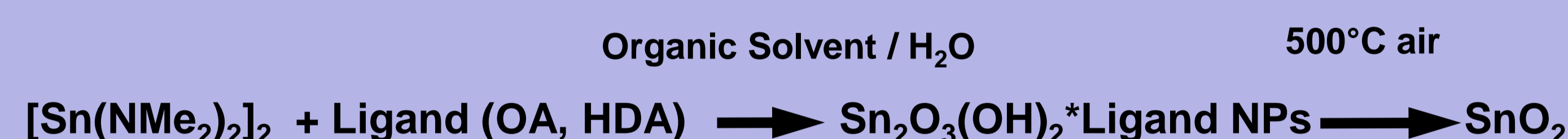
TEM images of ZnO nanoparticles with various morphology: a. ZnO CL, b. ZnO NPs (NP1), c. ZnO NRs (NR1)



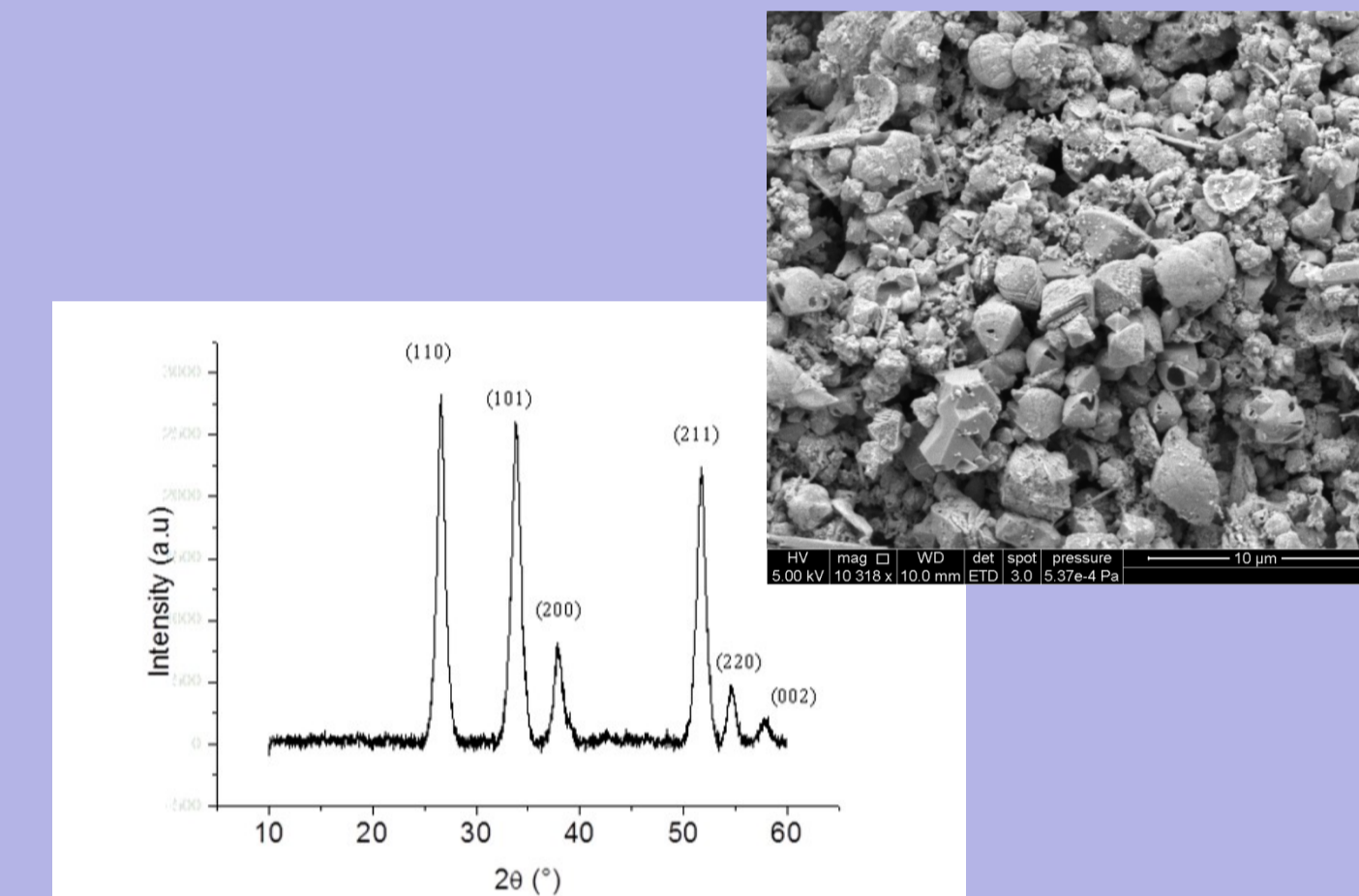
XRD diagrams of ZnO nanoparticle a. cloudy-like structures, b. isotropic nanoparticles, c. nanorods

Results

SnO₂ Nanoparticles synthesis



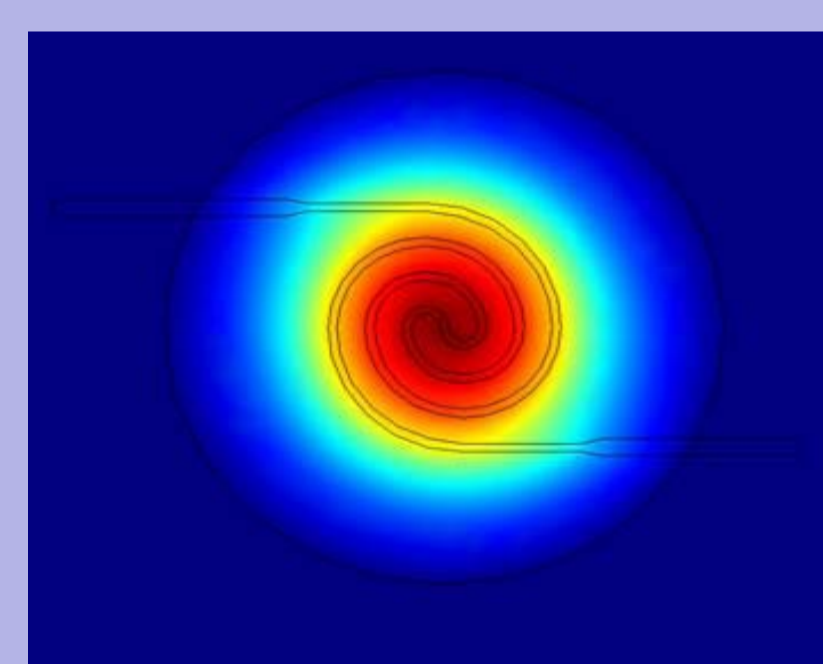
XRD diagram of Sn₂O₃(OH)₂



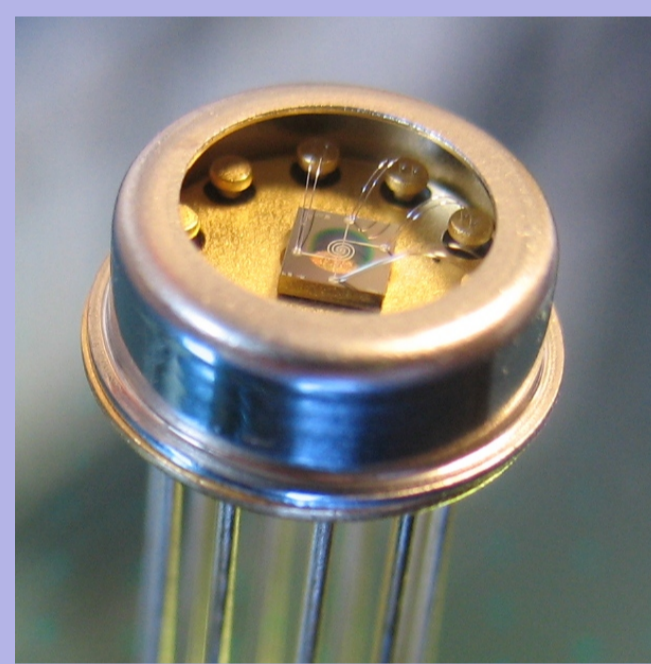
XRD diagram of SnO₂

Micromachined silicon platform³ and sensitive layer deposition

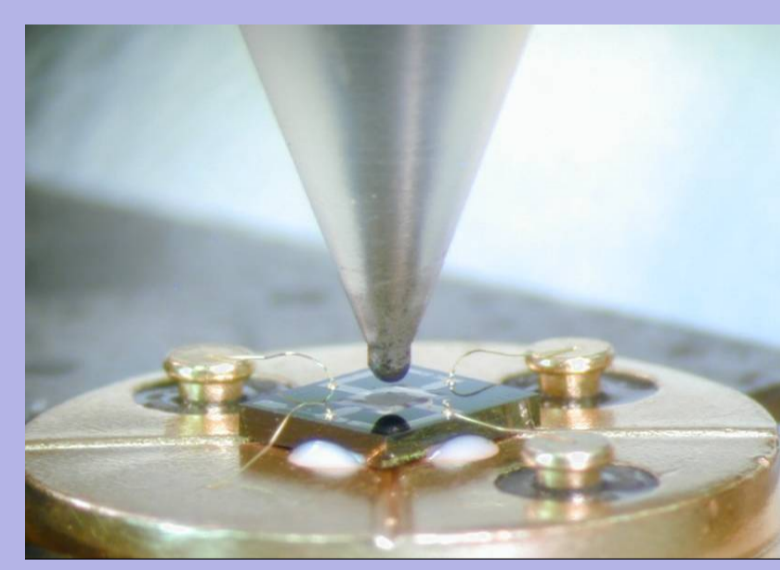
Design of the round shaped platinum heater and interdigitated electrodes for the sensitive layer contact



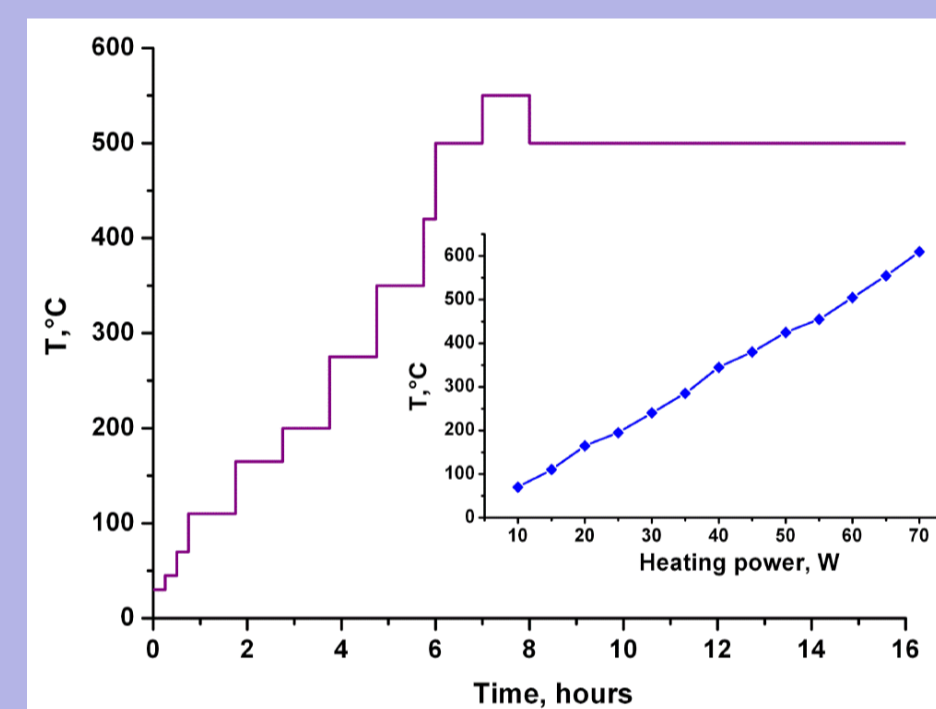
Thermal homogeneity of the heater operating at 400°C



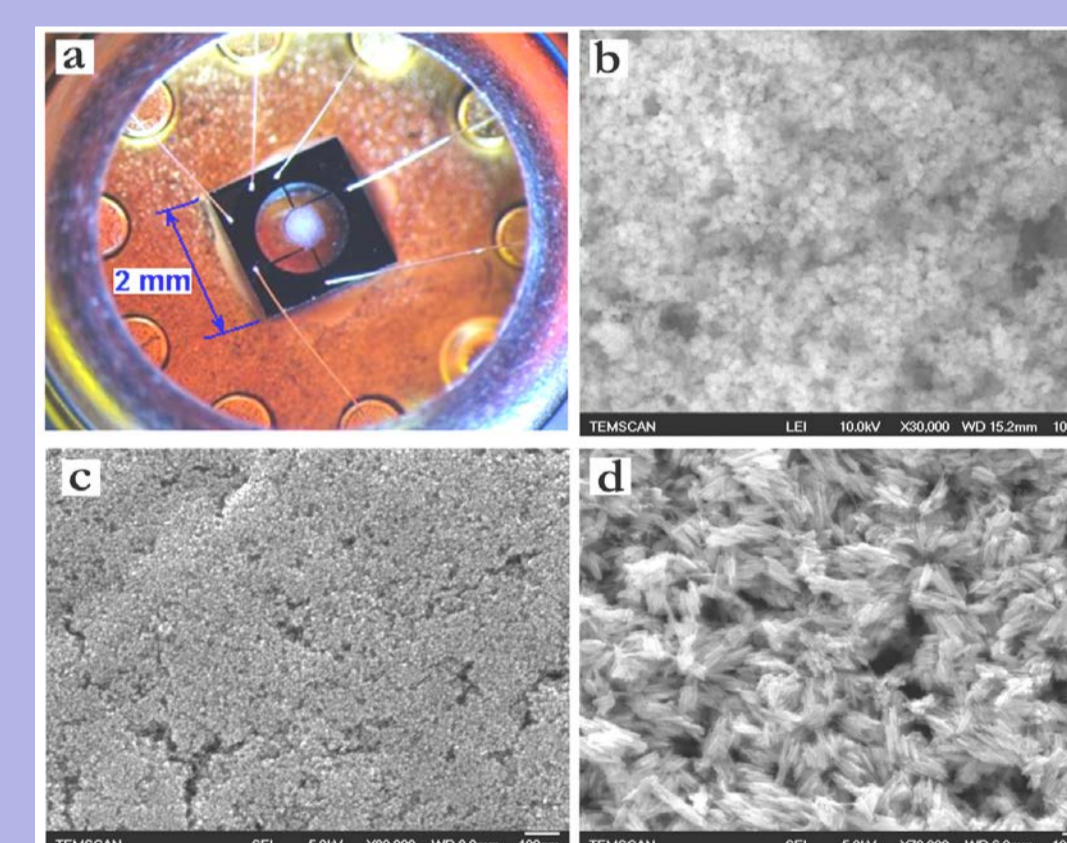
Gas sensor silicon platform on TO5 package.



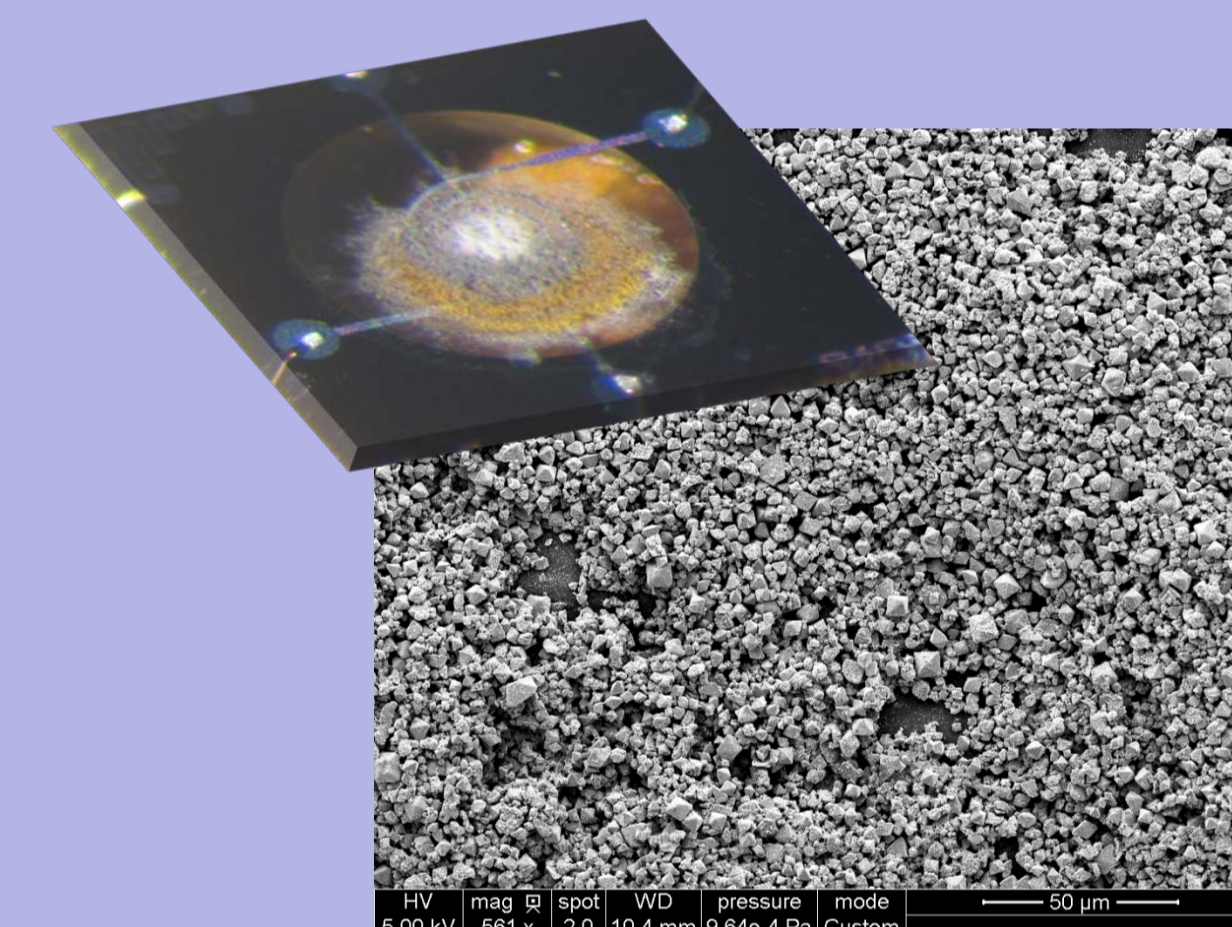
Drop deposition of the metal oxide nanoparticles on the silicon platform



Temperature profile of annealing and stabilization procedure of sensing layers

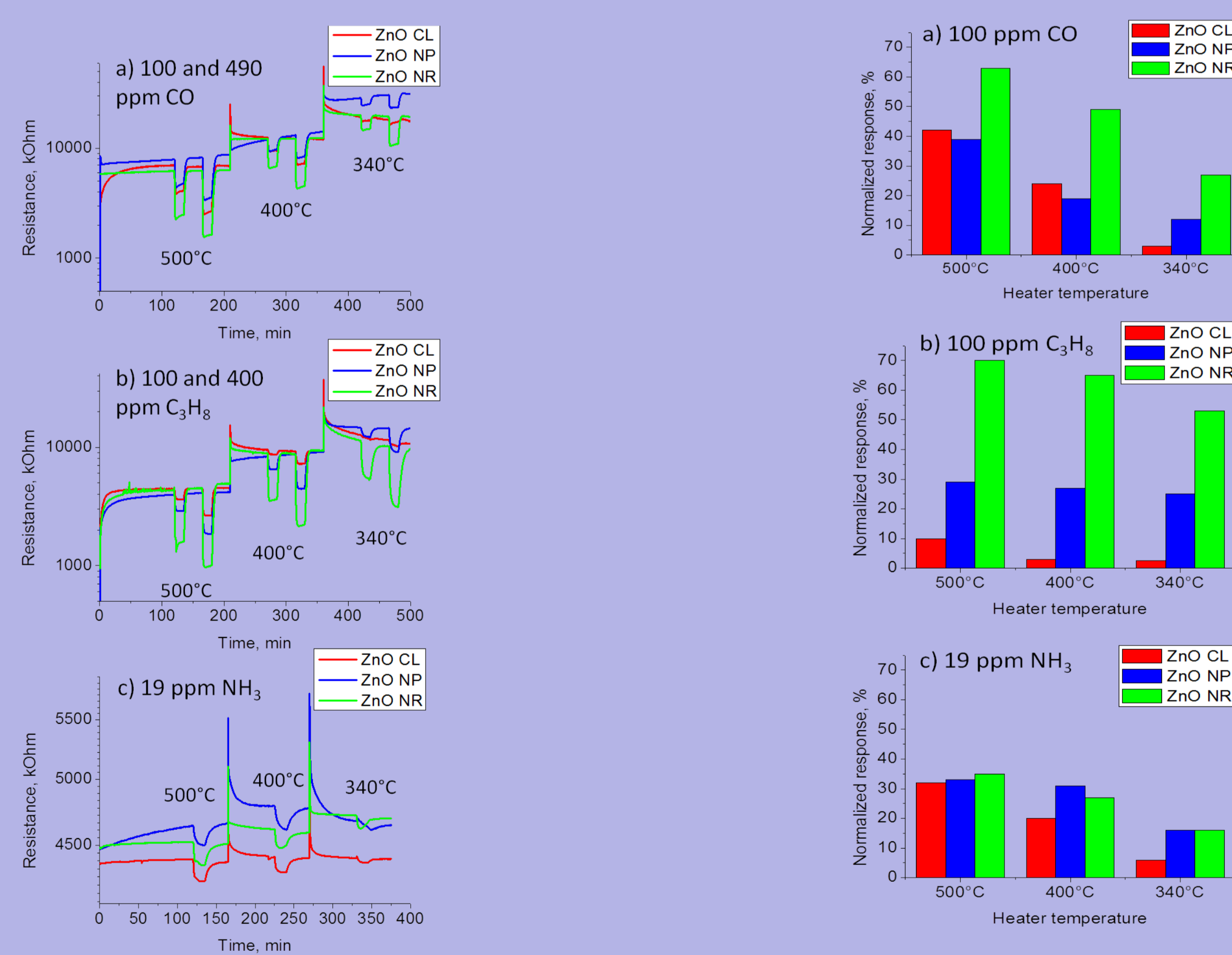


Optical image of sensor with ZnO sensitive layer and SEM-FEG images of b. ZnO CL, c. ZnO NPs, d. ZnO NRs



Optical image of sensor with SnO₂ sensitive layer and SEM-FEG characterization

ZnO Nanoparticles gas sensors

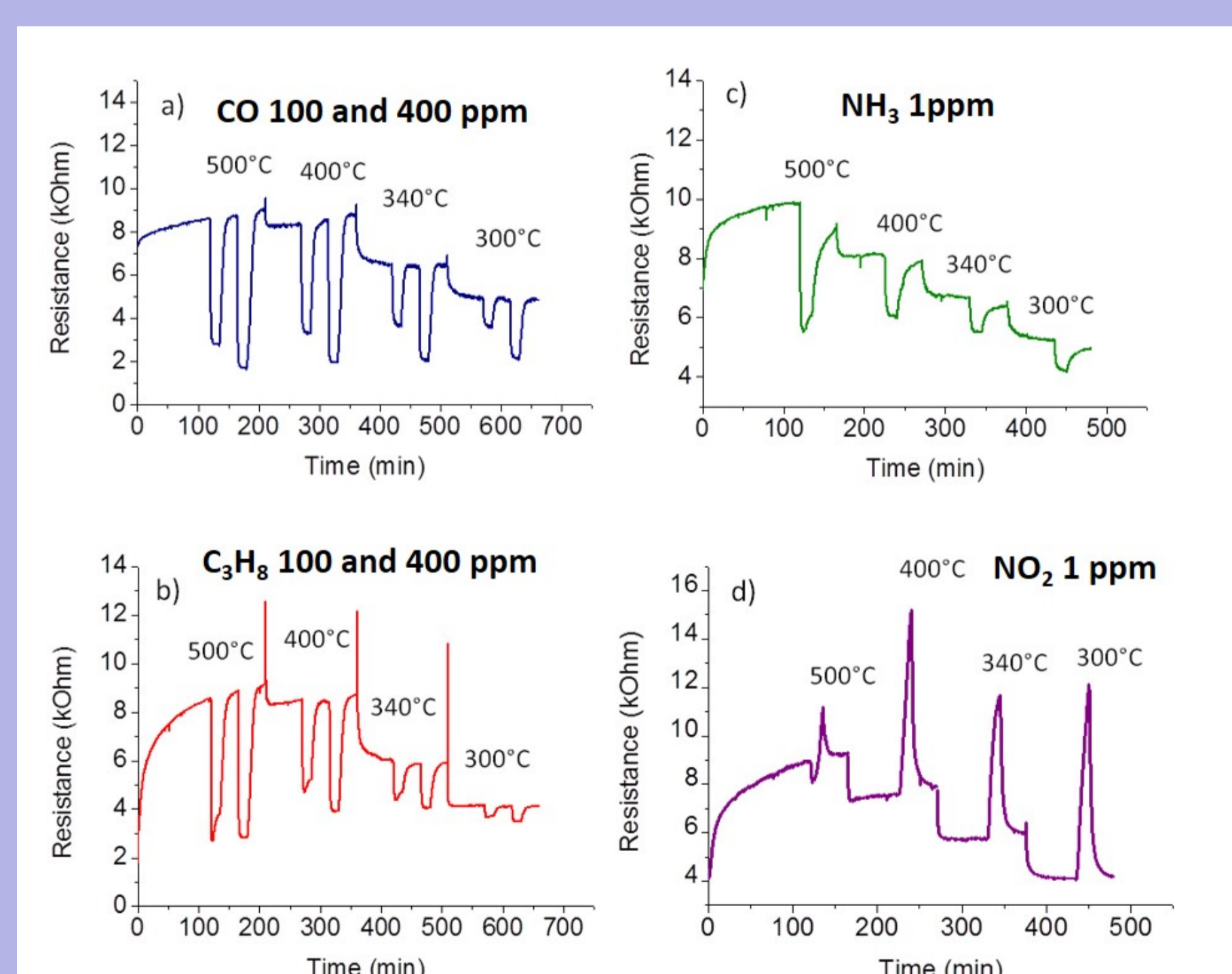


Sensors responses obtained with ZnO CL, NP, and NR at different operating temperatures (500, 400 and 340°C) and relative humidity 50% (Y scale in log plot). (a) 100 and 490 ppm CO, (b) 100 and 400 ppm C₃H₈, (c) 19 ppm NH₃.

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 C₃H₈, (c) 19 ppm NH₃

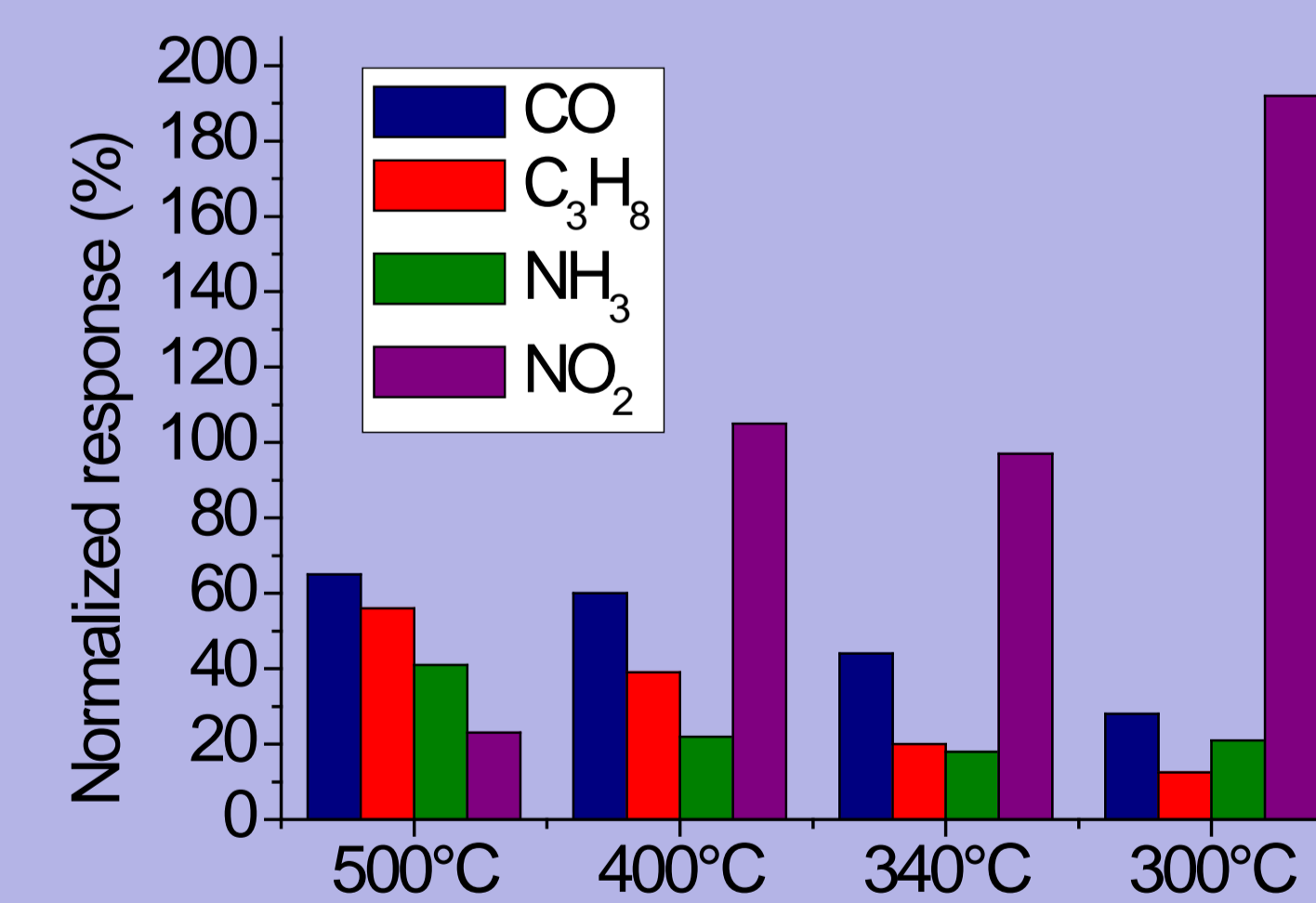
gas responses

$$S = (\text{Rair-Rgas}) / \text{R gas}$$



SnO₂ sensors responses to a) 100 and 490 ppm CO, b) 100 and 400 ppm C₃H₈, c) 5 ppm NH₃, d) 1 ppm NO₂ at different temperatures (RH 50%).

SnO₂ Nanoparticles gas sensors



SnO₂ sensors' normalized responses to 100 ppm CO, 100 ppm C₃H₈, 5 ppm NH₃ and 1 ppm NO₂ 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 NH₃ relatively to C₃H₈ when operating at 400°C. ZnO NR sensors display a high response to all tested gases with an optimum selectivity for C₃H₈ comparatively to CO and NH₃ when operating at 340°C. ZnO NP layers present the best stability of the response for C₃H₈ between 340 to 500°C.

Sn₂O₃(OH)₂ octahedra have been prepared from tin amidure precursor in mild conditions, and transforms into SnO₂ at 500°C. Gas sensing properties of SnO₂ sensor to CO, C₃H₈, NH₃, and NO₂ gases have been investigated. At 340°C, the sensors present the best selectivity between CO and other reducing gases (C₃H₈ and NH₃). At 300°C, the sensors are extremely sensitive and sensitive to 1 ppm of NO₂ (R_n = 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.

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