Embedding Palladium into flame-made & leached SnO_2 drastically enhances Gas Sensing

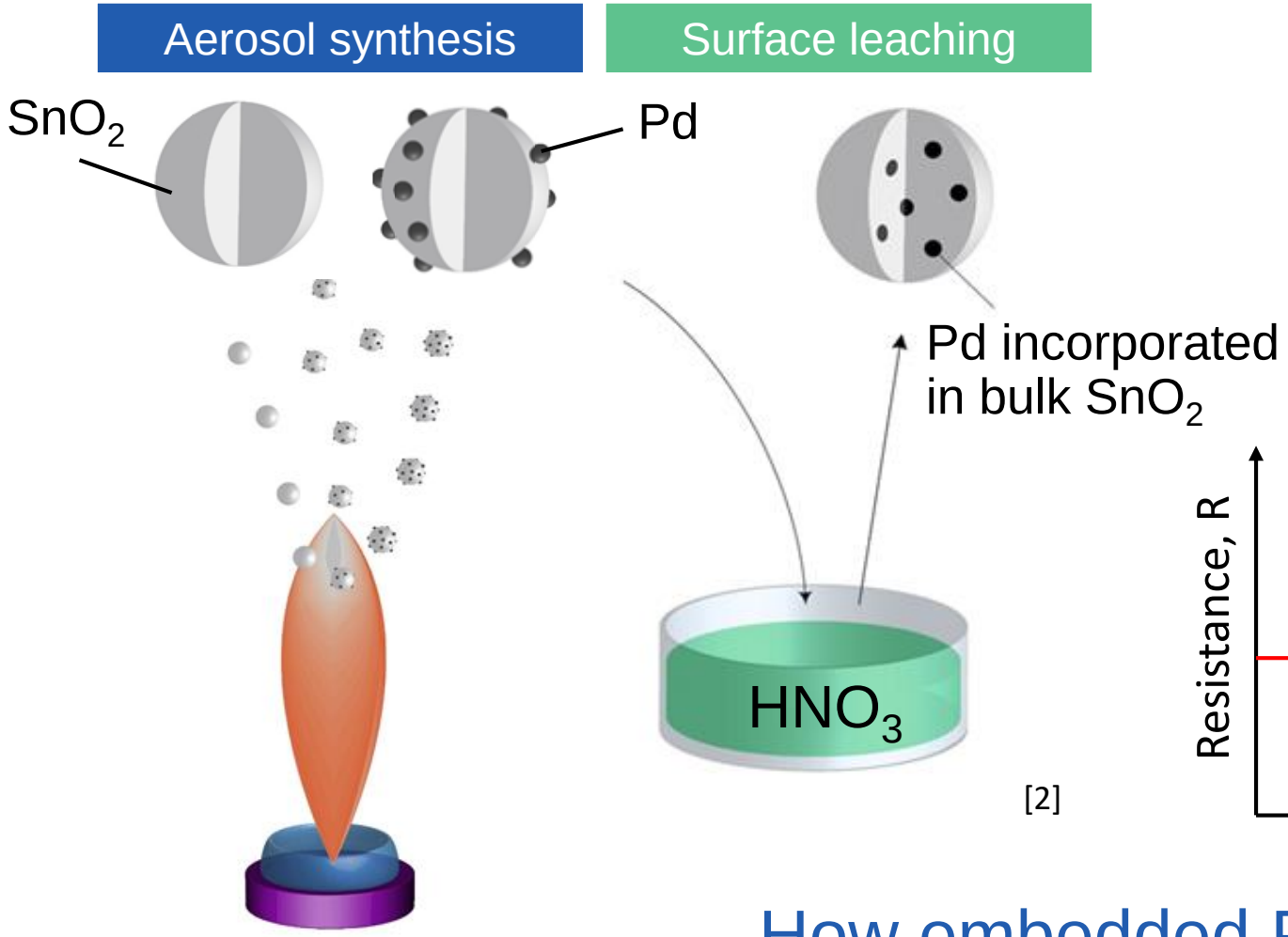
Katarzyna Jabłczyńska[1], Christian M.P. Kubsch, Alexander Gogos[2], Sotiris E. Pratsinis

[1]Faculty of Chemical and Process Engineering, Warsaw University of Technology, Warsaw, Poland

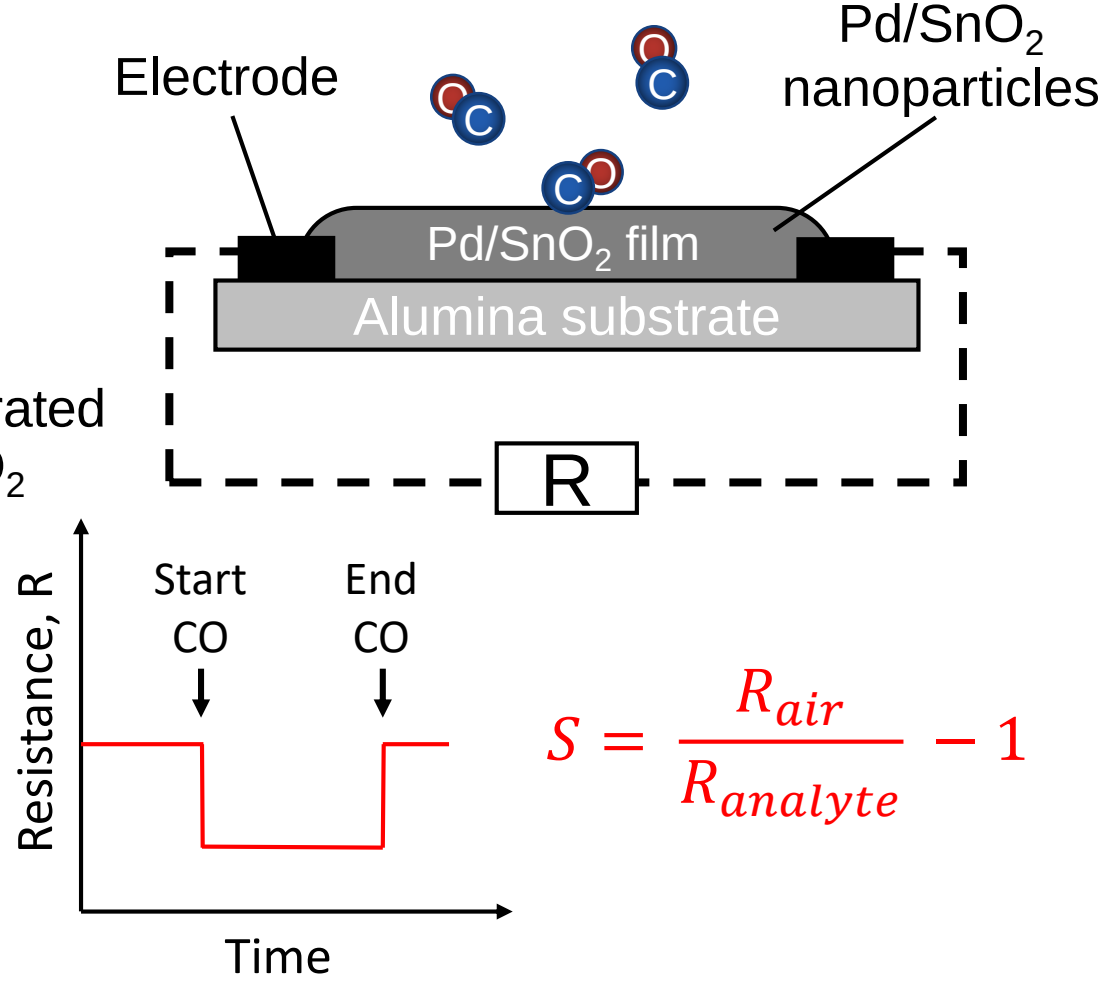
[2]Swiss Federal Laboratories for Materials Science and Technology (Empa), CH-9014 St. Gallen, Switzerland.

Particle Technology Laboratory, Dept. of Mechanical & Process Eng'g, ETH Zurich, Switzerland

Pd-containing tin dioxide (SnO_2) nanoparticles for gas sensing



[2]



$$S = \frac{R_{air}}{R_{analyte}} - 1$$

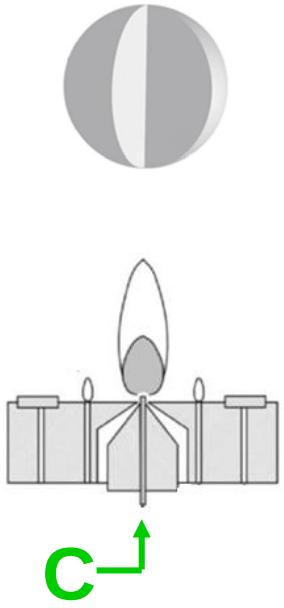
FSP uniquely embeds noble metals in ceramics[1]

How embedded Pd affects sensor performance?

How can we control the surface & embedded Pd fractions?

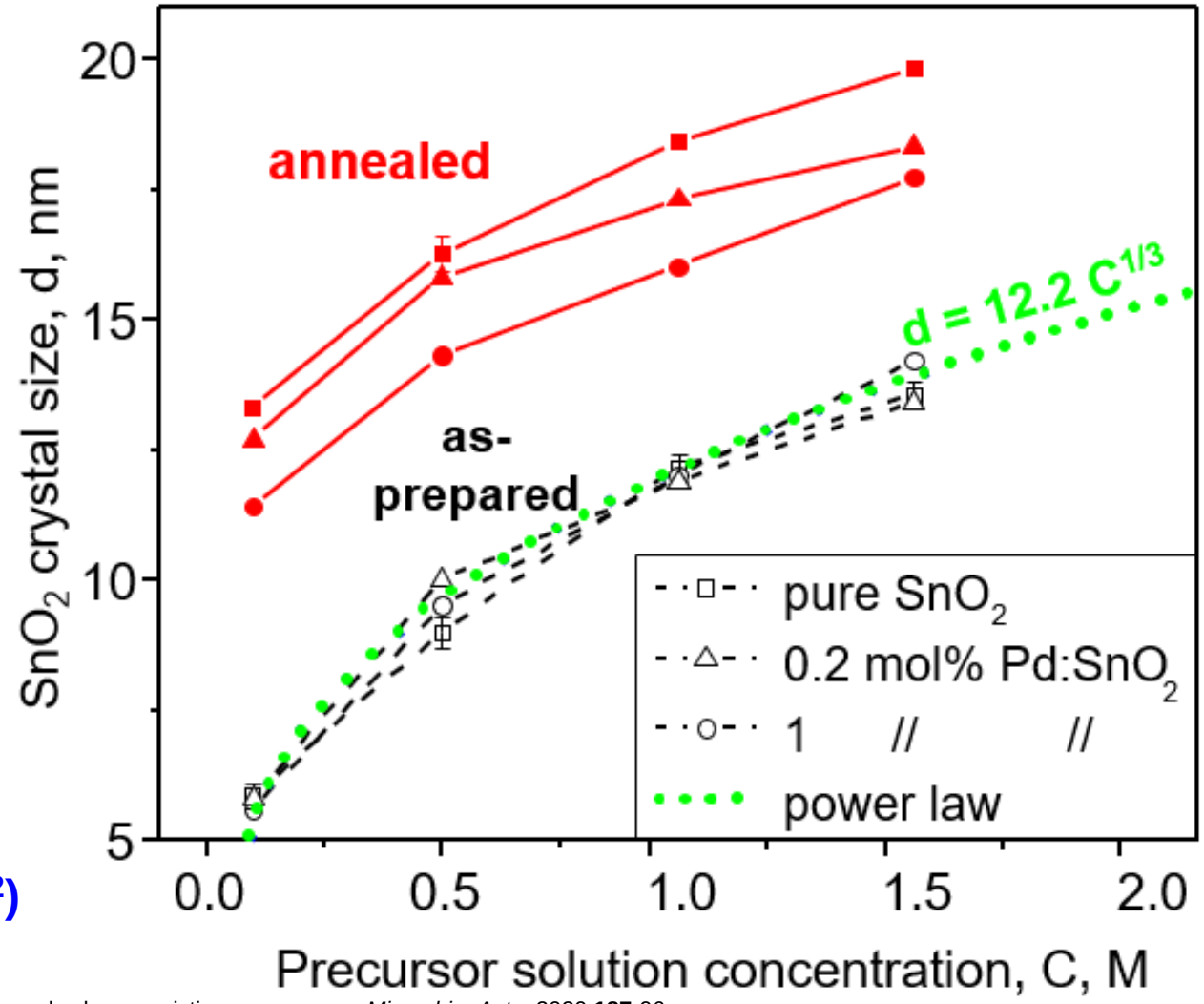
1. van Vegten, N.; Maciejewski, M.; Krumeich, F.; Baiker, A., Structural properties, redox behaviour and methane combustion activity of differently supported flame-made Pd catalysts. *Appl Catal B-Environ* **2009,** *93* , 38-49.
2. Pineau NJ, Keller SD, Güntner AT, Pratsinis SE. Flame-made chemoresistive gas sensors and devices. *Microchim Acta*. 2020;187:96.

Control of SnO_2 crystal size by Precursor solution concentration. C



Pd doesn't affect as-prepared SnO_2 particle size but decreases its annealed crystal size[1]

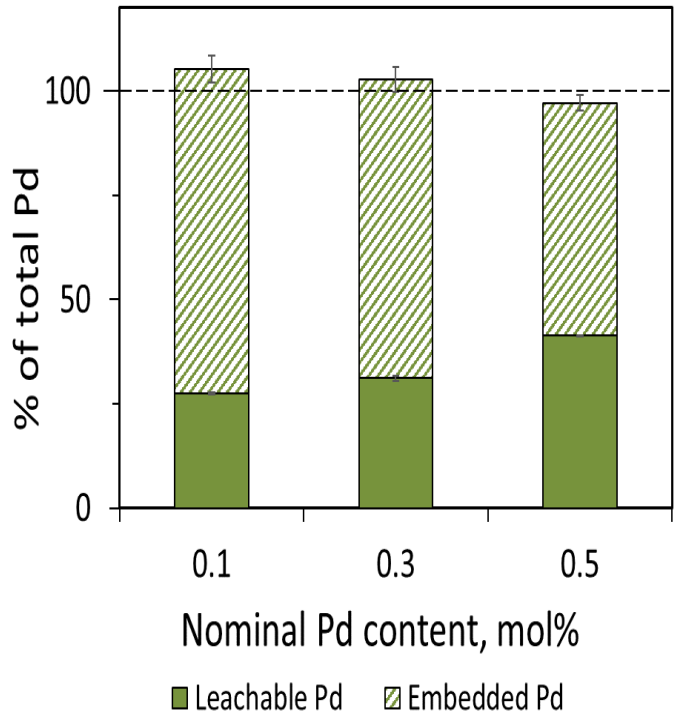
$d \sim C^{1/3}$ → particle growth by droplet-to-particle formation (microexplosions[2]) rather than coagulation-sintering $d \sim C^{2/5}$

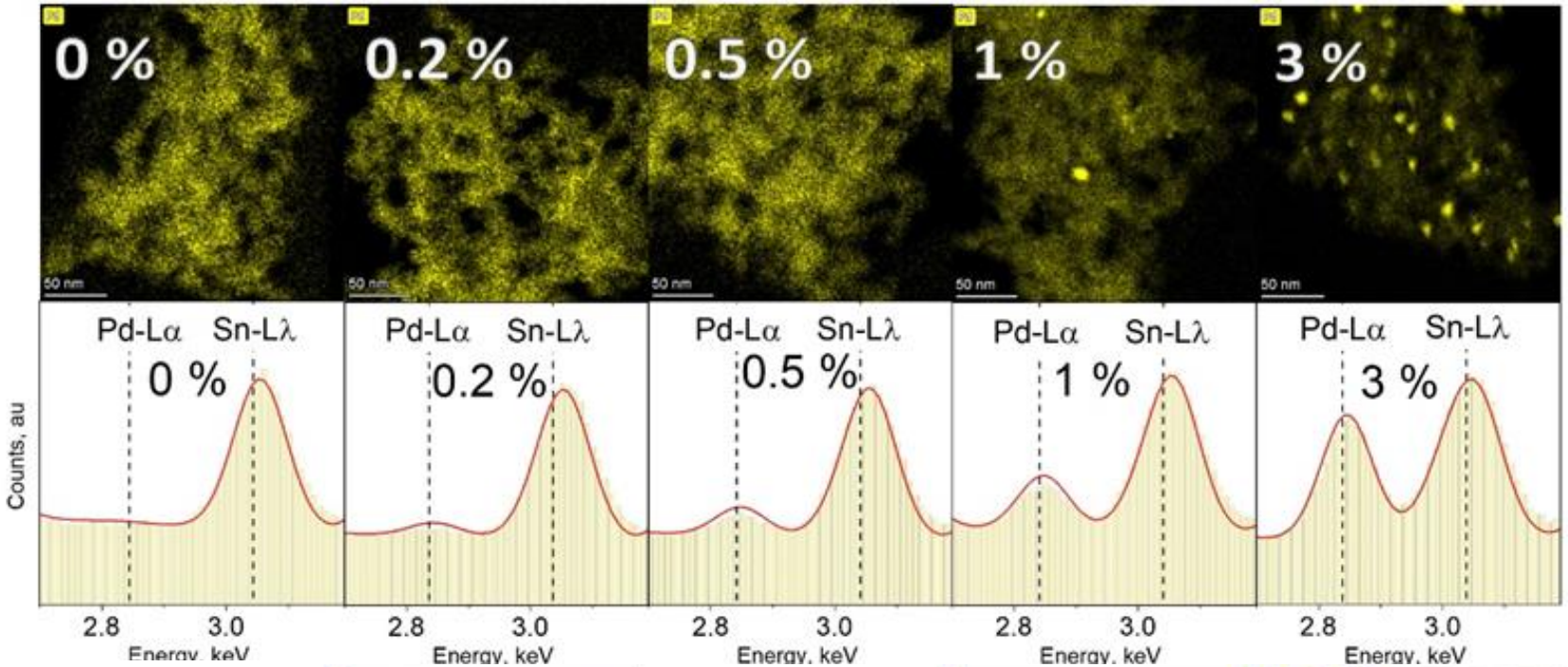


1. Pineau NJ, Keller SD, Güntner AT, SEP. Palladium embedded in SnO_2 enhances the sensitivity of flame-made chemoresistive gas sensors. *Microchim Acta*. 2020;**187:**96

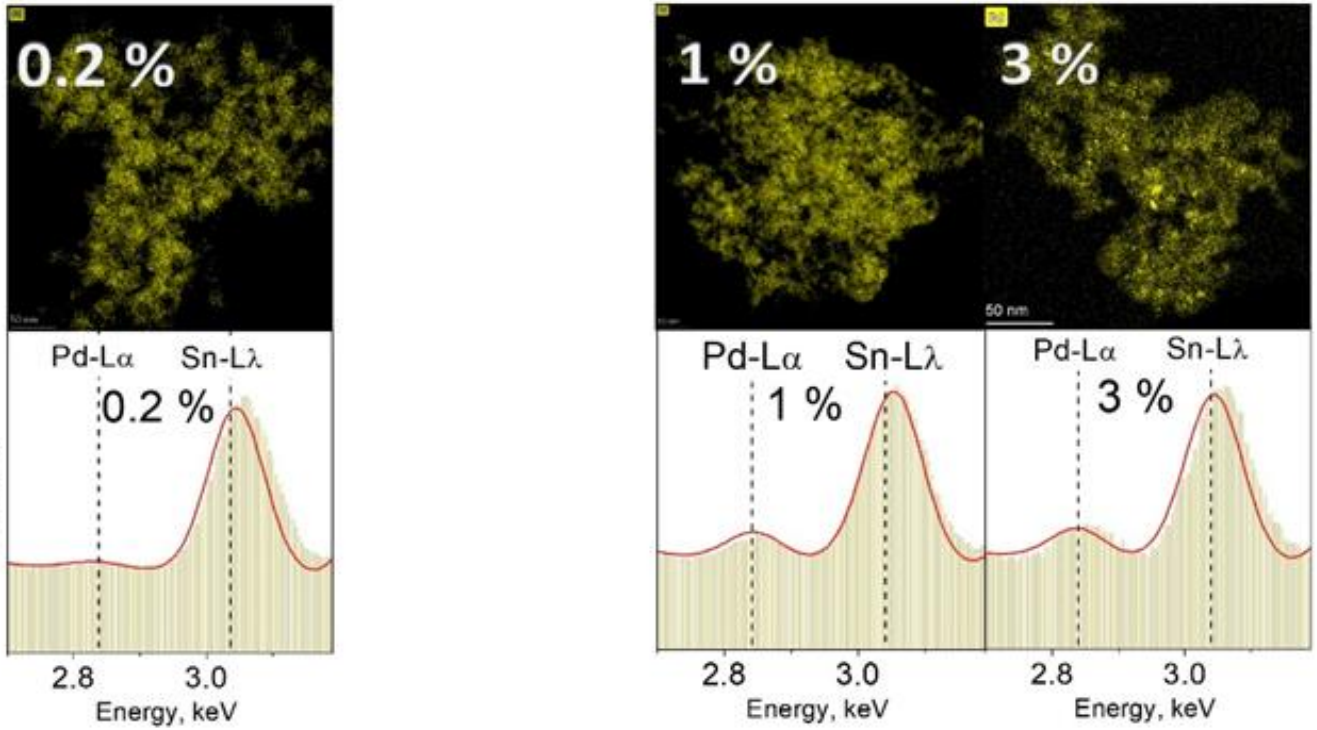
2. C.D. Rosebrock, T. Wriedt, L. Mädler, K. Wegner, The role of microexplosions in flame spray synthesis for homogeneous nanopowders from low-cost metal precursors, *AIChE J.*, 2016, **62**, 381-391.

C=0.5 M, P/D=5/5
ICP-OES of leachate and digested solution



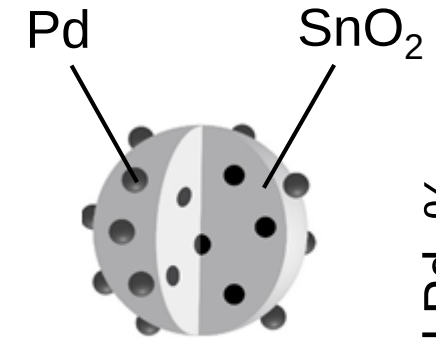


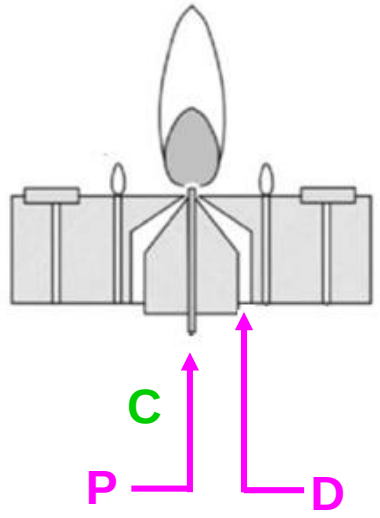
Before leaching



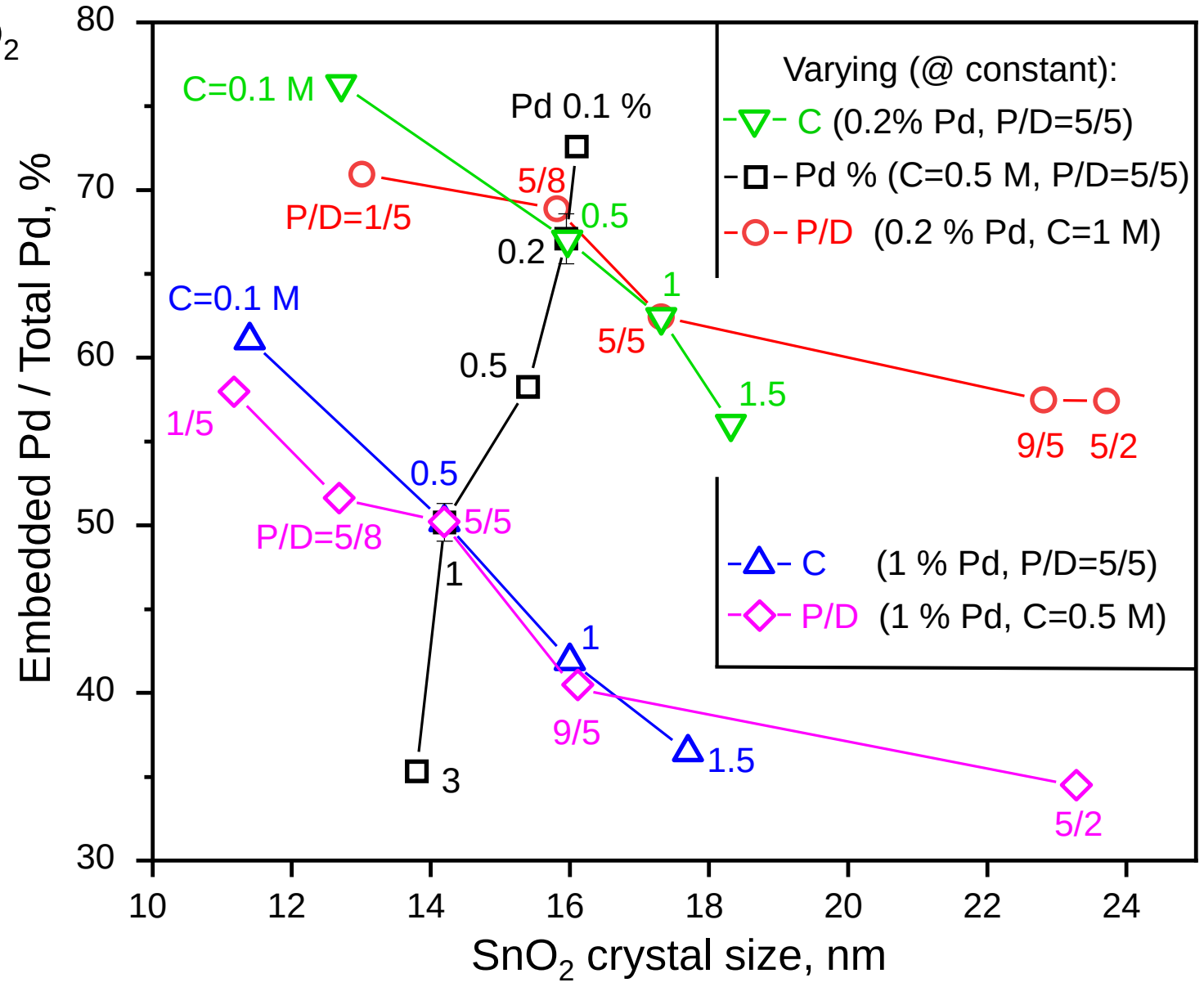
After leaching

The Pd Fraction embedded in FSP-made Pd-containing SnO_2





[1]

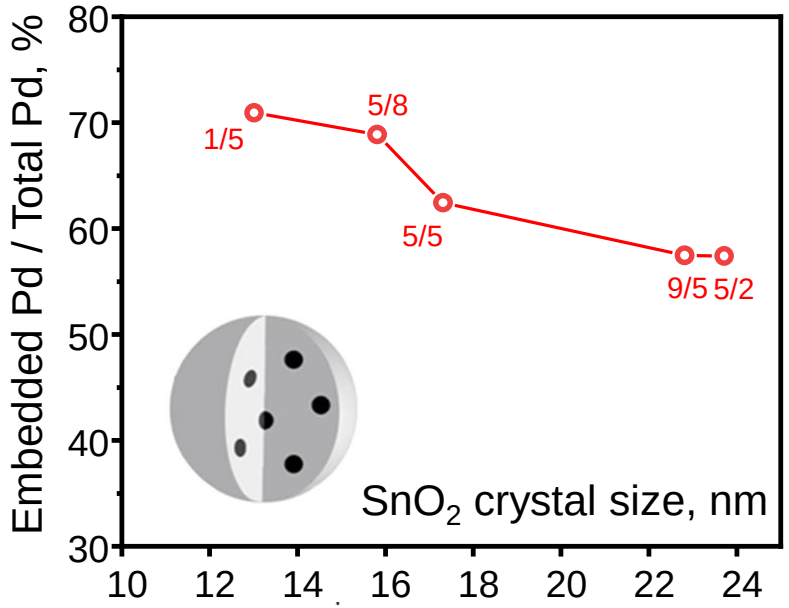


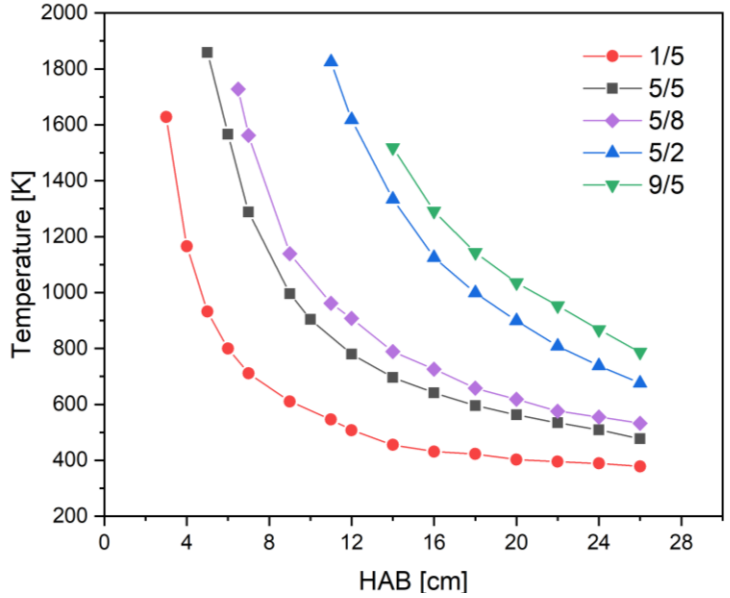
30 – 80 % of Pd embedded into or 20 – 70 % on the surface of SnO_2!

1. Mädler, Roessler, SEP, Sahm, Gurlo, Barsan, Weimar, Direct formation of highly porous gas-sensing films by in situ thermophoretic deposition of flame-made Pt/SnO_2 nanoparticles. *Sens. Act., B.* **2006**;114:283-295

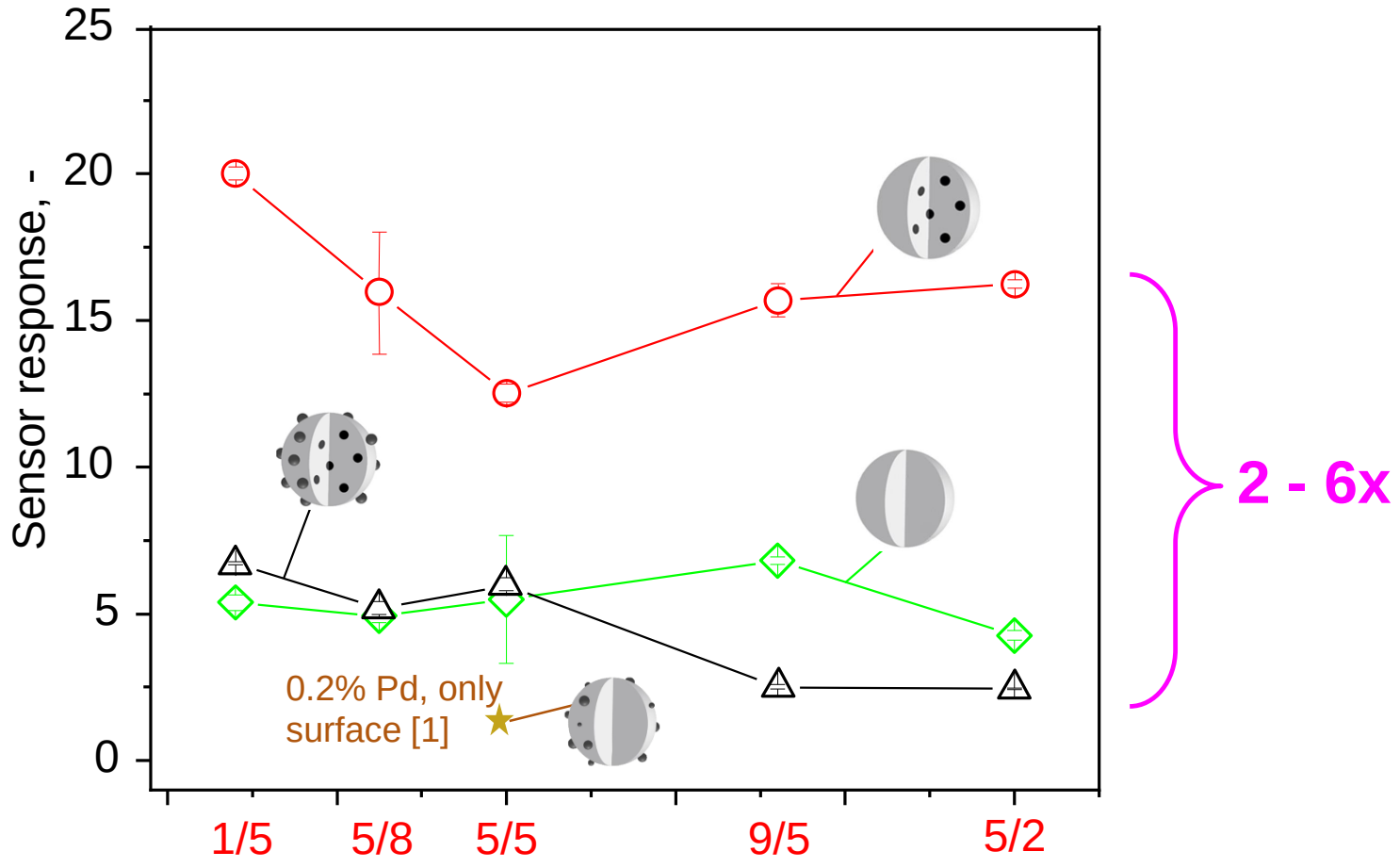
Gas sensing performance

Varying the precursor / oxygen flow rate (P/D) @ 0.2 % Pd & C = 1 M





1 ppm Acetone (50% RH, 350 °C)



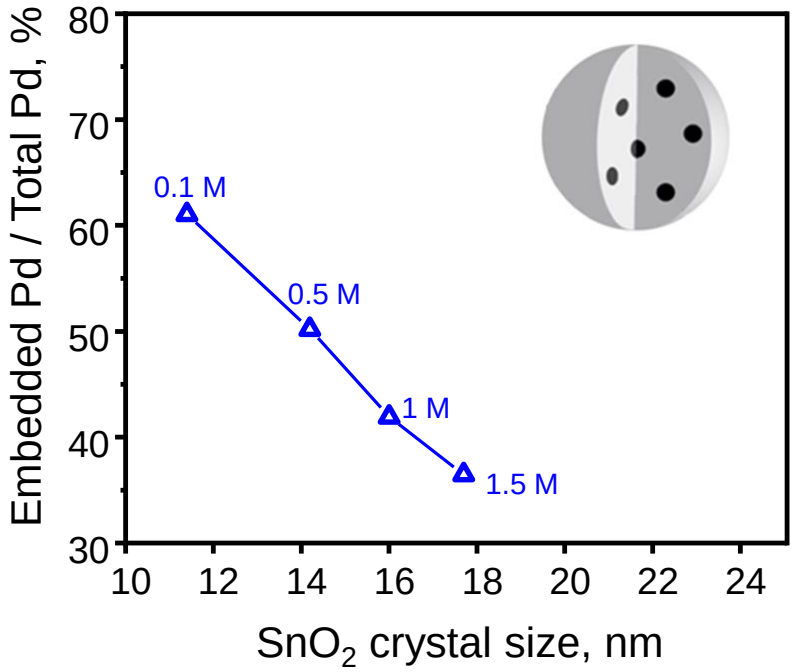
[1] Gschwend P, Schenk F, Gogos A, SEP, Acetone Sensing and Catalytic Conversion by Pd-Loaded SnO_2. *Materials* **2021**;14:5921.

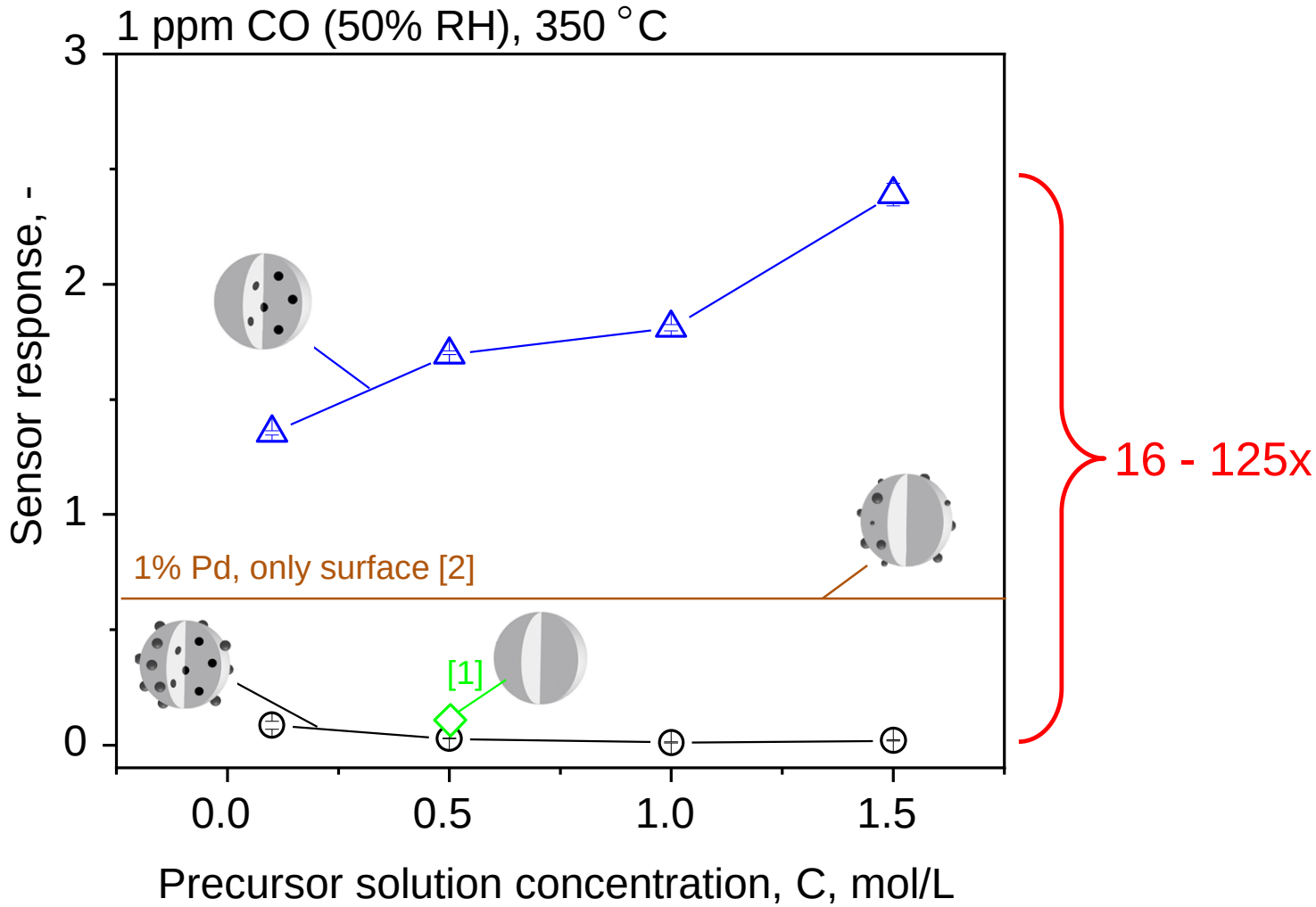
Effect on precursor concentration on sensing performance

Varying the concentration (C)

1 % Pd

P/D = 5/5



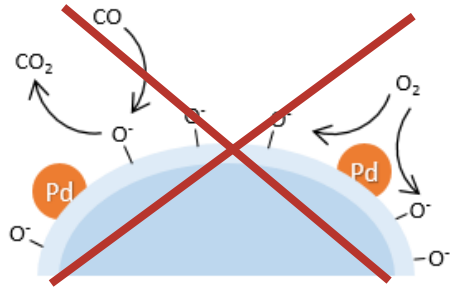


[1] Pineau NJ, Keller SD, Güntner AT, Pratsinis SE. Palladium embedded in SnO_2 enhances the sensitivity of flame-made chemoresistive gas sensors. *Microchim Acta*. 2020;187:96

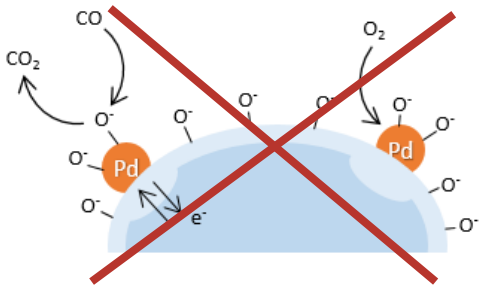
[2] Yuasa M et al. Nano-sized PdO loaded SnO_2 nanoparticles by reverse micelle method for highly sensitive CO gas sensor. *Sensor Actuat B*. 2009;136:99-104.

Possible mechanisms of enhancement by embedded Pd

Loading (Pd clusters):

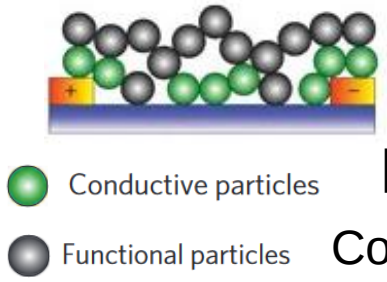


Spillover effect

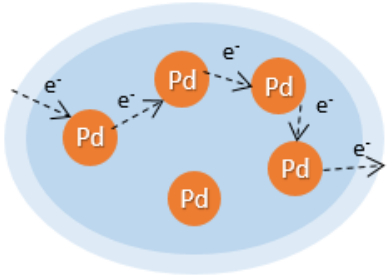


Surface Fermi level control

[1]

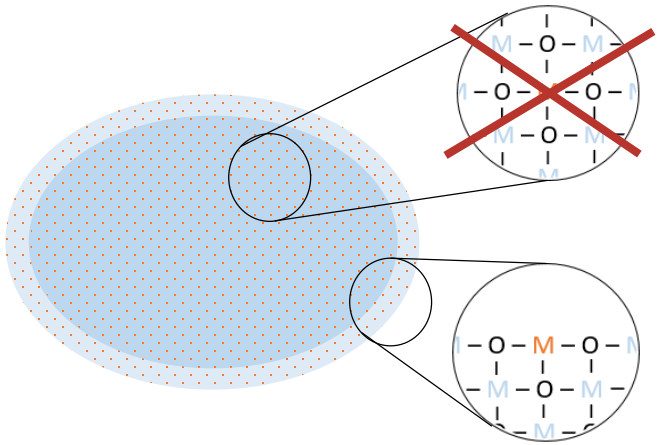


[4]



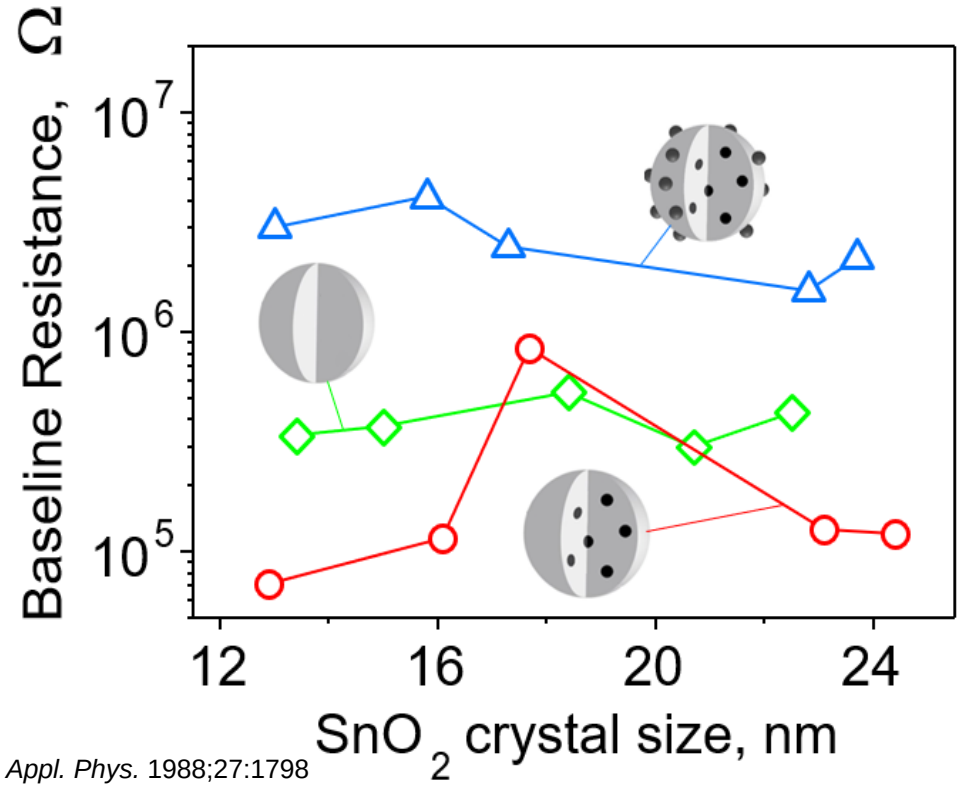
Conductive domains (nanoelectrodes)

Doping (Pd ions):



New acceptor and donor states [2]

Direct activation of oxygen [3]



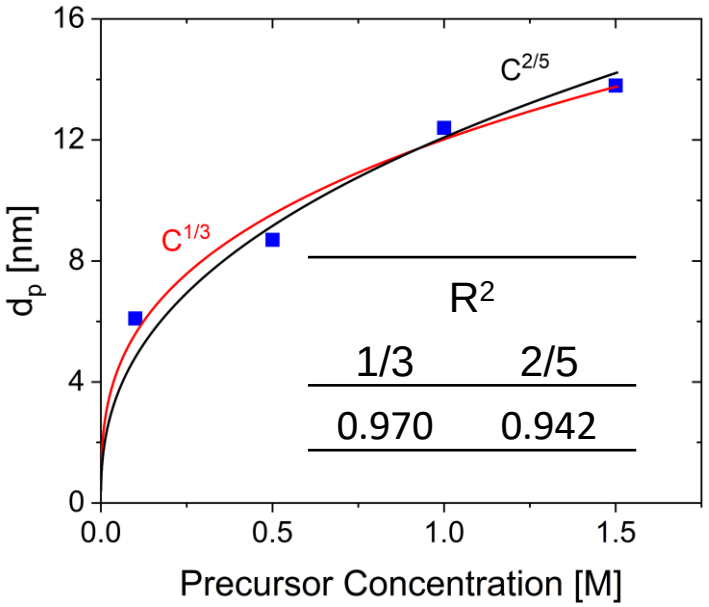
[1] Matsushima Sh, Teraoka Y, Miura N, Yamazoe N. Role of Additives on Alcohol Sensing by Semiconductor Gas Sensor. *Jpn. J. Appl. Phys.* 1988;27:1798

[2] Degler D, Pereira de Carvalho HW, Weimar U, Barsan N, Pham D, Mädler L, Grunwaldt J-D. Structure–function relationships of conventionally and flame made Pd-doped sensors studied by X-ray absorption spectroscopy and DC-resistance.*Sensor Actuat B-Chem*. 2015; 219:315-23.

[3] Koziej D, Hübner M, Barsan N, Weimar U, Sikora M, Grundwaldt J-D. Operando X-ray absorption spectroscopy studies on Pd-SnO_2 based sensors. *Phys. Chem. Chem. Phys*. 2009;11:8620-8625.

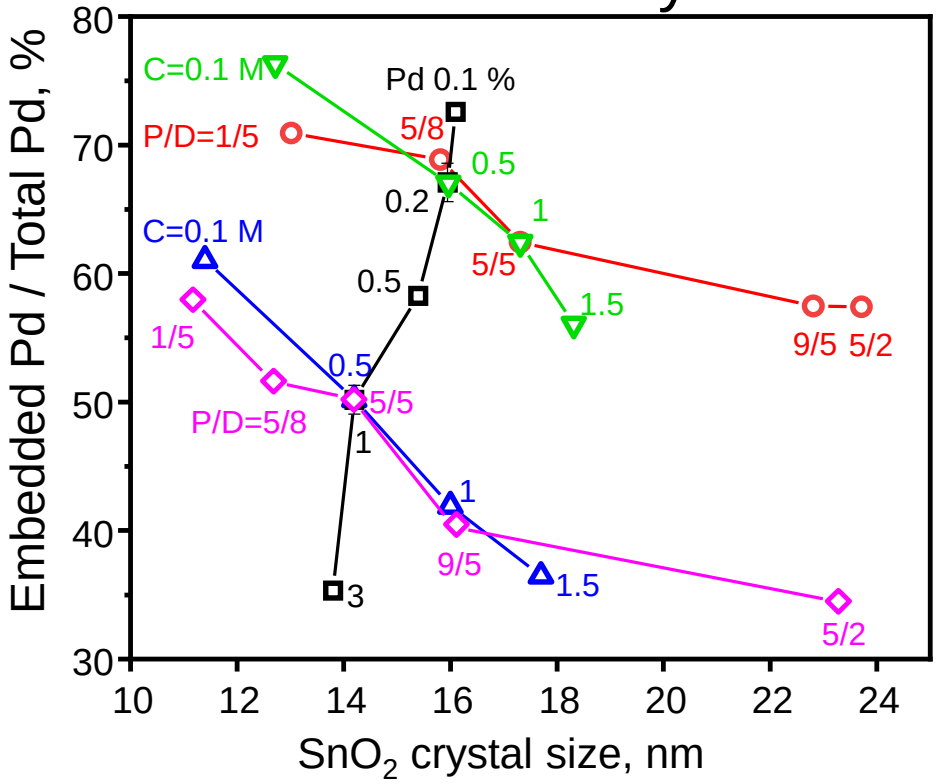
[4] Tricoli A, Pratsinis SE. Dispersed nanoelectrode devices. *Nature Nanotechnol*. 2010;5:54-60

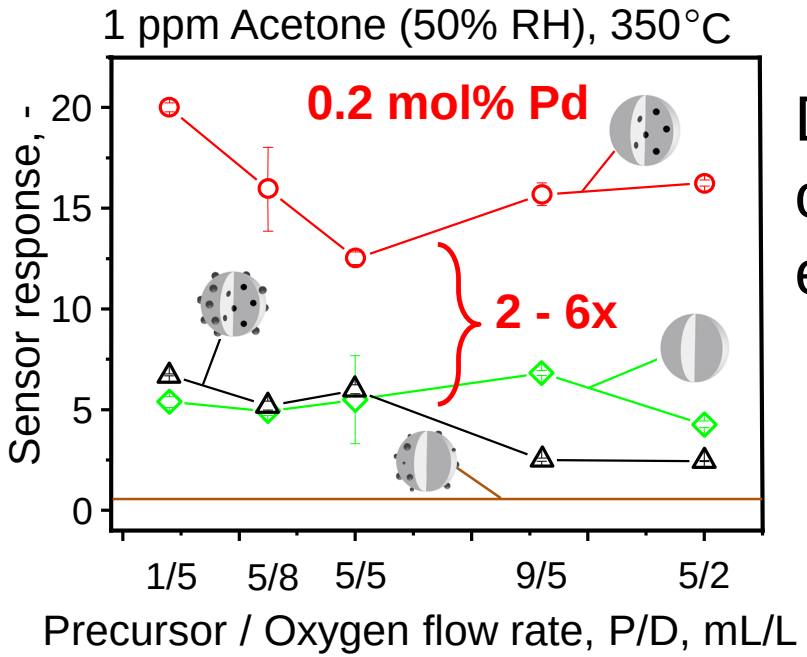
Conclusions



FSP-made SnO_2 seems to form by droplet microexplosions followed by droplet-to-particle conversion rather than by coagulation-coalescence

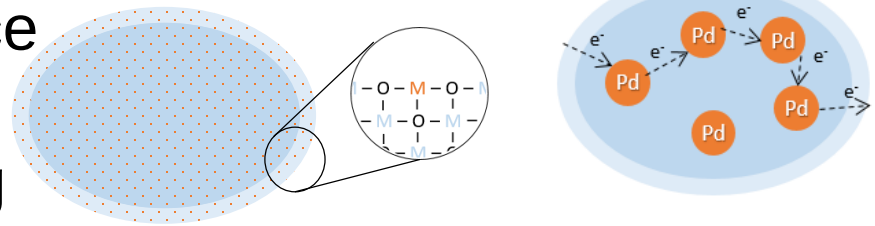
Close control of Pd embedded fraction & crystal size



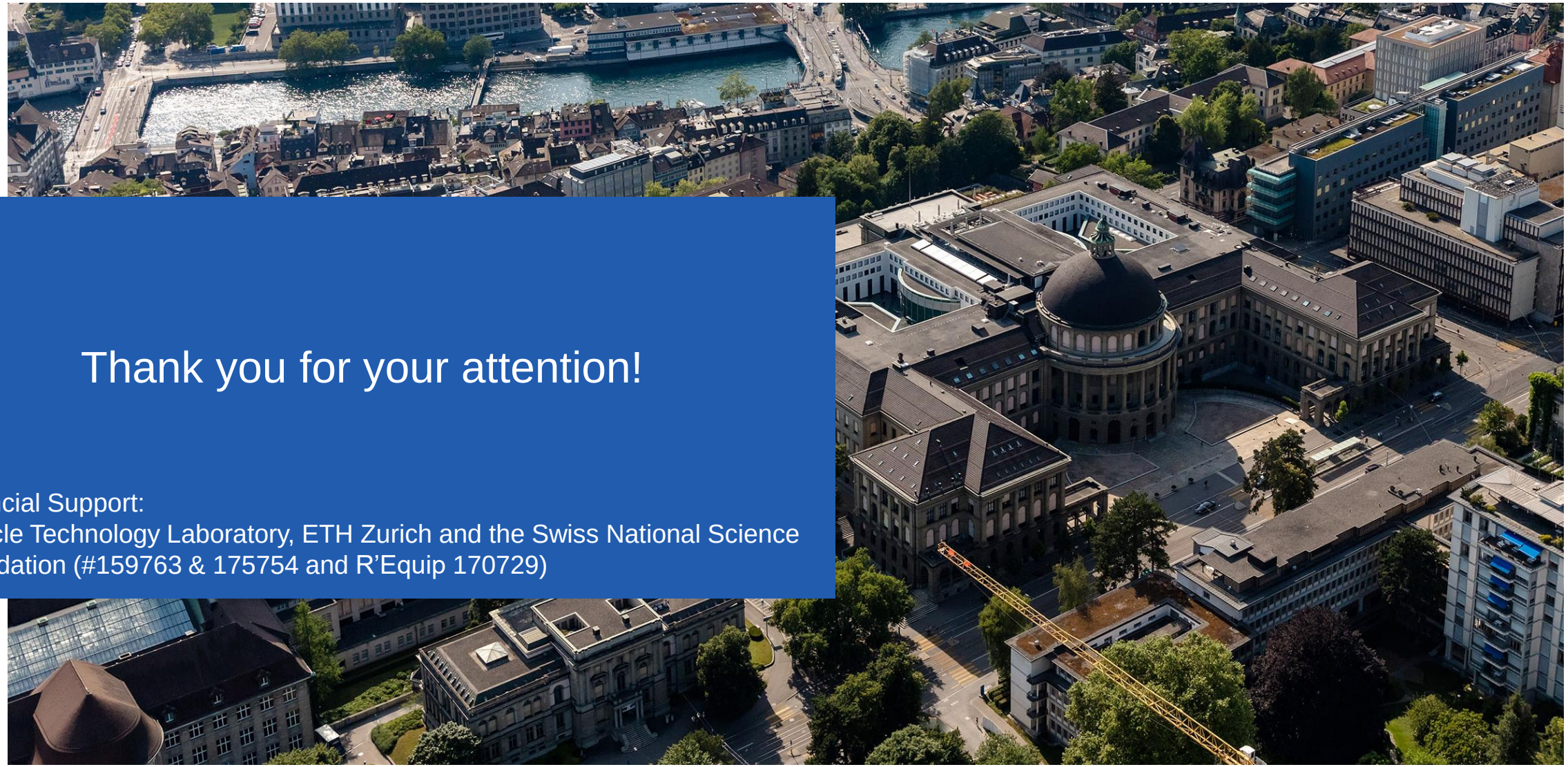


Drastic enhancement of gas sensing after embedding of Pd

Bulk and/or surface mechanisms enhanced sensing



ETH zürich



Thank you for your attention!

Financial Support:
Particle Technology Laboratory, ETH Zurich and the Swiss National Science Foundation (#159763 & 175754 and R'Equip 170729)

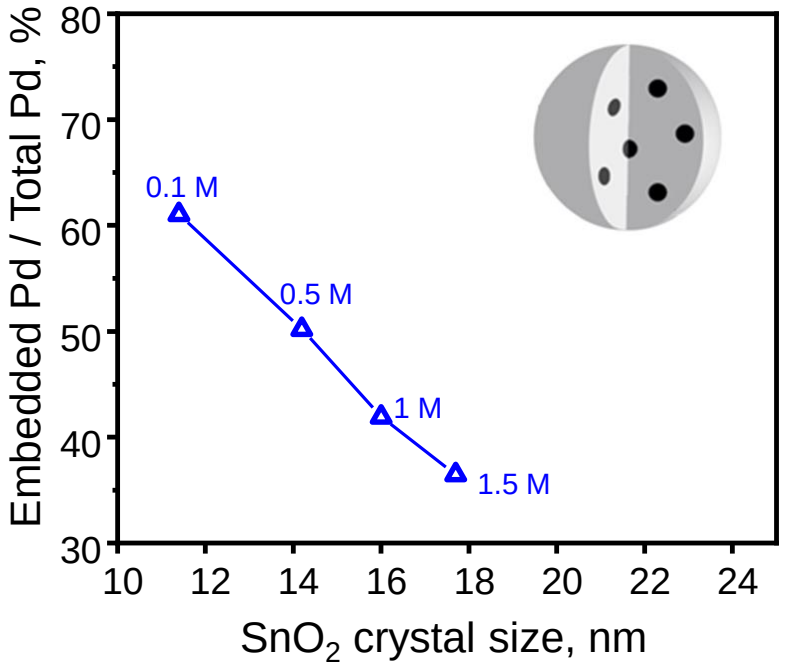
K. Jabłczyńska, A. Gogos, C.M.P. Kubsch, S.E. Pratsinis, Embedding Pd into SnO_2 drastically enhances gas sensing, *Nanoscale Advances.*, **6**, 1259-1268 (2024).

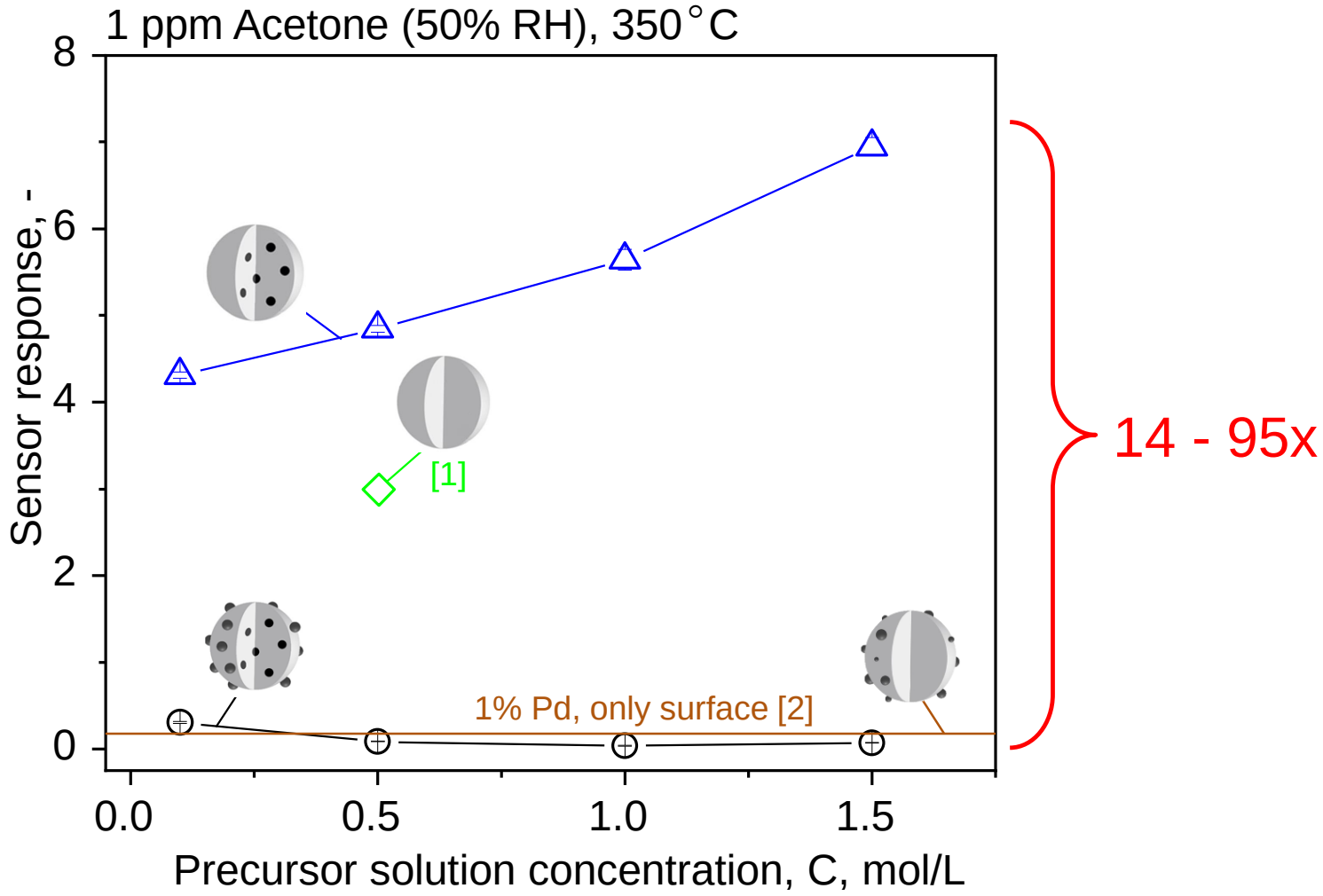
Effect on precursor concentration on sensing performance

Varying the concentration (C)

1 % Pd

P/D = 5/5

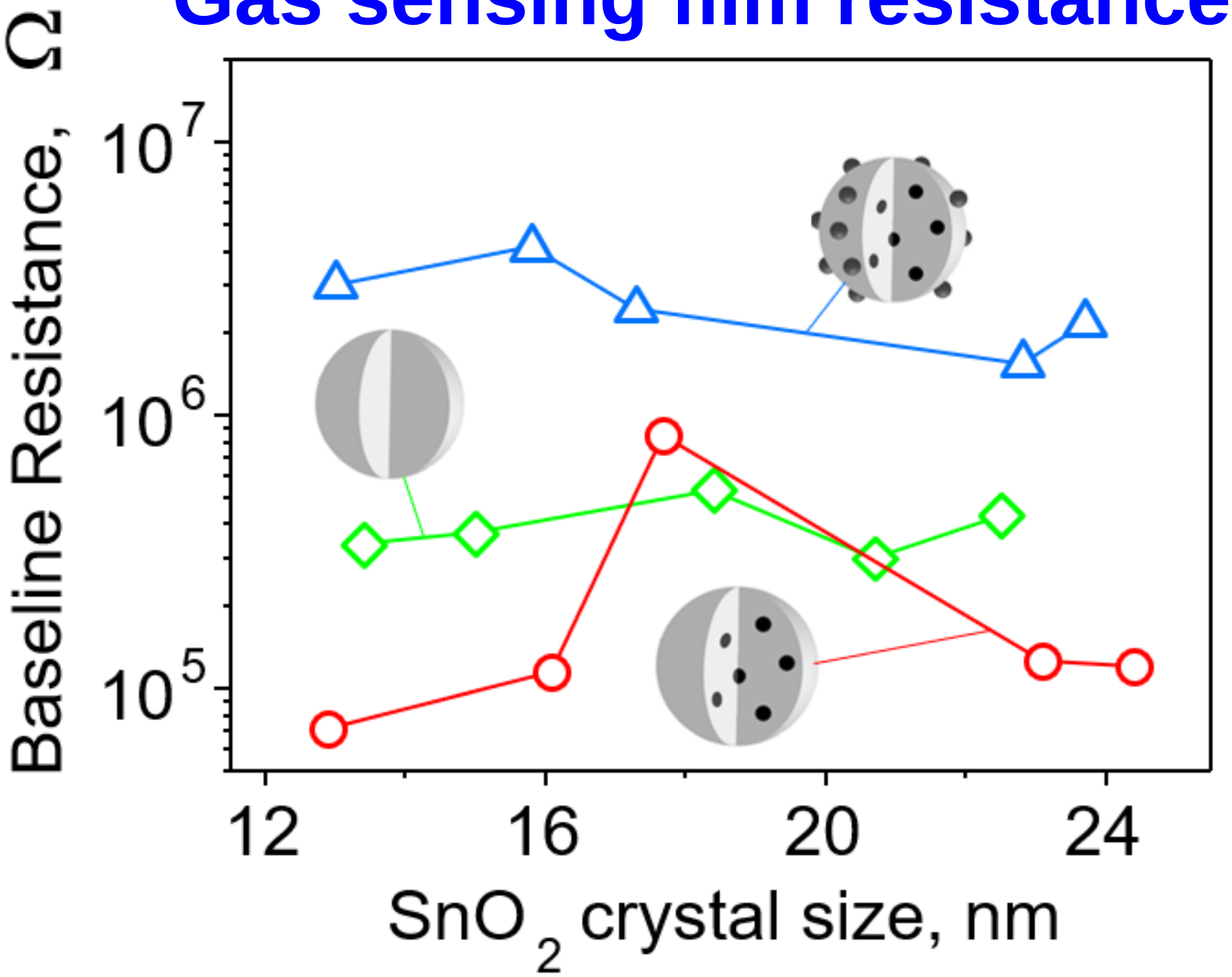




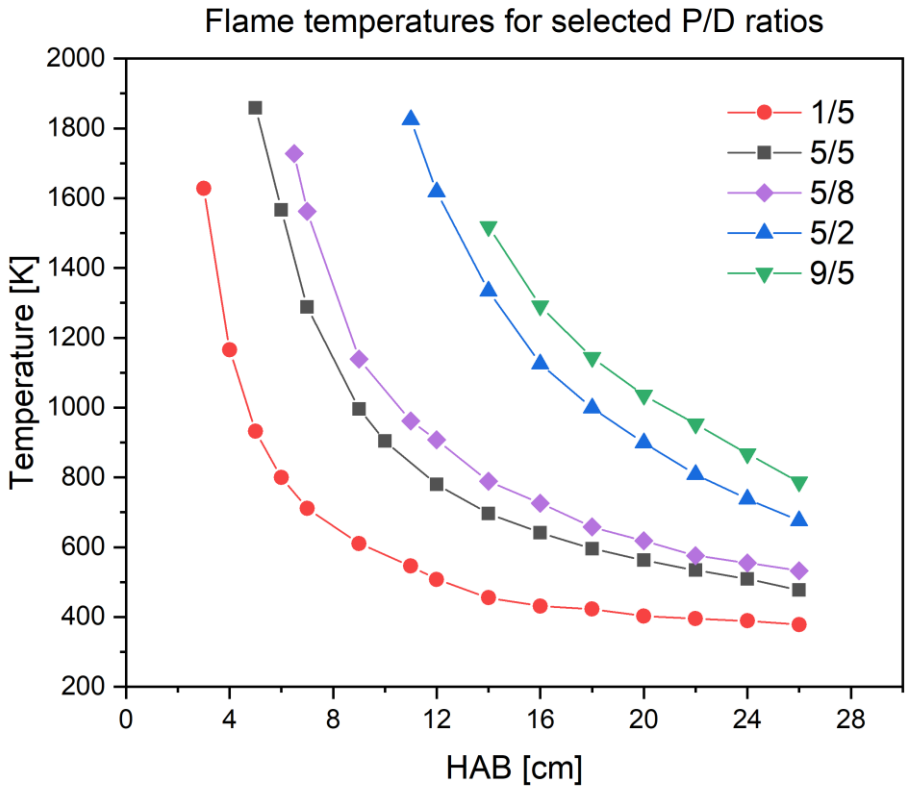
[1] Pineau NJ, Keller SD, Güntner AT, Pratsinis SE. Palladium embedded in SnO_2 enhances the sensitivity of flame-made chemoresistive gas sensors. Microchim Acta. 2020;187:96

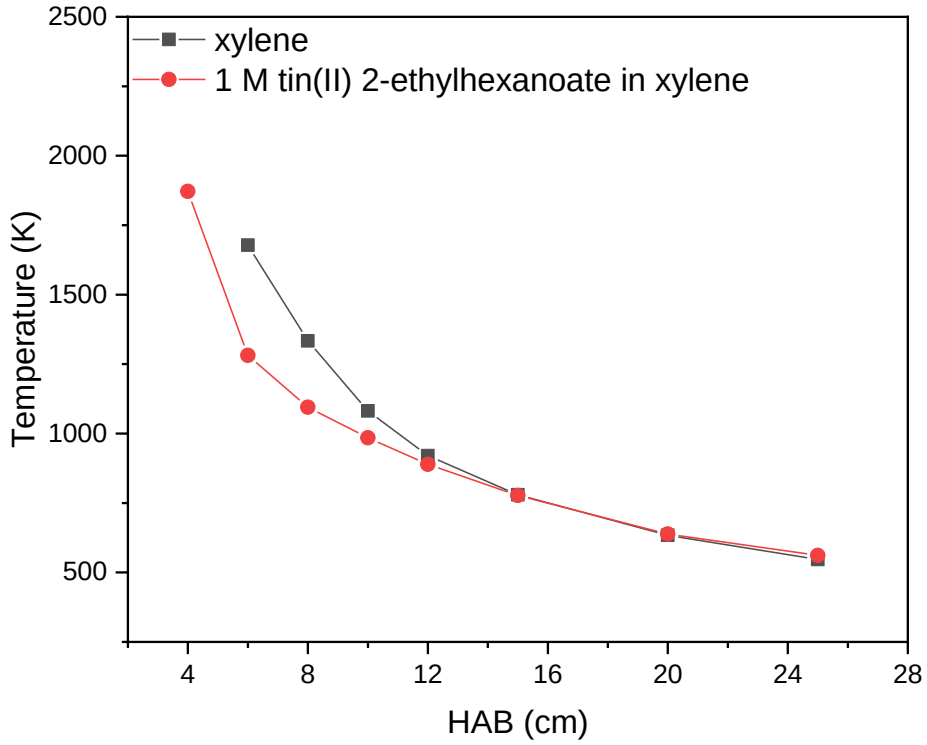
[2] Gschwend P, Schenk F, Gogos A, Pratsinis SE, Acetone Sensing and Catalytic Conversion by Pd-Loaded SnO_2. *Materials* 2021;14:5921.

Gas sensing film resistance



Flame temperature profiles

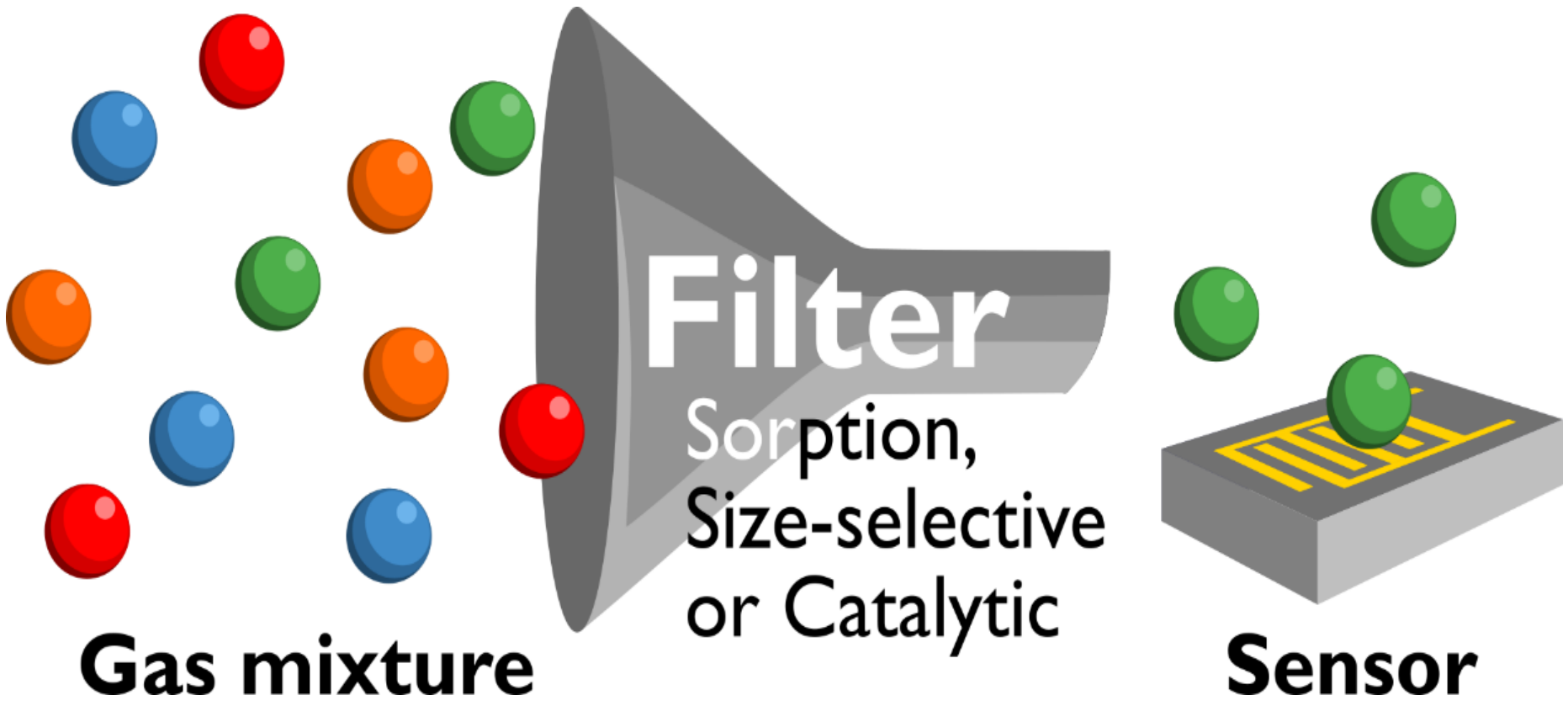




Boiling points of metallic and oxidized Pd and Sn

	T_b [K]
Pd	3236
Sn	2875
SnO2	2173
SnO	1698
PdO	1023 (decomposition)

Filter- or Concentrator-enhanced sensor selectivity

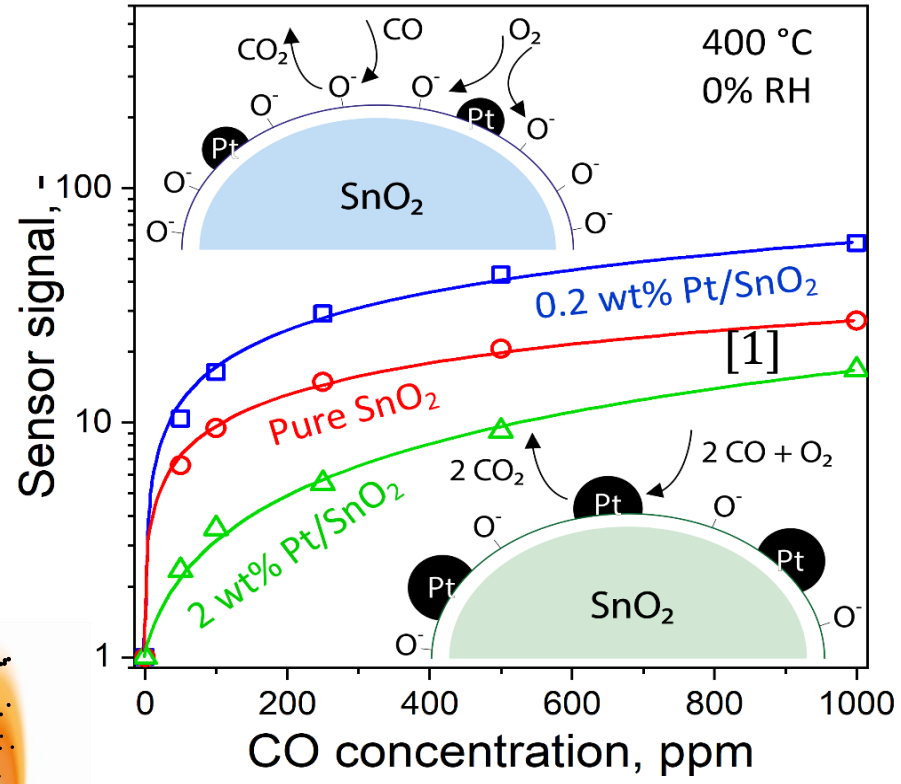


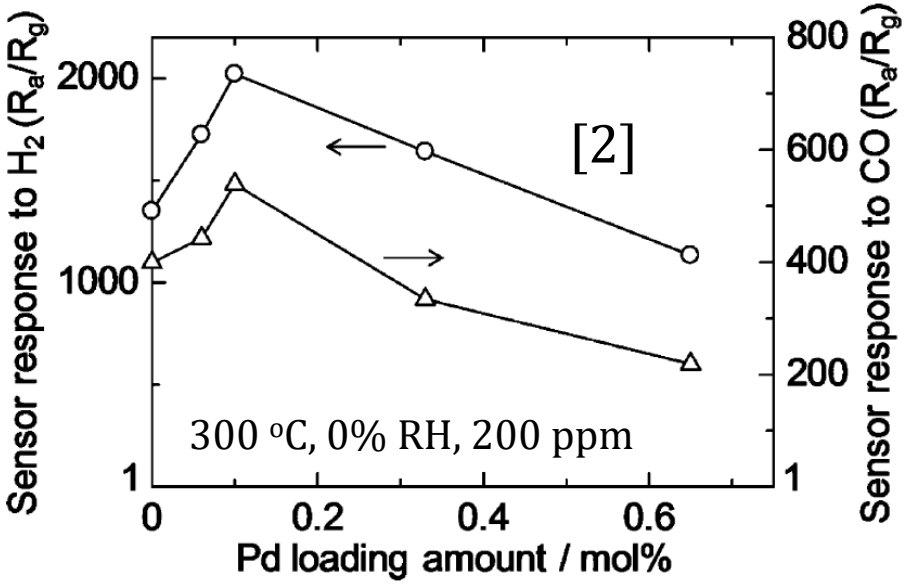
van den Broek J, Weber IC, Güntner AT, SEP. *Mater Horiz.* Highly selective gas sensing enabled by filters, **2021**;8:661-84

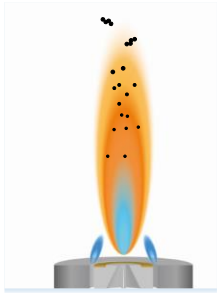
Noble metal content in SnO_2 gas sensors

Korotcenkov G, Brinzari V, Boris Y, Ivanov M, Schwank J, Morante J. Thin Solid Films. 2003;436(1):119-126

spill-over" effect (i.e. *chemical sensitization*)







Flame spray pyrolysis

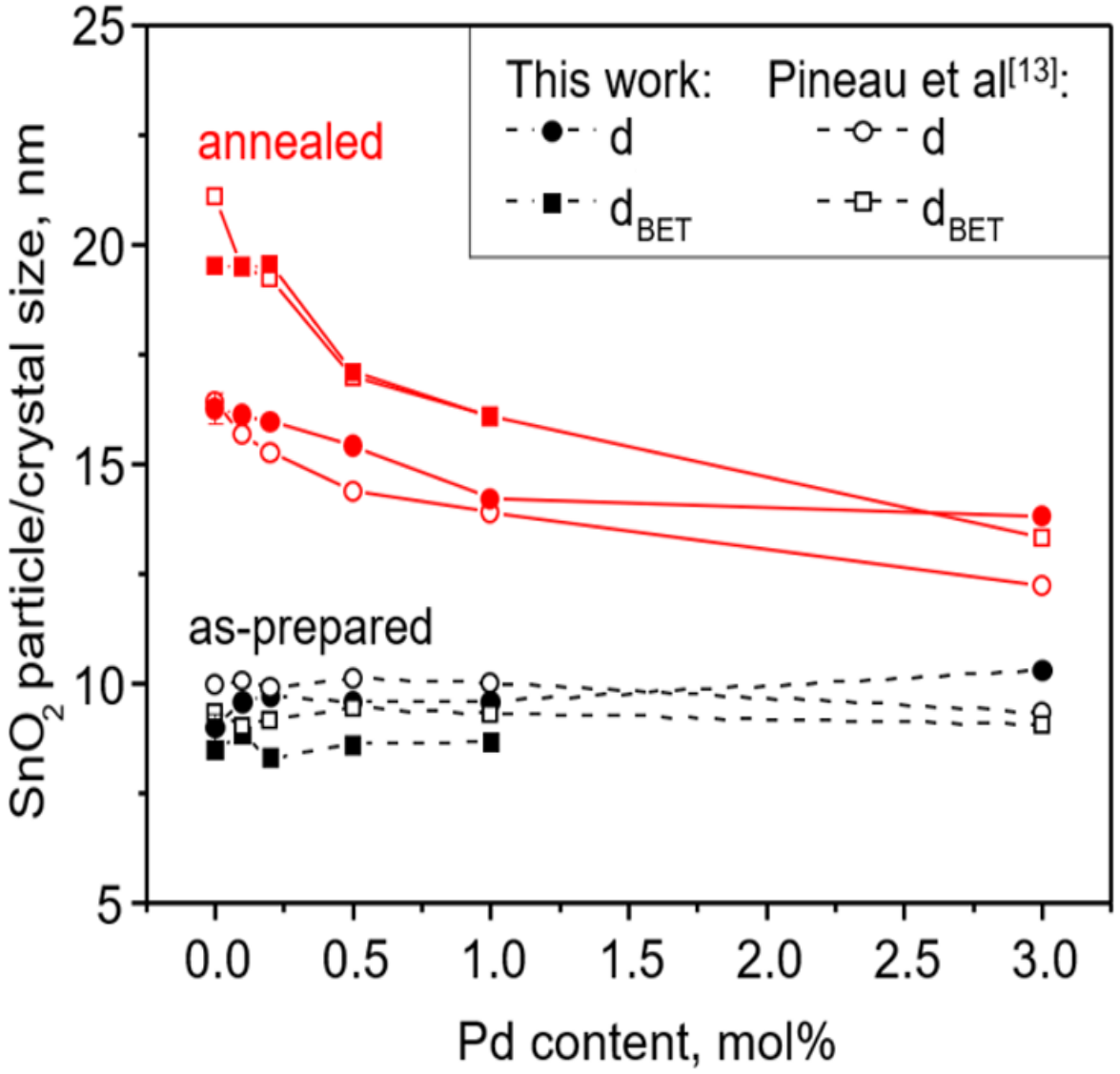
Wet made (precipitation) Pd on SnO_2

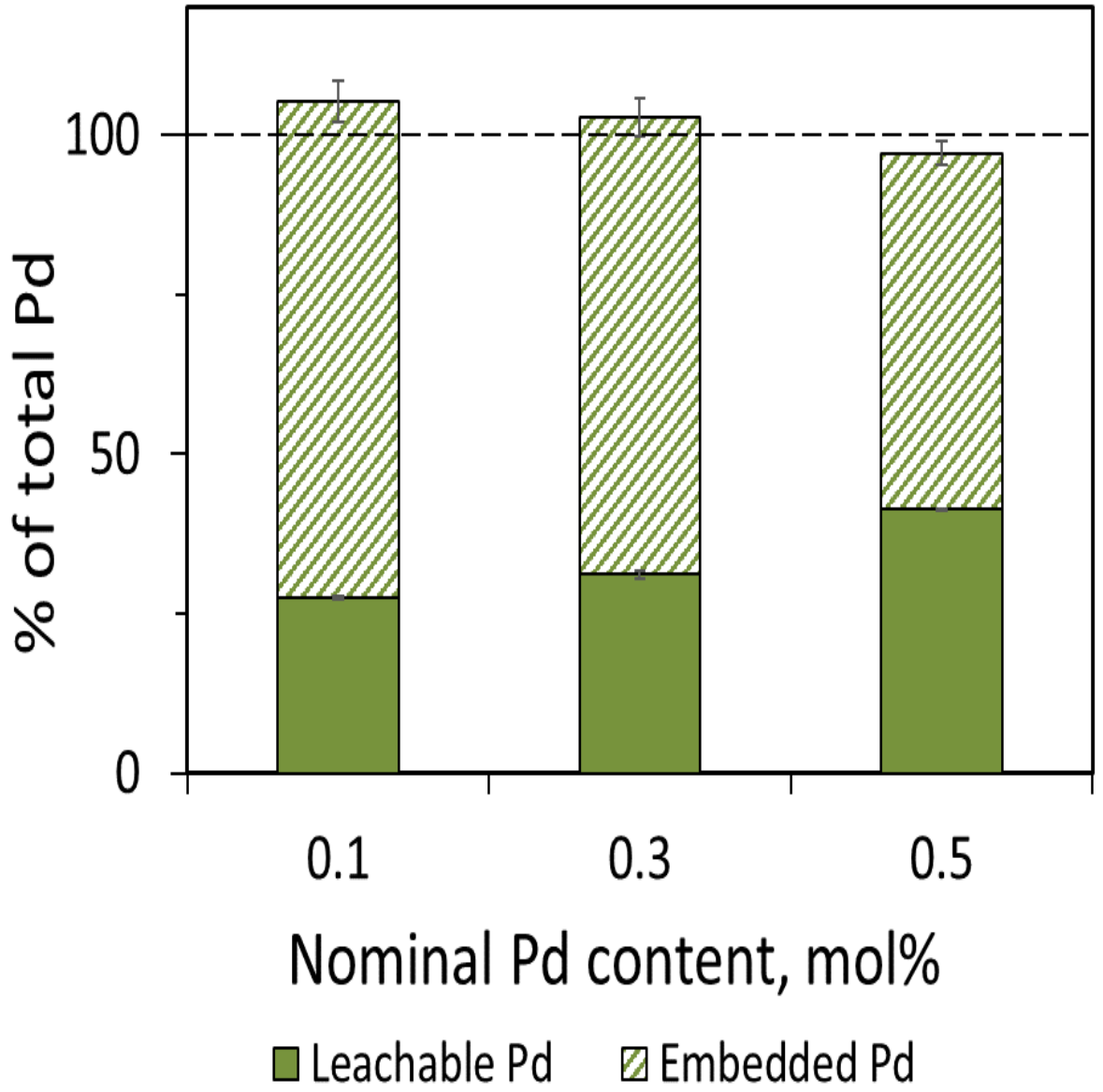
- optimum at 0.15 mol% Pd
- sensor response enhanced with surface Pd

Low noble metal concentrations most effective in gas sensing

[1] Mädler L, Sahm T, Gurlo A, Grunwaldt JD, Barsan N, Weimar U, SEP. J Nanopart Res. **2006;**8:783-96,

[2] Suematsu, K.; Shin, Y.; Hua, Z.Q.; Yoshida, K.; Yuasa, M.; Kida, T.; Shimanoe, K., *ACS Appl Mater Inter,* **2014,** *6*:5319-5326





C=0.5 M, P/D=5/5
IICP-OES of leachate
and digested solution