Charge transport in layers of ZnO nanotetrapods and porous nanosheets comparatively investigated by impedance spectroscopy measurements

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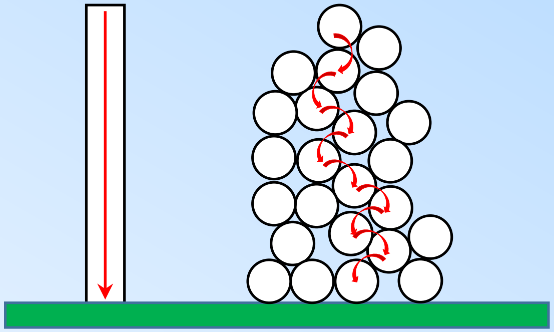
Introduction

- ZnO exhibits a unique combination of potentially interesting properties (large energy bandgap, high bulk electron mobility) joined to the probably richest variety of nanostructures.
- ZnO nanostructures are used for applications such as gas sensors and solar cells due to their high surface-to-volume ratio.
- The performances of ZnO nanoparticle-based solar cells are superior than those of nanorod-based devices, in spite of the slower electron transport of nanoparticles due to the presence of grain boundaries.

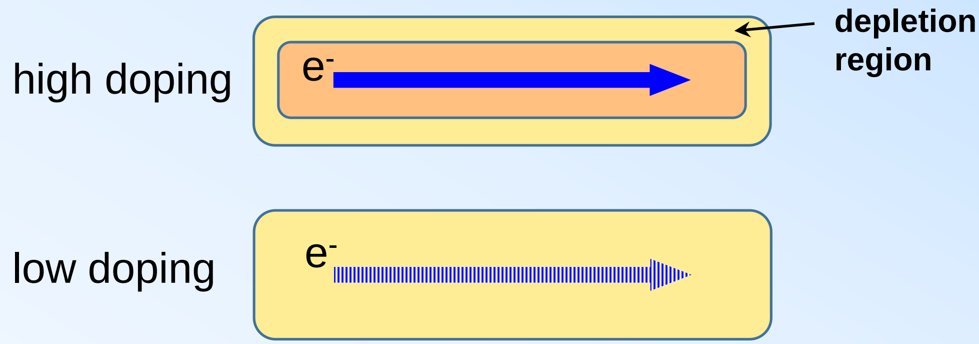


- Gas sensing involves adsorption of atmospheric oxygen on the oxide surface that extracts electrons from the semiconductor leading to a change in carrier density and conductivity.
- The exact fundamental mechanism causing a gas response is still controversial.

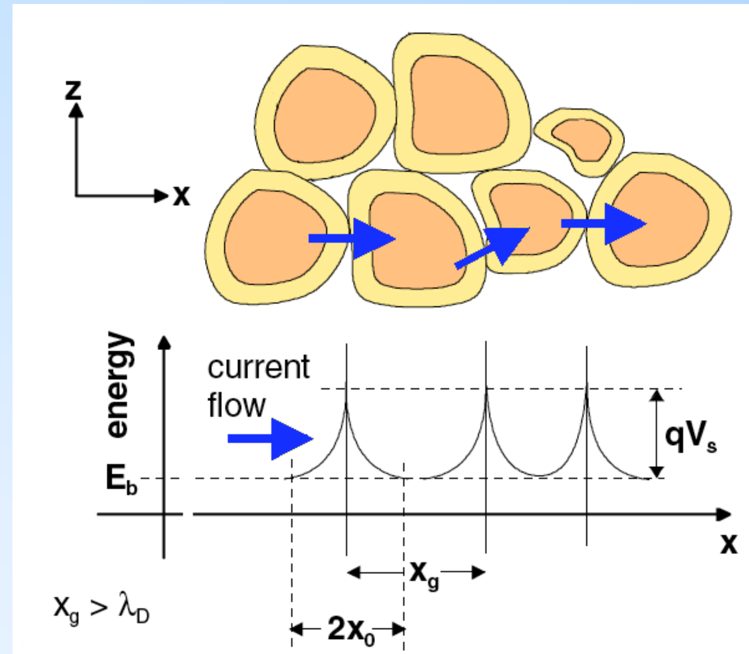
Charge transport in nanostructured layers

charge transport depends on morphology and doping

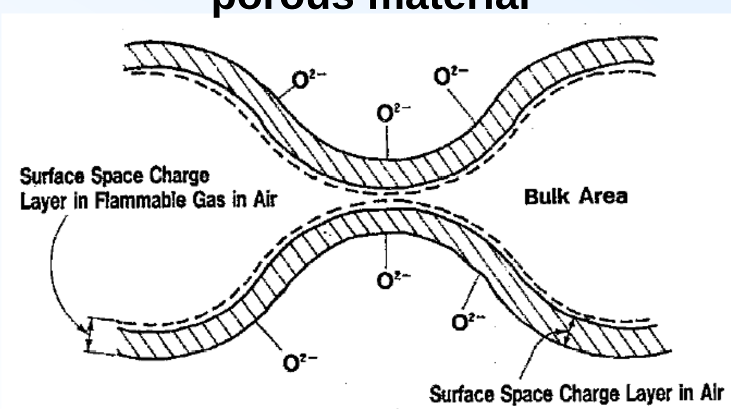
partly or completely depleted nanostructures



nanostructured layer



porous material



Studying the detailed mechanisms of responses from different nanostructure morphologies may be a tool to understand charge transport in these layers.

We report about an ongoing investigation performed by impedance spectroscopy (IS) on layers made of:

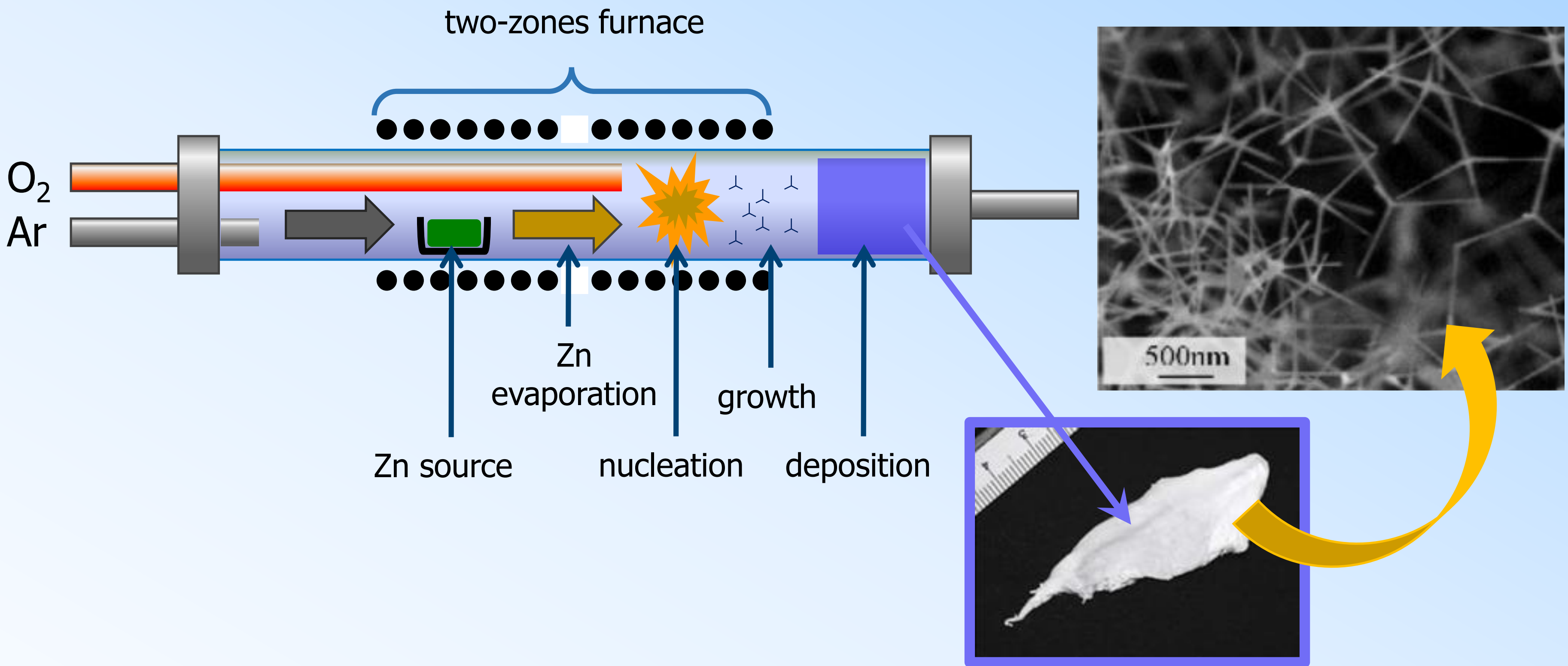
- ZnO nanotetrapods (TPs) grown by vapour phase processes
- mesoporous ZnO nanosheets (NSs) obtained from hybrid organic-inorganic precursor nanostructures.

Outline

- Nanostructure preps & props
- IS in gas (EtOH, CO) and vs temperature
- One equivalent circuit for different nanostructures
- Conclusion

ZnO nanotetrapods

Growth of ZnO "nano-tetrapods" (TPs) by vapour phase processes

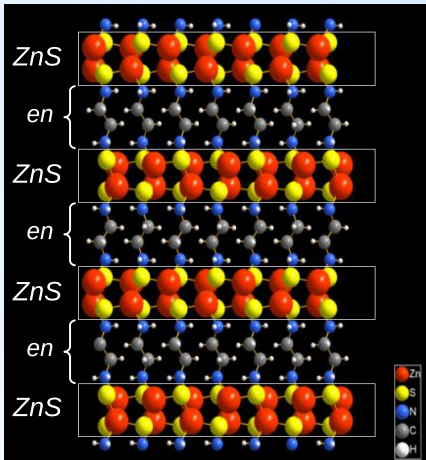


Optimized growth conditions:

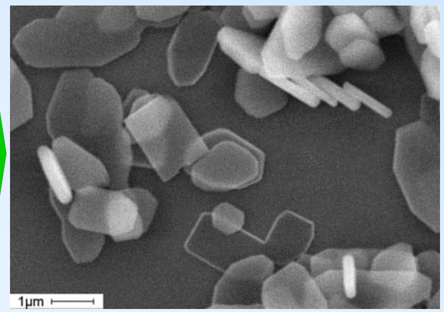
- Zn source is heated at 700°C in a 100 sccm Ar flow, while O_2 (10 sccm) is introduced farther in the reactor (T=500-600°C) in order to protect Zn source from early oxidation
- Tetrapods nucleate in the zone where O_2 is introduced, grow in ~1-2 minutes while floating toward the end of the reactor and, finally, deposit in the coldest zone on the quartz tube wall.

ZnO porous nanosheets

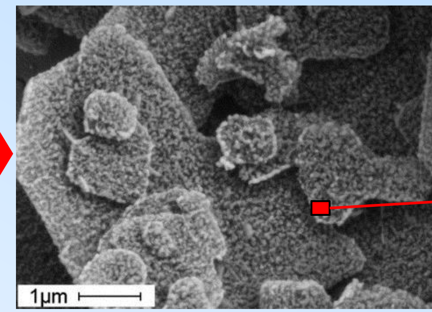
ZnO porous nanosheets are obtained from $ZnS(en)_{0.5}$ hybrid precursors synthesized via solvothermal routes

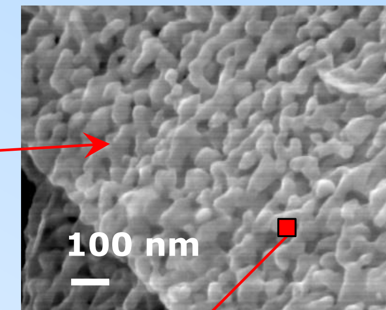


$ZnS(en)_{0.5}$ hybrid

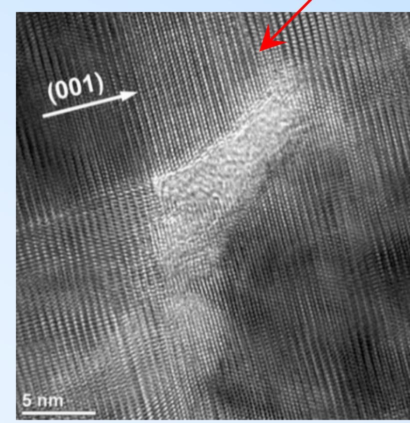


Porous ZnO

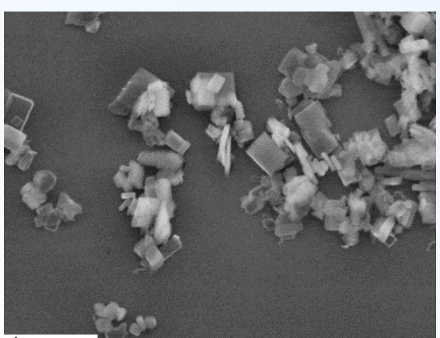




large nanosheets (**L-NSs**)



different Zn source



small nanosheets (**S-NSs**)

R. Mosca et al.

Cryst. Res. Technol. **4**6, 818 (2011)

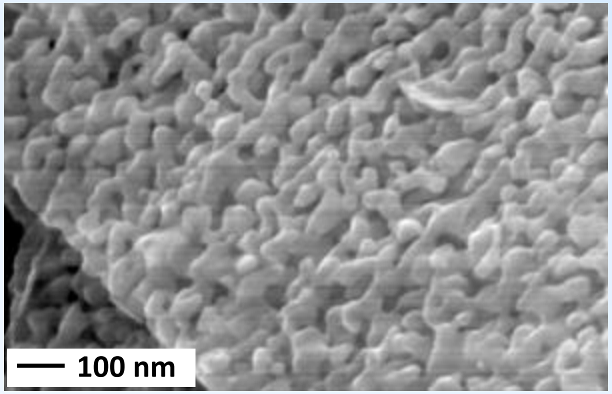
L. Nasi et al.

J. Phys. Chem. C **116,** 6960 (2012)

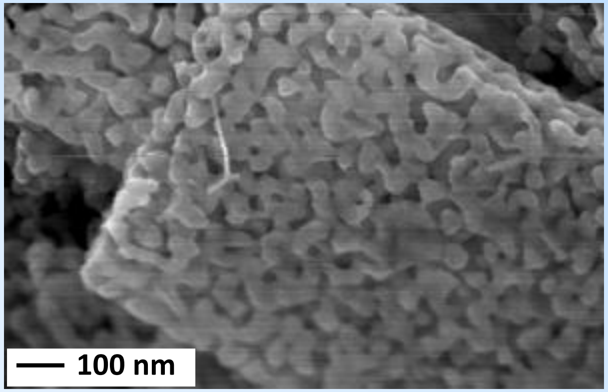
ZnO porous nanosheets

- Porosity is similar in large and small platelets.

Large NSs

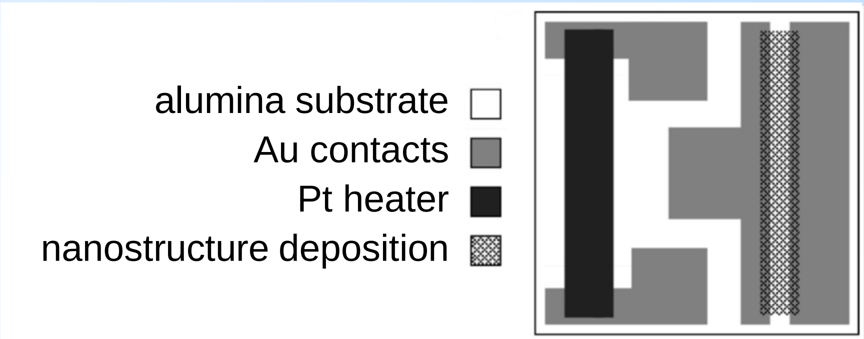


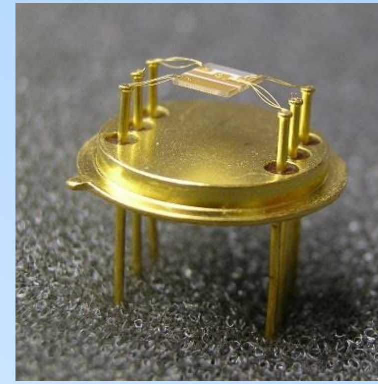
Small NSs



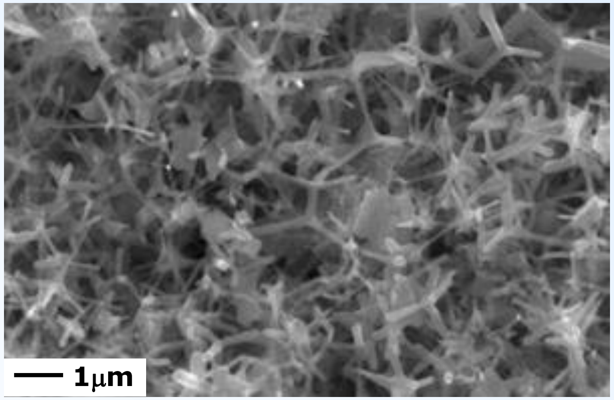
- Material size is in the 50 nm domain

Sensor structures as test devices

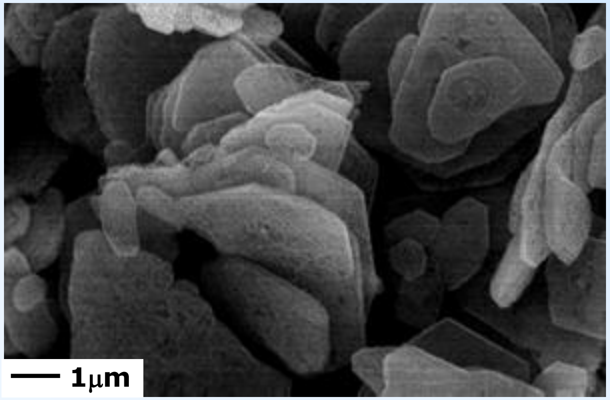




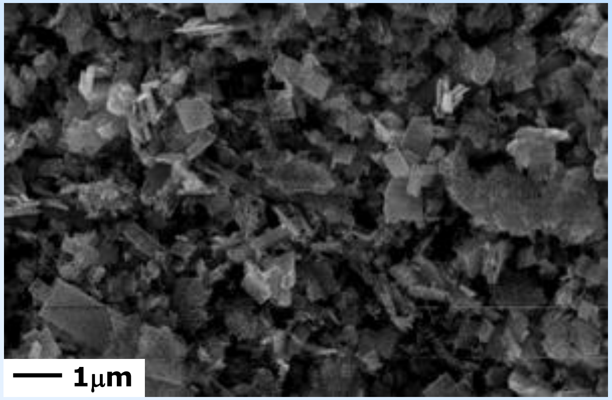
TPs



L-NSs



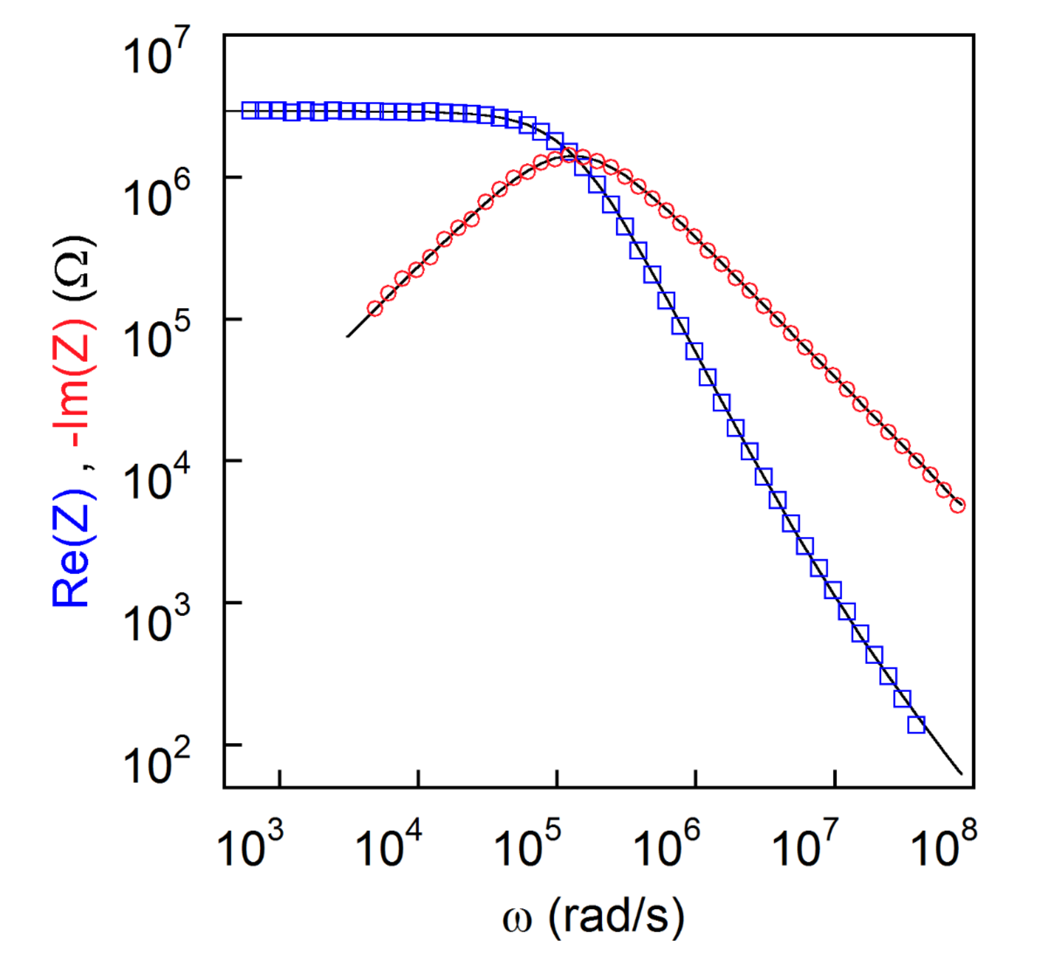
S-NSs

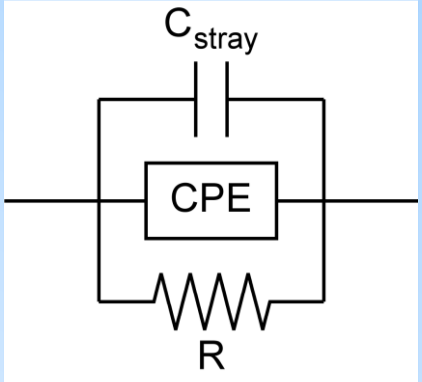


- TPs: legs are ~1 μm long and 30-200 nm large
- Large porous NSs: 0.5-5 μm large, ~ 200-300 nm thick.
- Small porous NSs: ≤500 nm large, <100 nm thick.

Impedance spectroscopy: TPs

TPs @ 400°C in dry air





$$Z_{CPE} = \frac{1}{A(i\omega^n)} = \frac{1}{A\omega^n}\left[\cos\left(\frac{n\pi}{2}\right) - i\sin\left(\frac{n\pi}{2}\right)\right]$$

R=2.91 MΩ

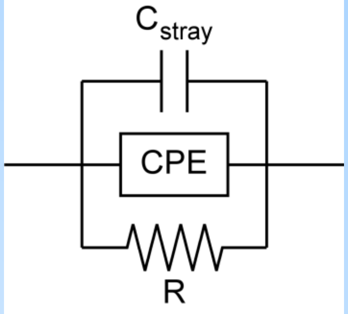
C_{stray}=2.4 pF

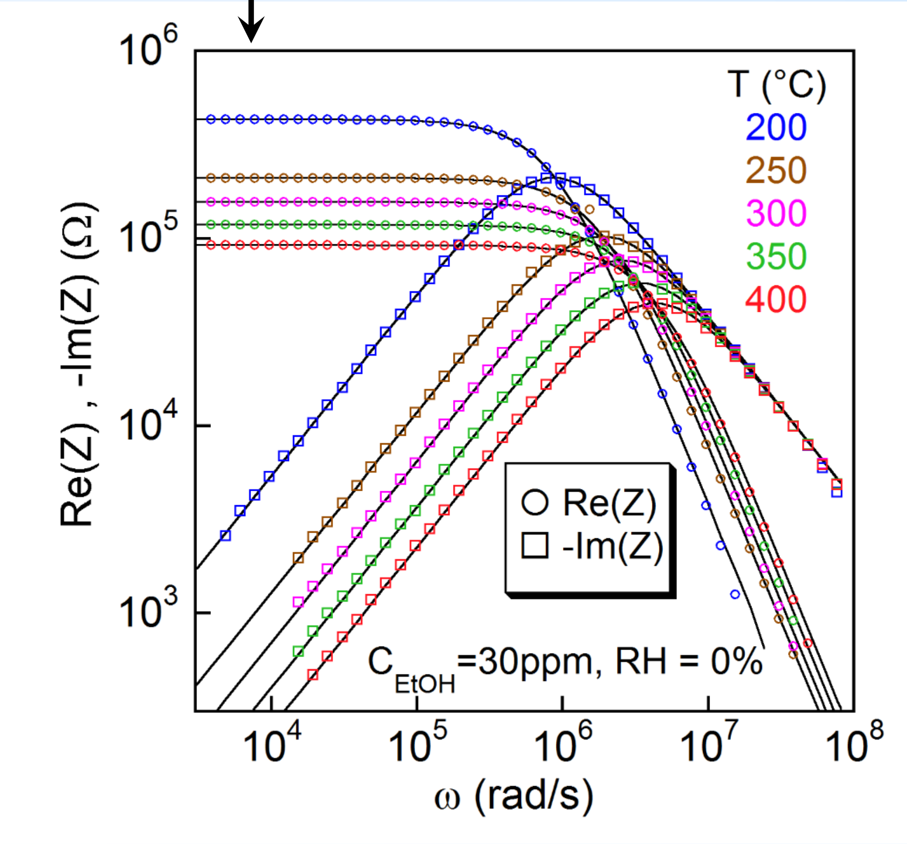
A=1.96 pF

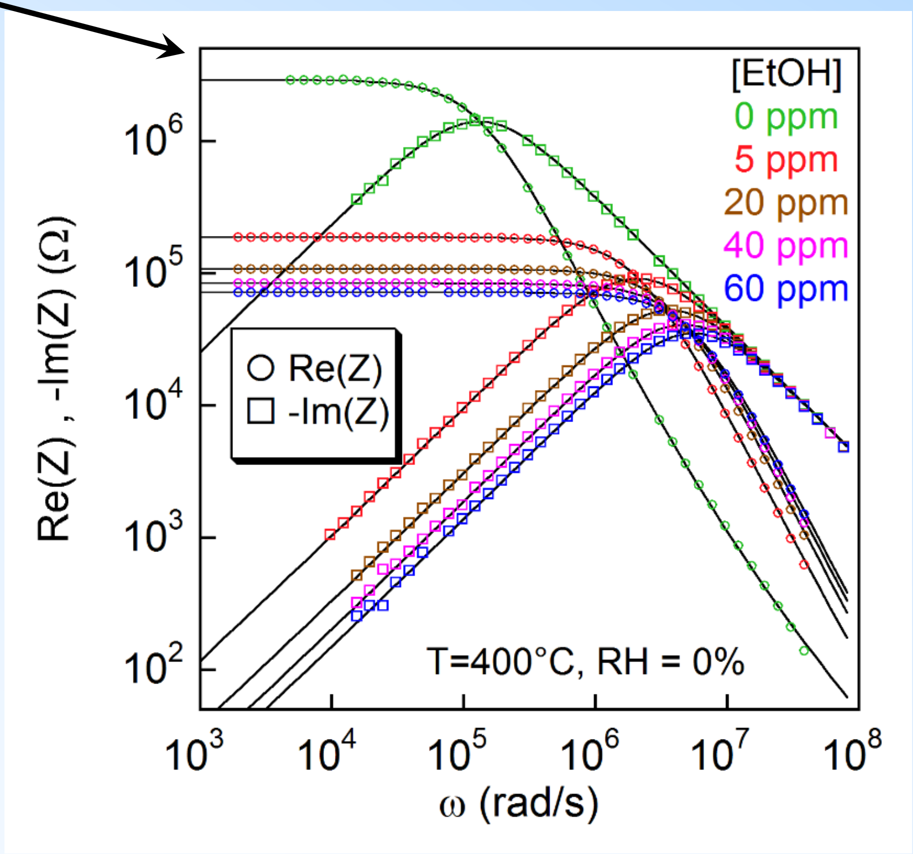
n=0.842

Impedance spectroscopy: TPs

The same equivalent circuit allows the impedance of the TP-based sensor to be modelled at different temperatures and ethanol contents in the atmosphere.

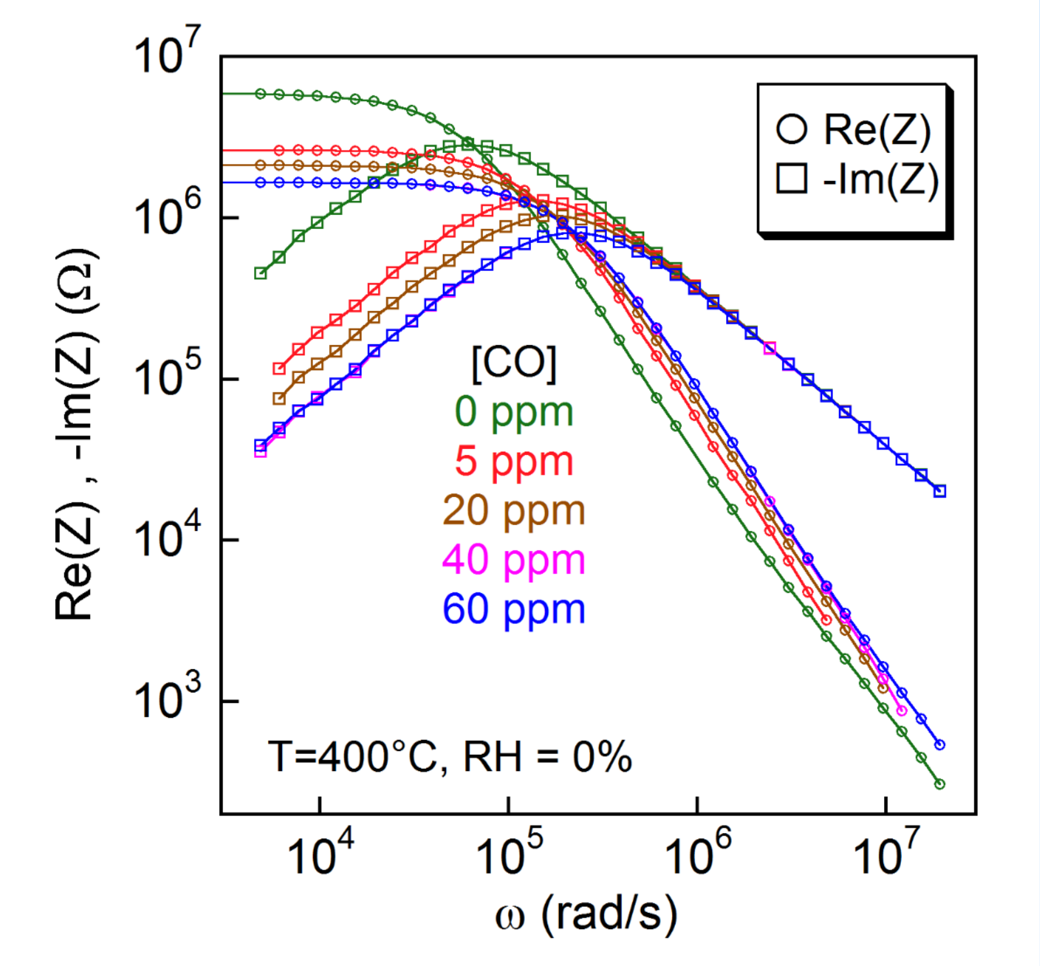




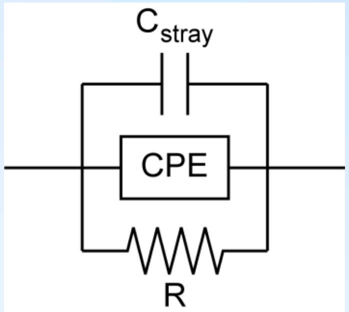


Impedance spectroscopy: TPs

Similar results were obtained by using CO instead of EtOH

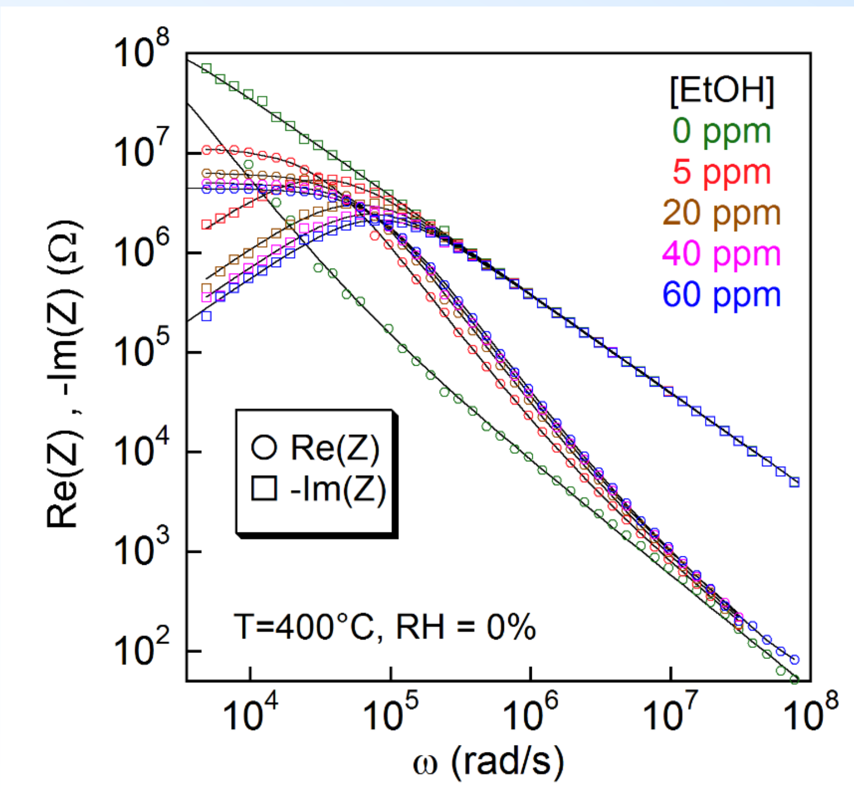


Impedance spectroscopy: NSs

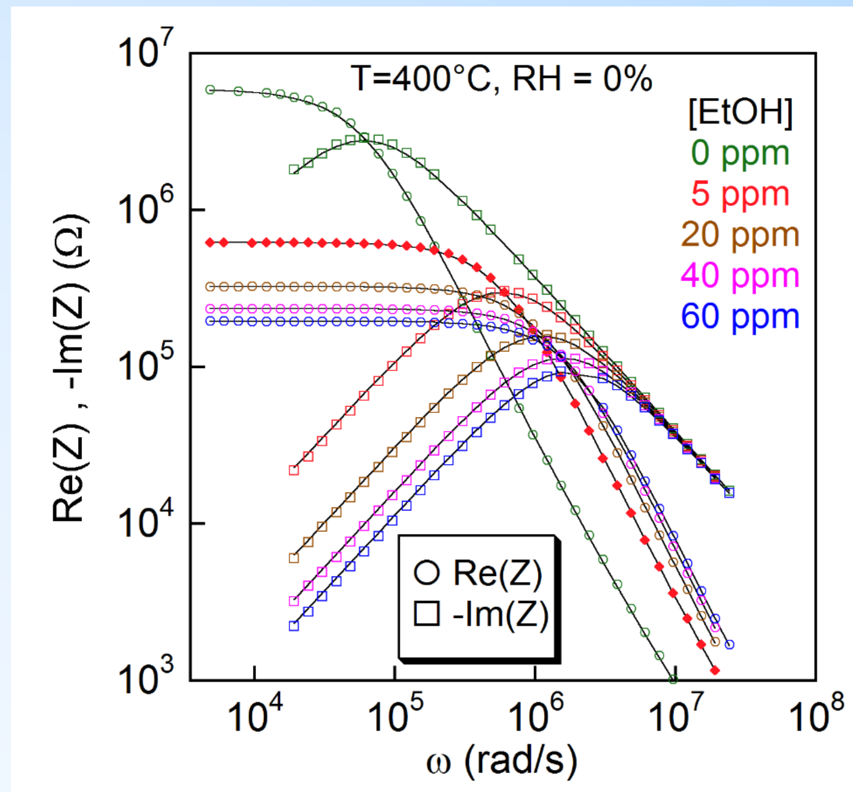


In spite of the different morphology, the same equivalent circuit is suitable for modelling also the impedance of the NS-based sensors (both L-NS and S-NS).

L-NSs

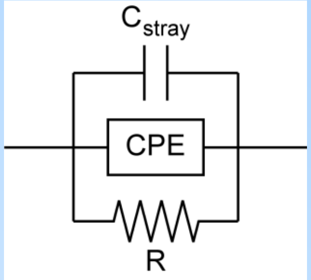


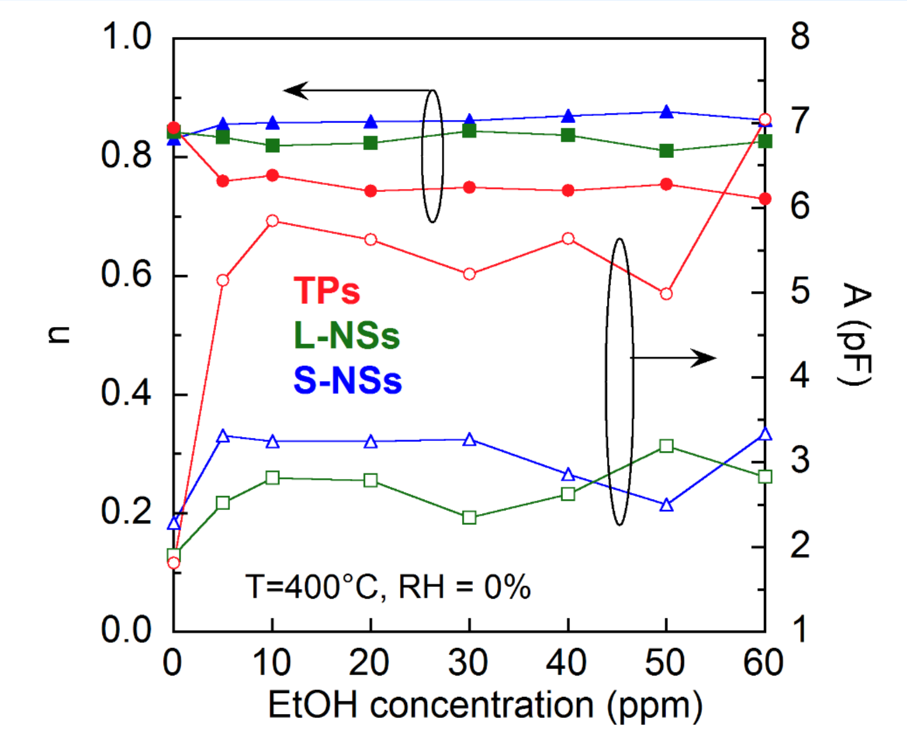
S-NSs

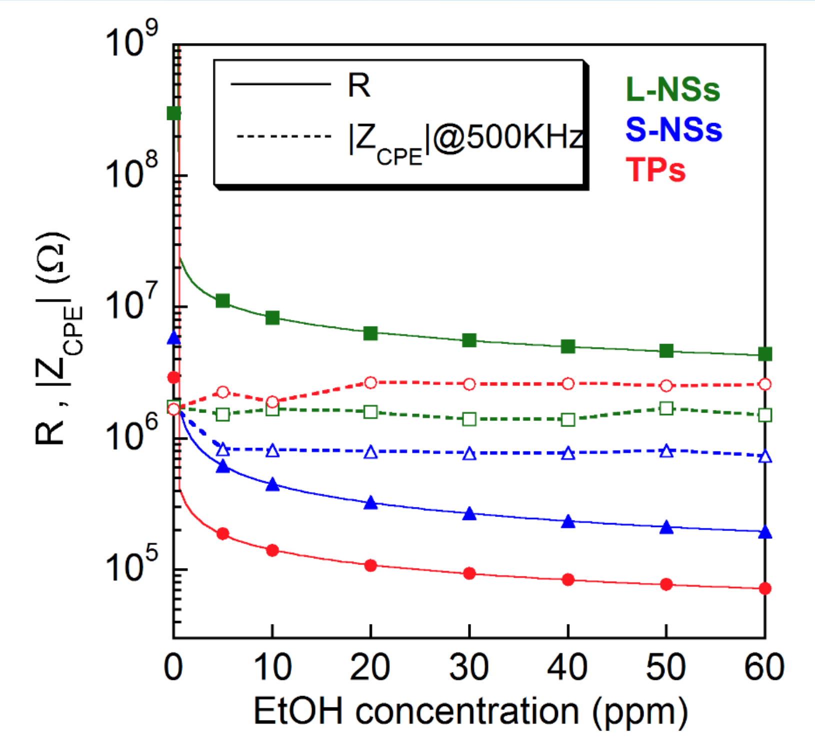


Impedance parameters

$$Z_{CPE} = \frac{1}{A\omega^n}\left[\cos\left(\frac{n\pi}{2}\right) - i\sin\left(\frac{n\pi}{2}\right)\right]$$



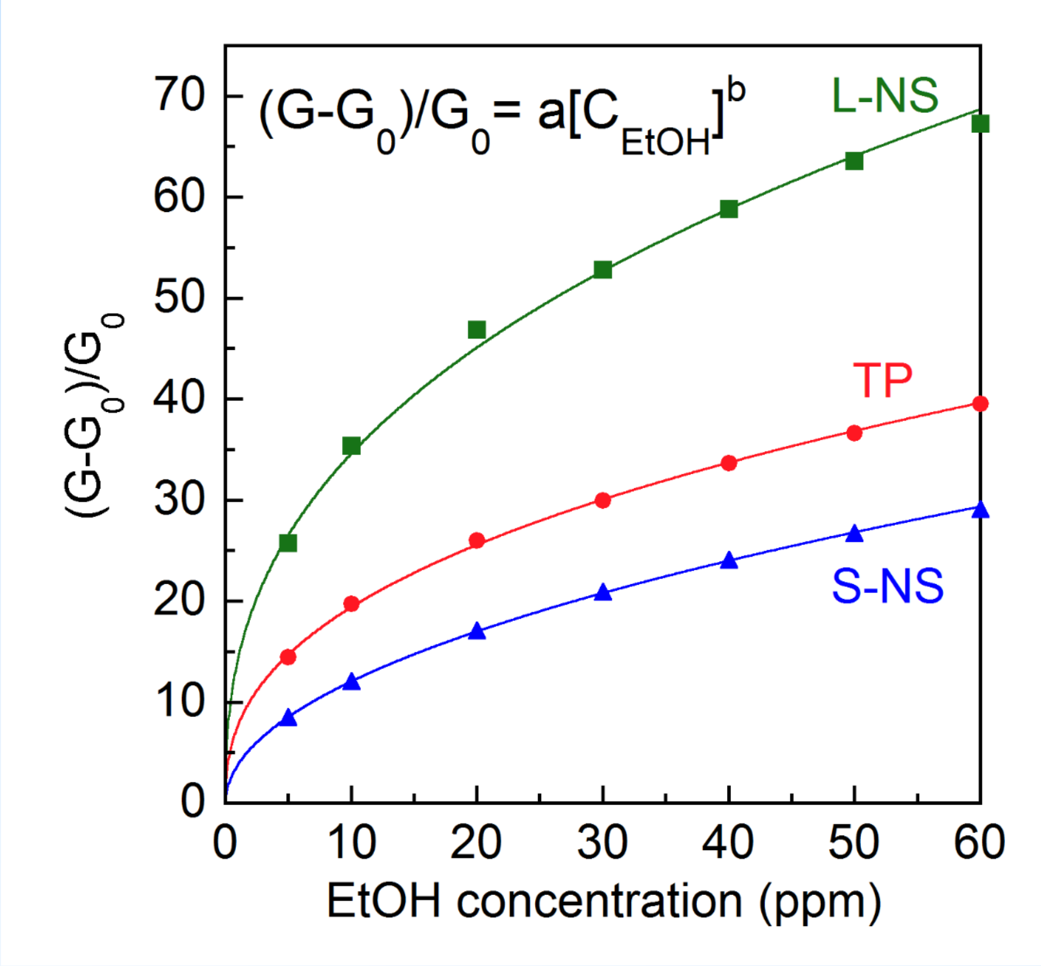




In all the samples response to EtOH is due mainly to R

Sensitivity to EtOH

- Large NS are the most sensitive and small NSs are the least sensitive to EtOH.
- The number of NS-to-NS barriers is larger in S-NS than in L-NS due to the smaller size.
- Nanostructure response to EtOH is not straightly related to the potential barrier at the interfaces between adjoining nanostructures
- Nanostructure complete depletion (low doping)?
- Similar porosity in L-NS and S-NS.



Does carrier recombination at the NS-to-NS interface affect charge transport?

Conclusions

- ✓ We are investigating the charge transport mechanisms in layers made of ZnO nanostructures (tetrapods or nanosheets).
- ✓ In spite of the huge differences in shape and size of nanostructures, the same equivalent circuit provides an excellent description of the behavior of TPs- and NSs-based sensors, for all the conditions considered.
- ✓ NS sensitivity to EtOH suggests that the potential barrier between adjoining nanocrystals is not involved in the gas sensing transduction.
- ✓ Work is under way to identify the physical mechanisms causing the parallel R-CPE circuit element and the decrease of R upon exposure to EtOH.