6th NANO Boston Conference (Virtual)

Nanostructured composites of semiconductor metal oxides with noble metals (Au, Pt): comparison of sensitivity to volatile organic compounds

Artem Marikutsa

Chemistry Department, Moscow State University, Vorobyevy gory 1-3, Moscow 119234, Russia

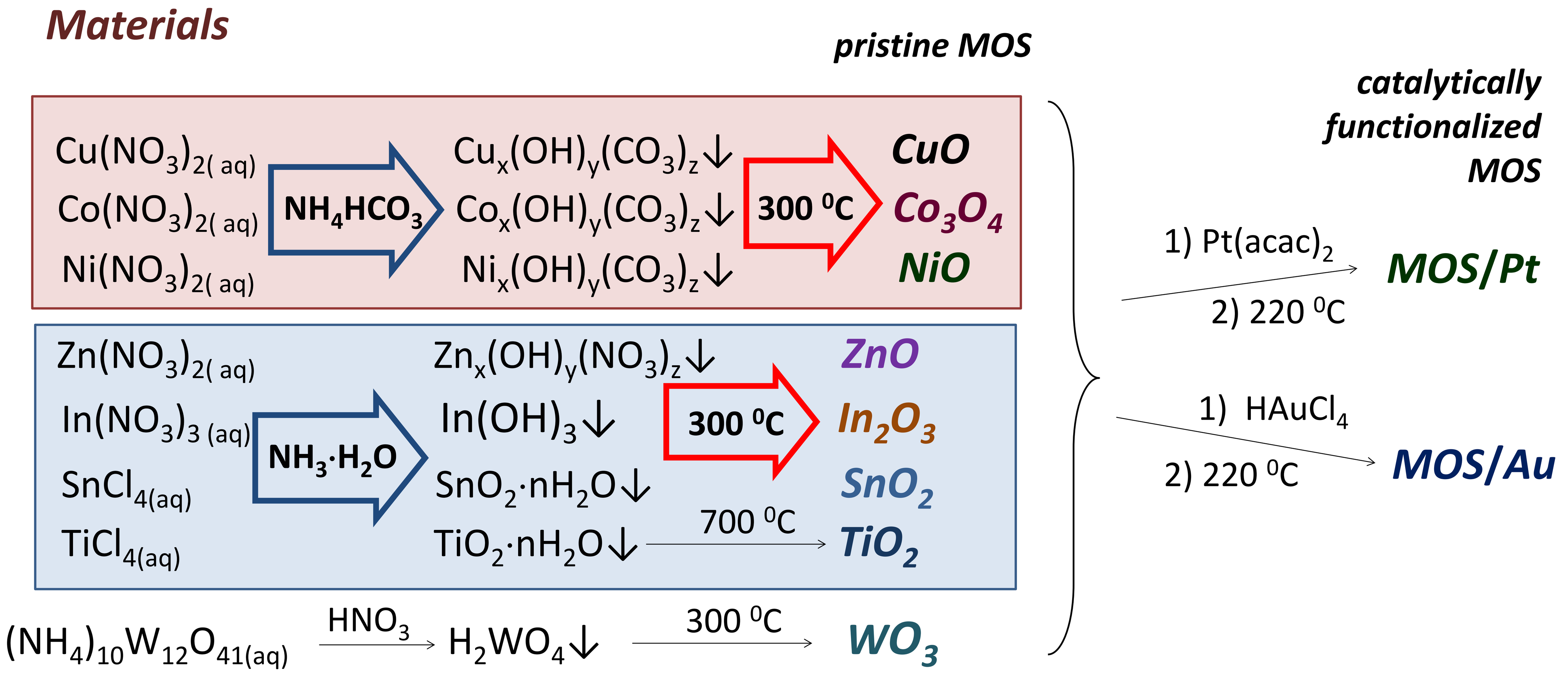
artem.marikutsa@gmail.com

Introduction

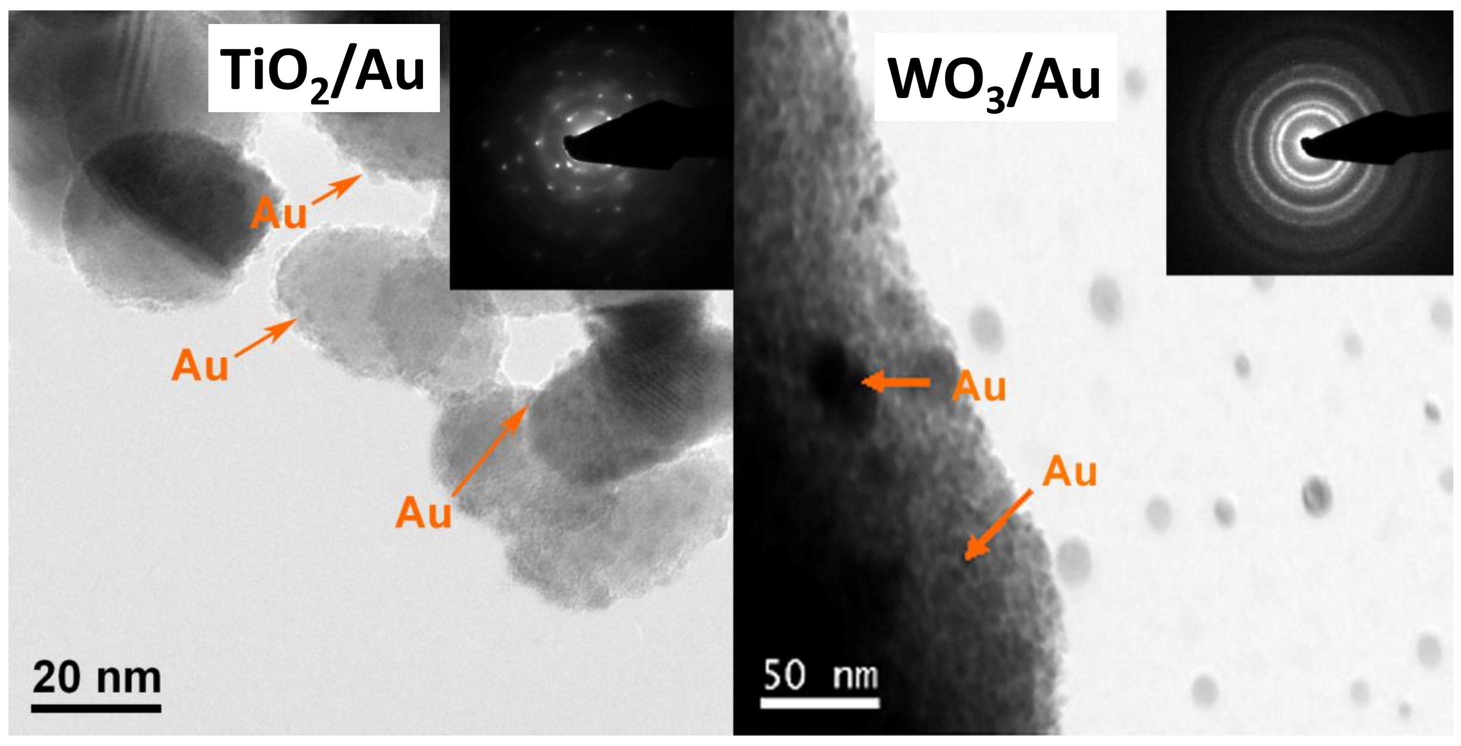
Metal oxide semiconductors (MOS) functionalized by catalytic noble metals are promising for gas sensors of volatile organic compounds (VOC). However, the relations of materials composition and sensing behavior is unclear. In this work, we compare the sensitivity and selectivity of different MOS and composites MOS/Au, MOS/Pt to methanol and acetone. Nanoparticles of *p*-type (NiO, CuO, Co_3O_4) and *n*-type (In_2O_3, ZnO, SnO_2, TiO_2, and WO_3) MOS were obtained by conventional aqueous deposition method. Active sites (surface oxygen species and acid sites) were analyzed. Metal-oxygen bond energy (E_{M-O}) was chosen as a descriptor for the observed difference in active sites concentration and gas sensitivity. The interaction routes of methanol and acetone with materials surfaces were examined by diffuse-reflectance infrared spectroscopy (DRIFT). Oxidation of methanol and acetone to CO, formate and acetate species was revealed, roles of active sites in these reactions were rationalized.

MOS	Type	E_{M-O}, eV	Band gap, eV	Grain size, nm	BET area, m^2/g
NiO	p-type	4.8	3.5	7	110
CuO		7.1	1.6	15	30
Co_3O_4		9.3	1.5	12	70
In_2O_3	n-type	9.3	2.8	8	105
ZnO		10.4	3.4	35	10
SnO_2		15.5	3.6	5	100
TiO_2		20.7	3.2	30-40	8
WO_3		36.6	2.7	7-10	30

Materials

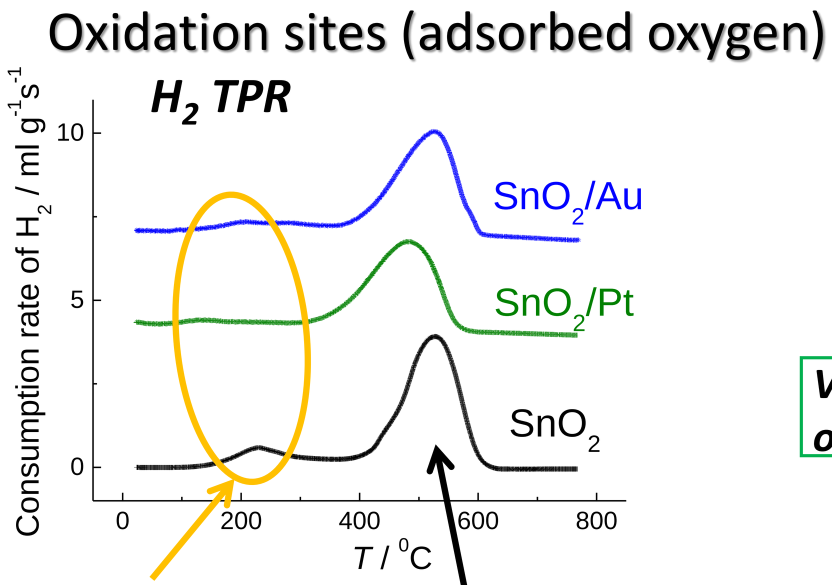


TEM micrographs



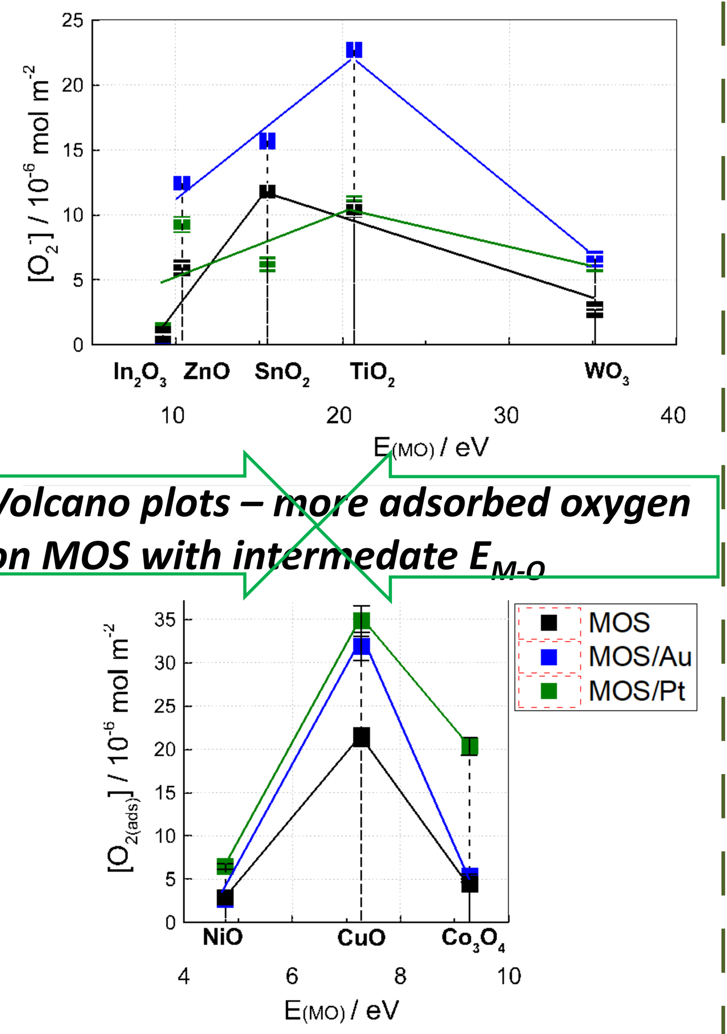
Active surface sites

Oxidation sites (adsorbed oxygen)

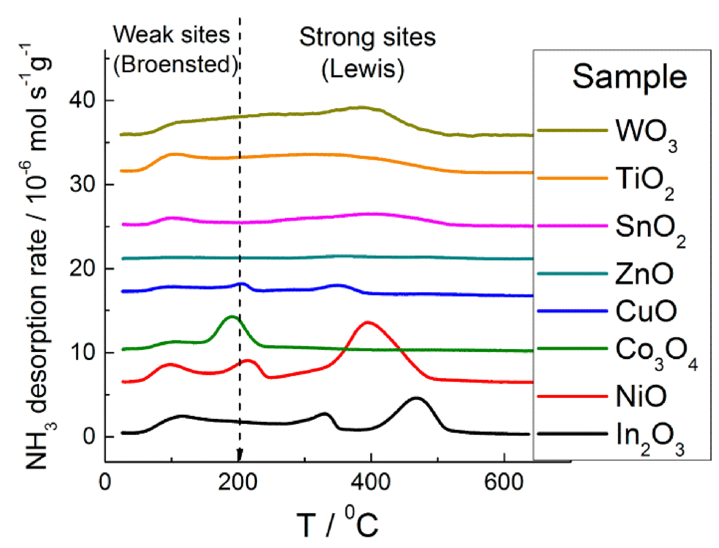


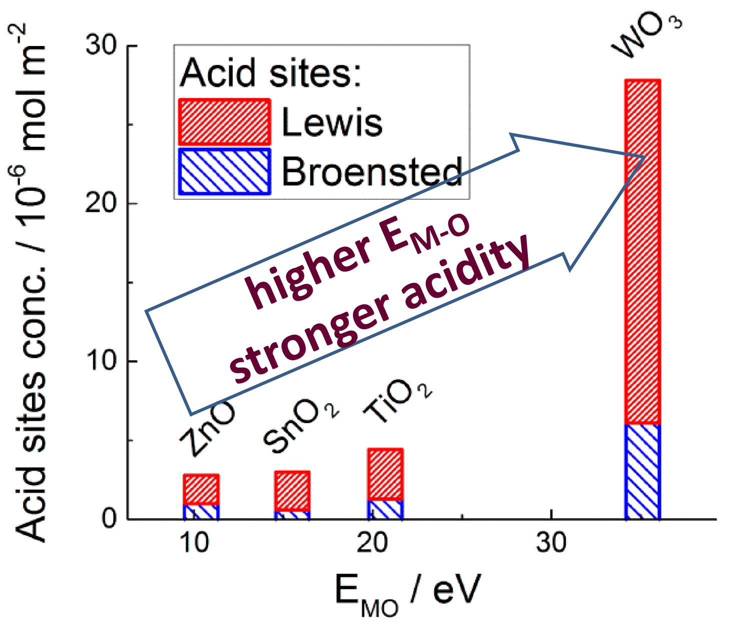
$O_{2(ads)} + 2H_2 = 2H_2O$

$MO_x + x\ H_2 = M + x\ H_2O$

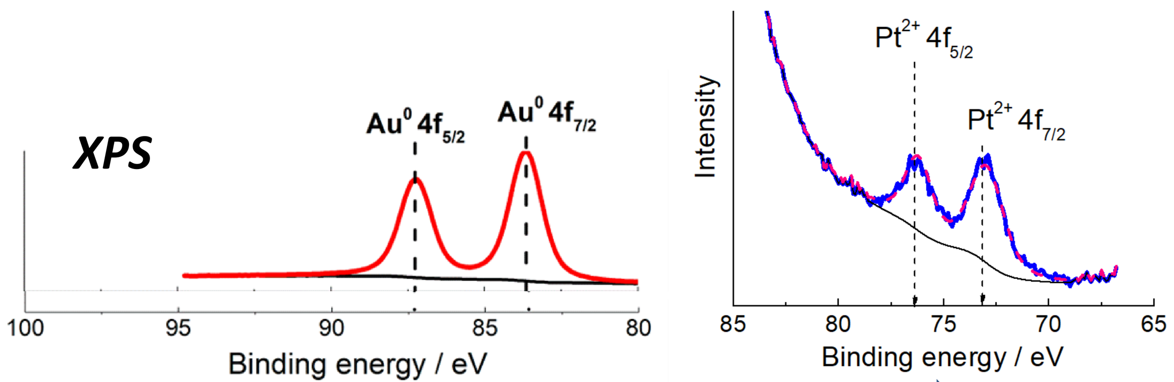


Acid sites





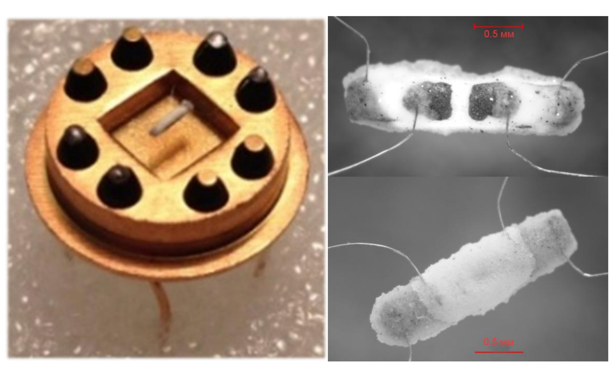
Noble metals – oxidation states

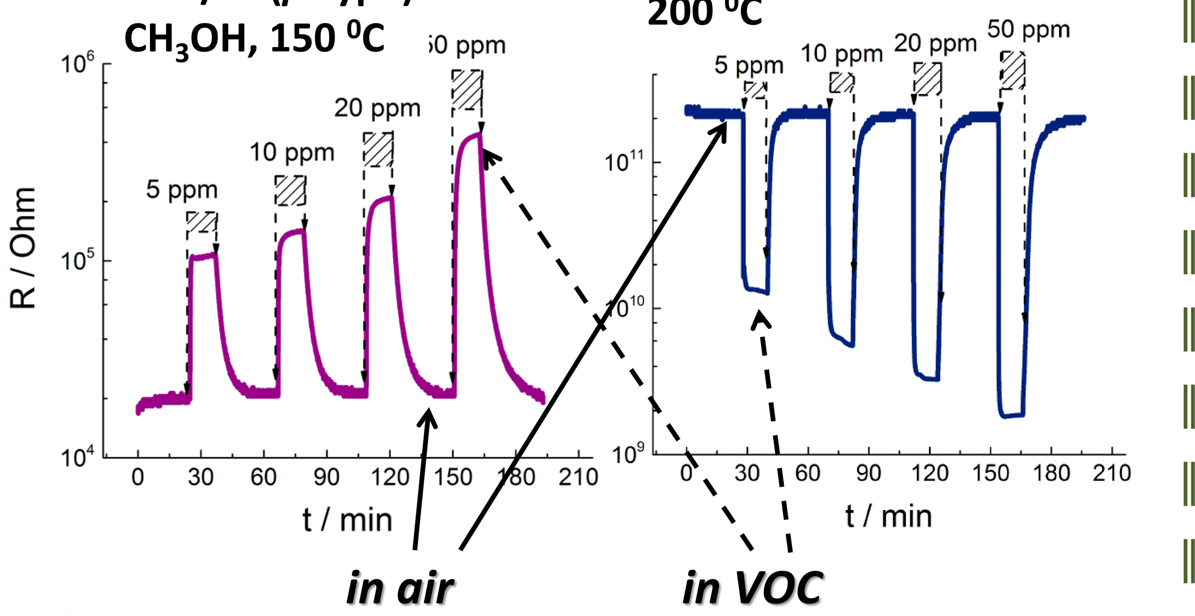


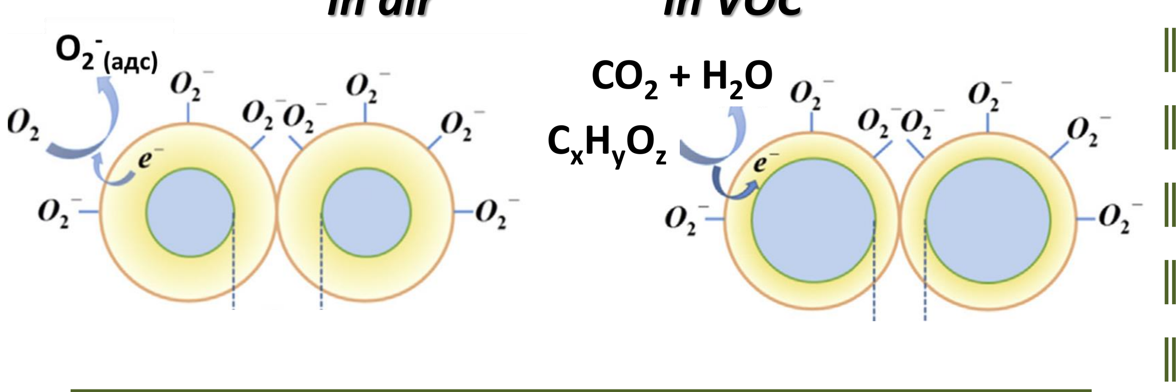
MOS/Au: E_{Au-O} = 2.3 eV — *Au is metallic*

MOS/Pt²⁺: E_{Pt-O} = 4.1 eV — *Pt is oxidizied by adsorbed oxygen*

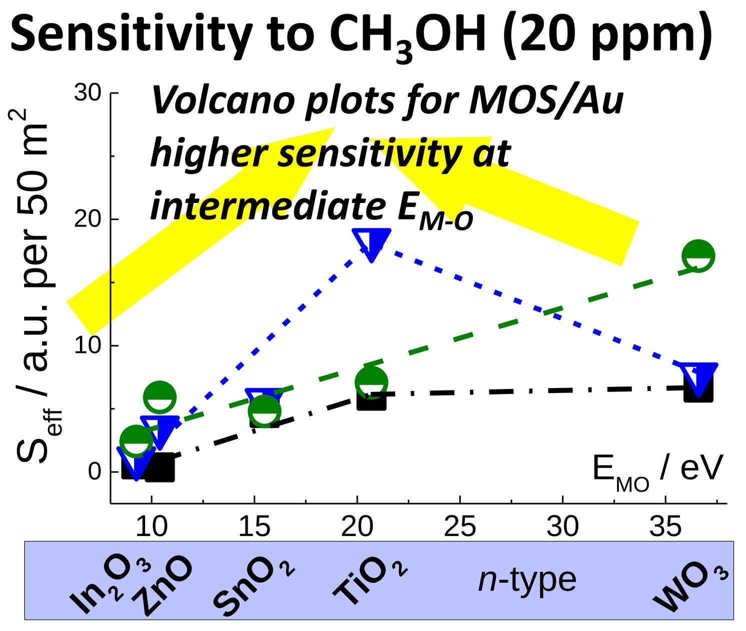
Gas sensitivity to VOC

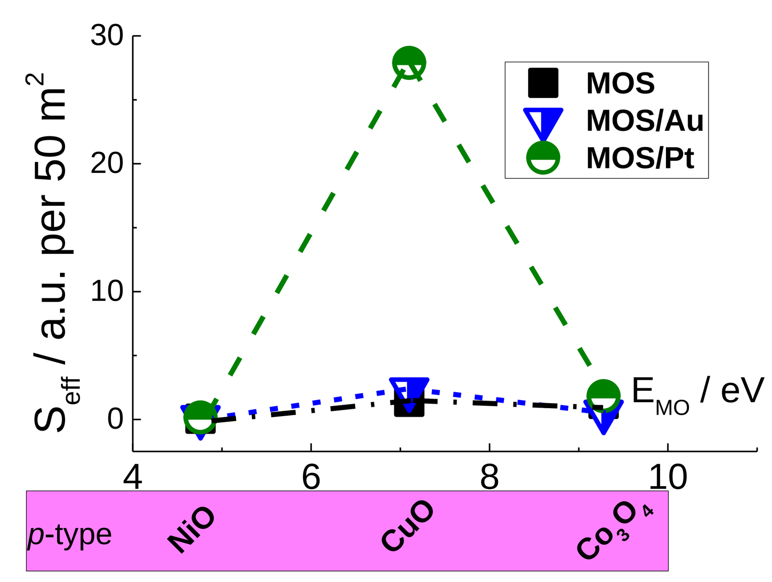




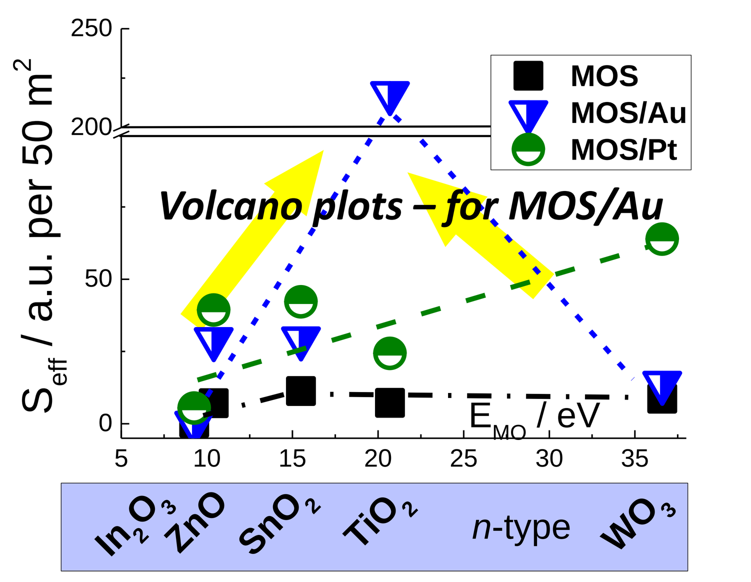


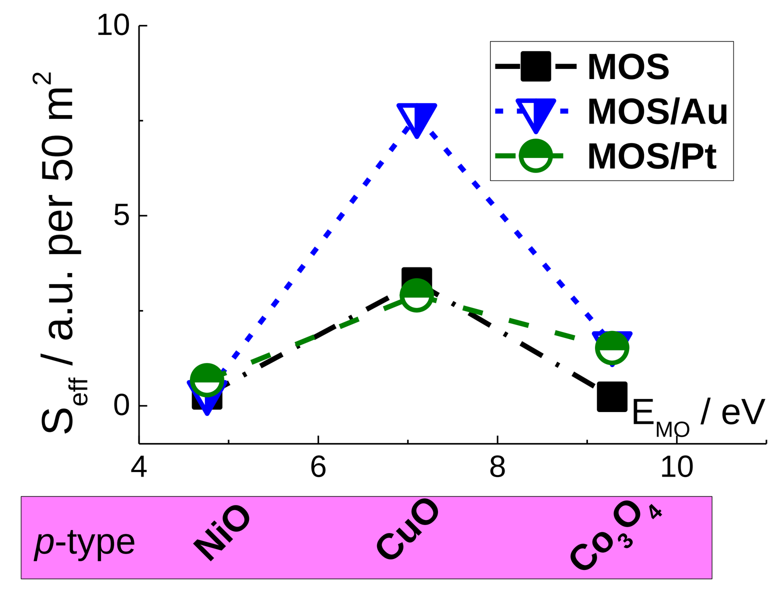
Sensitivity to CH_3OH (20 ppm)



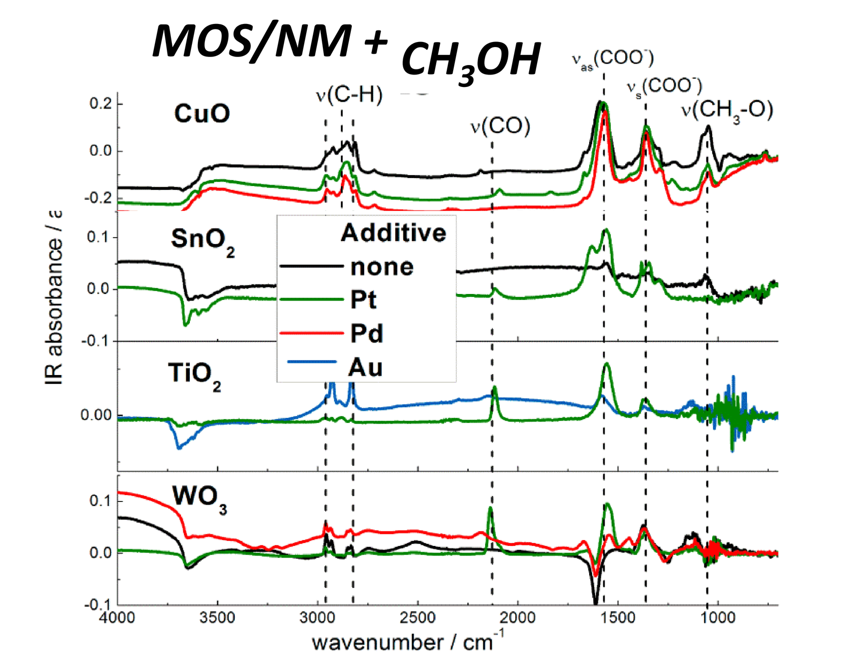


Sensitivity to CH_3COCH_3 (20 ppm)



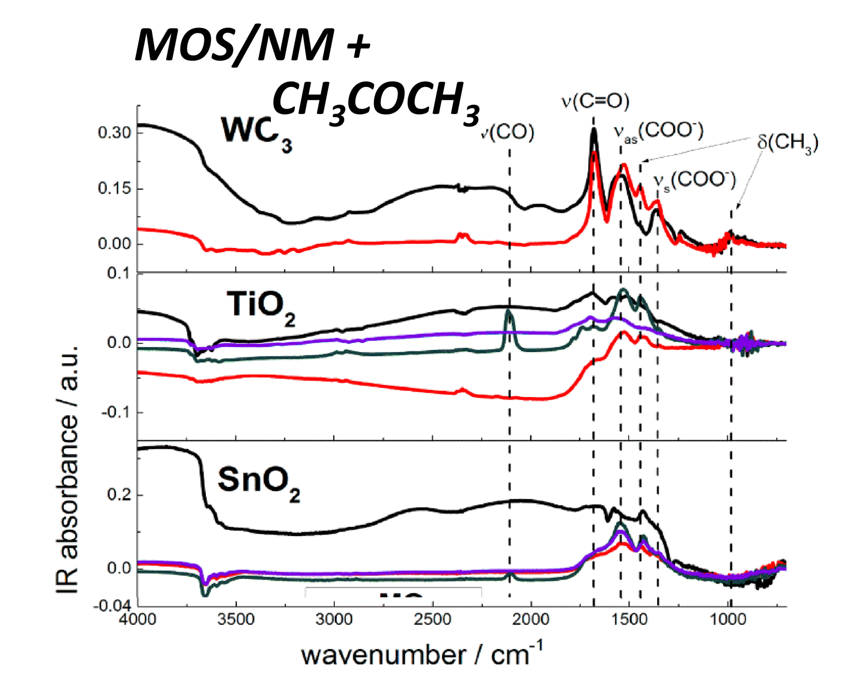


DRIFT study of sensing mechanism



$4\ CH_3OH + 5\ O_2^- = 4\ HCOO^- + 6\ H_2O + e^-$

$CH_3OH + Pt + O_2^- = Pt\text{-}CO + 2\ H_2O + e^-$ more on acidic MOS



$4\ CH_3COCH_3 + 9\ O_2^- = 4\ CH_3COO^- + 4\ CO_2 + 6\ H_2O + 9\ e^-$

$CH_3COCH_3 + 3\ Pt + 3\ O_2^- = 3\ Pt\text{-}CO + 3\ H_2O + 3\ e^-$ (on acidic MOS)

Conclusions

- Nanaparticles of MOS, nanocomposites MOS/Au and MOS/Pt were obtained with different metal-oxygen energies
- Au is metallic due to low Au-O bond energy, oxidized PtO is in the nanocomposites due to higher Pt-O bond energy
- Higher concentration of adsorbed oxygen was on MOS with average E_{M-O} and increaed in presence of Pt and Au due to spillover-effect
- Surface acidity of MOS increased with the bond energy E_{M-O}, the acid sites favor adsorption of VOC molecules CH_3OH and CH_3COCH_3
- Sensitivity to VOC followed the volcano-like dependence on E_{M-O} for *p*-type MOS-based sensors and *n*-type MOS/Au sensors due to increased concentration of adsorbed oxygen on these materials
- Sensitivity to VOC increased with E_{M-O} for *n*-type MOS/Pt due to Pt-catalyzed conversion of VOC to CO on the acidic metal oxides