A novel low-concentration isopropanol gas sensor based on Fe-doped ZnO nanoneedles

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Content

Introduction: Project PATHACOV

Interreg France-Wallonie-Vlaanderen
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PATHACOV

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HUMAN DISEASES DIAGNOSIS BY VOC ANALYSIS IN BREATH

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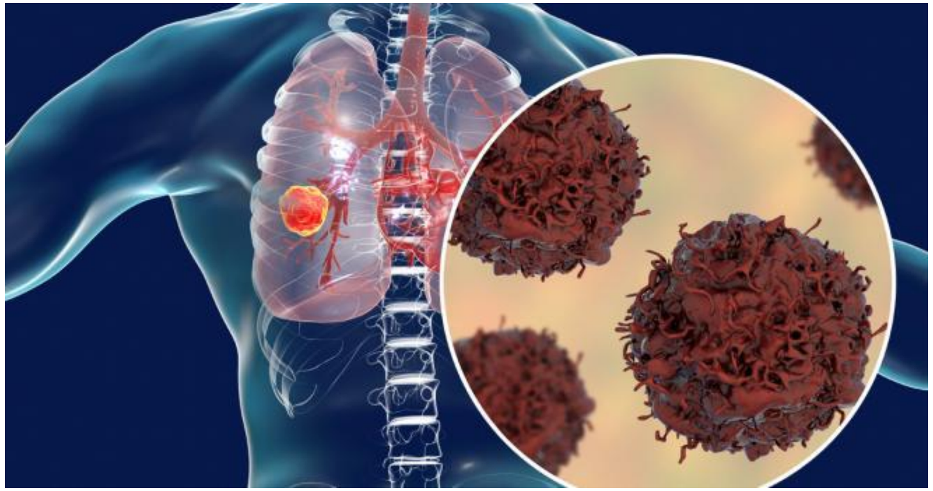
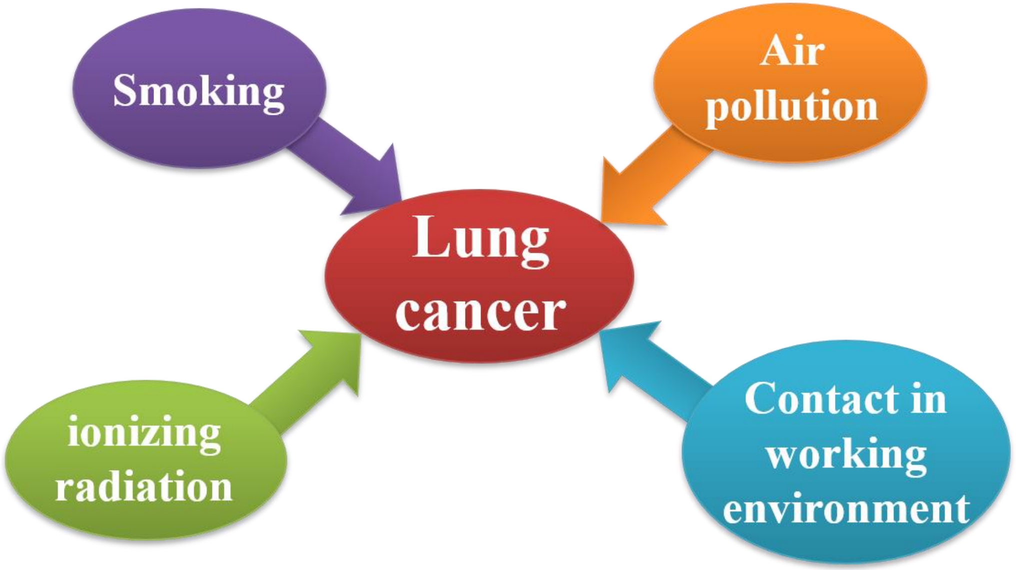
Door mensen gedreven

Background

Lung cancer



- Lung cancer: fastest increase in morbidity and mortality
- 28% of the cancers are lung cancer
- Patients increase 45% to 190% until 2030.
- Average 5-year survival chance: 14%
- 16% of the patients can get early diagnosis.

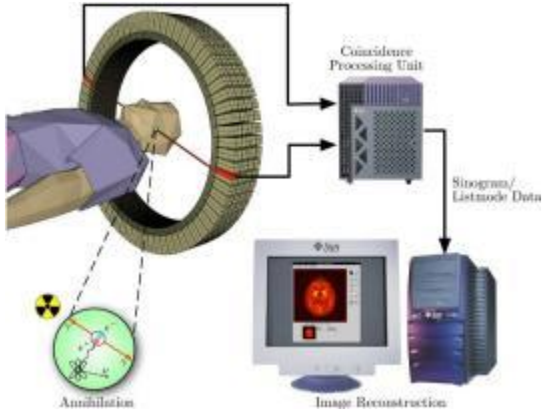


Distribution of the number of people who died of trachea, bronchitis and lung cancer in 2012

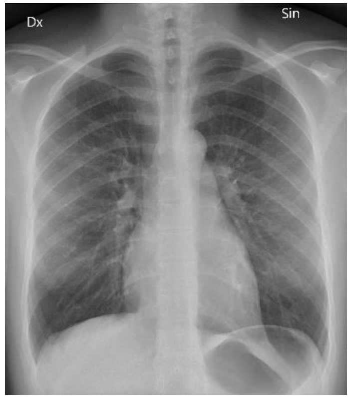
Common lung cancer detection method

CT (LDCT)

Lung Cancer



PET-CT



Chest X-ray

Breath analysis

Concentrations (ppb) of VOCs contains in Lung cancer patients

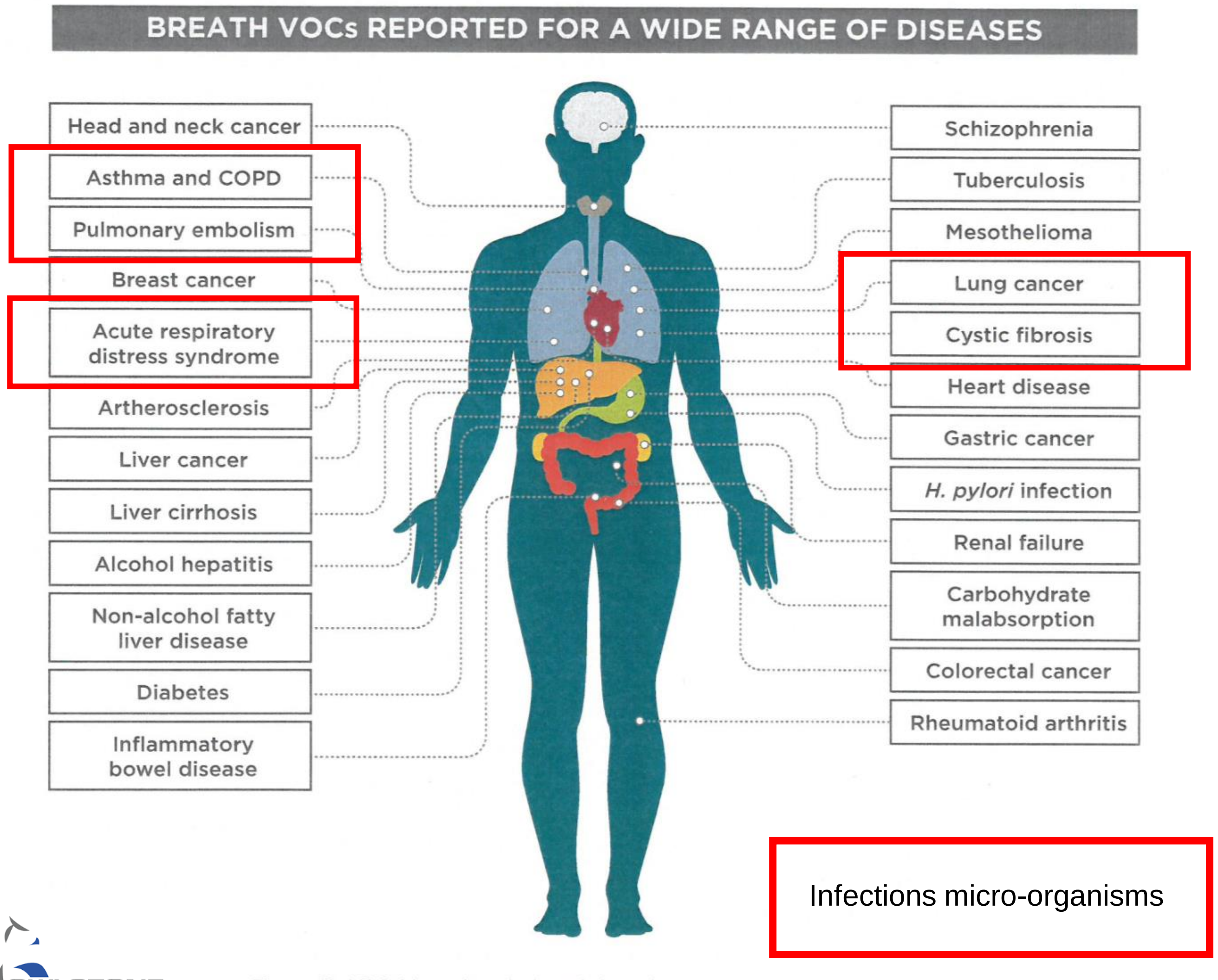


Figure 12. VOC biomarkers in breath have been reported for a large number of diseases in the literature [53,54], highlighting the wide disease relevance of Breath Biopsy®.

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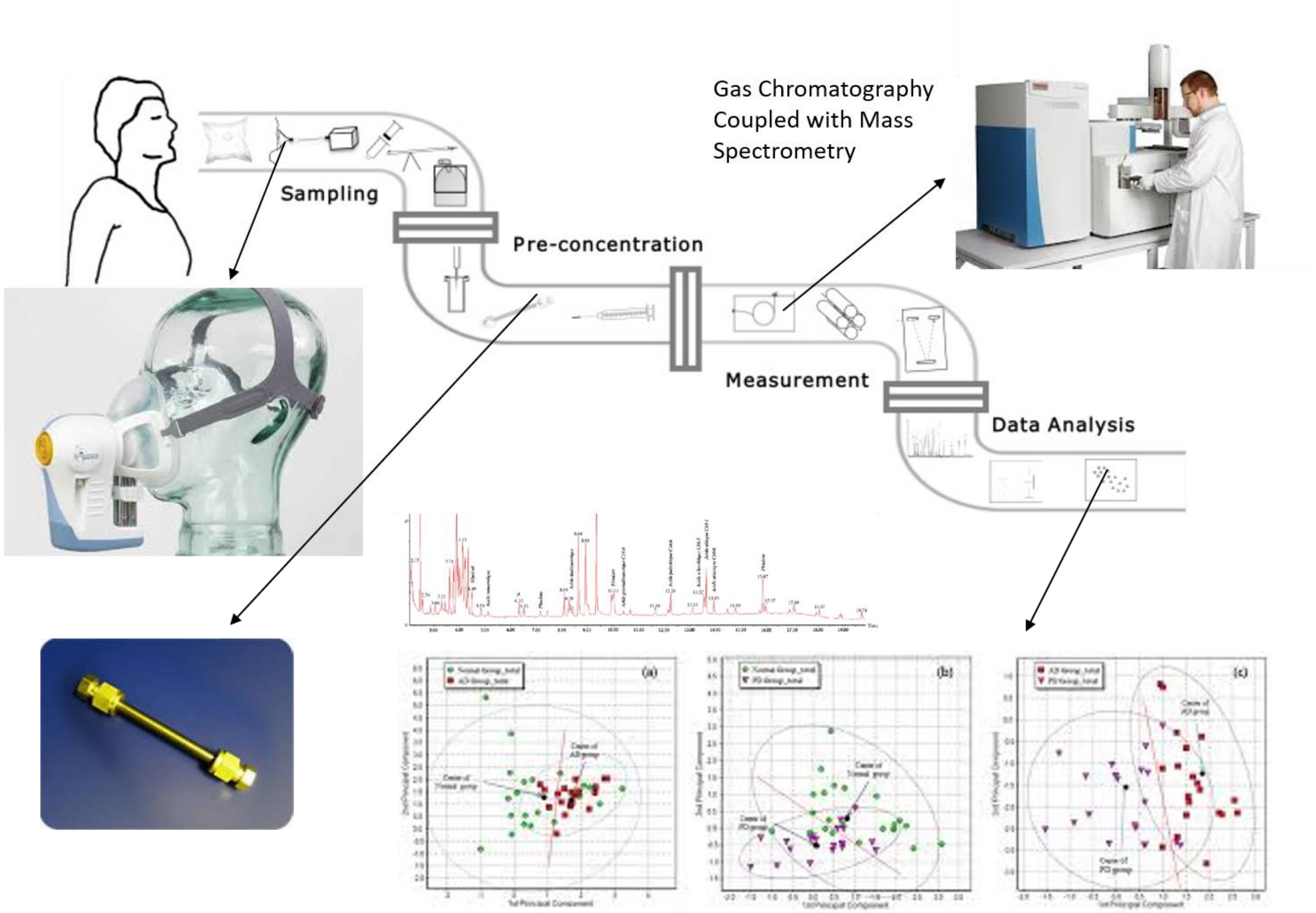
VOC groups	VOCs	Patients	Healthy
Straight chain alkanes	Pentane	0.73-17.50	6.84-94.36
	2-methylpentane	0.31-3.77	2.37-107.80
	Hexane	0.82-1.88	1.75-6.31
	Decane	0.06-62.9	0.26-18.5
Alcohol	Propanol	5.6-473	0-7
	Isopropanol	8.7-989.9	3.0-14.17
Ketone	Acetone	34.6-390.6	14.4-531.5
	Butanone	3.8-38.8	0.5-2.9
Aromatic hydrocarbons	Benzene	0.08-3.82	1.15-14.97
	Toluene	1.51-17.10	1.45-37.21
	Ethylbenzene	1.45-3.16	2.22-18.38
Unsaturated hydrocarbon	Isoprene	3130-8863	1399-6859

Traditional method for breath analysis



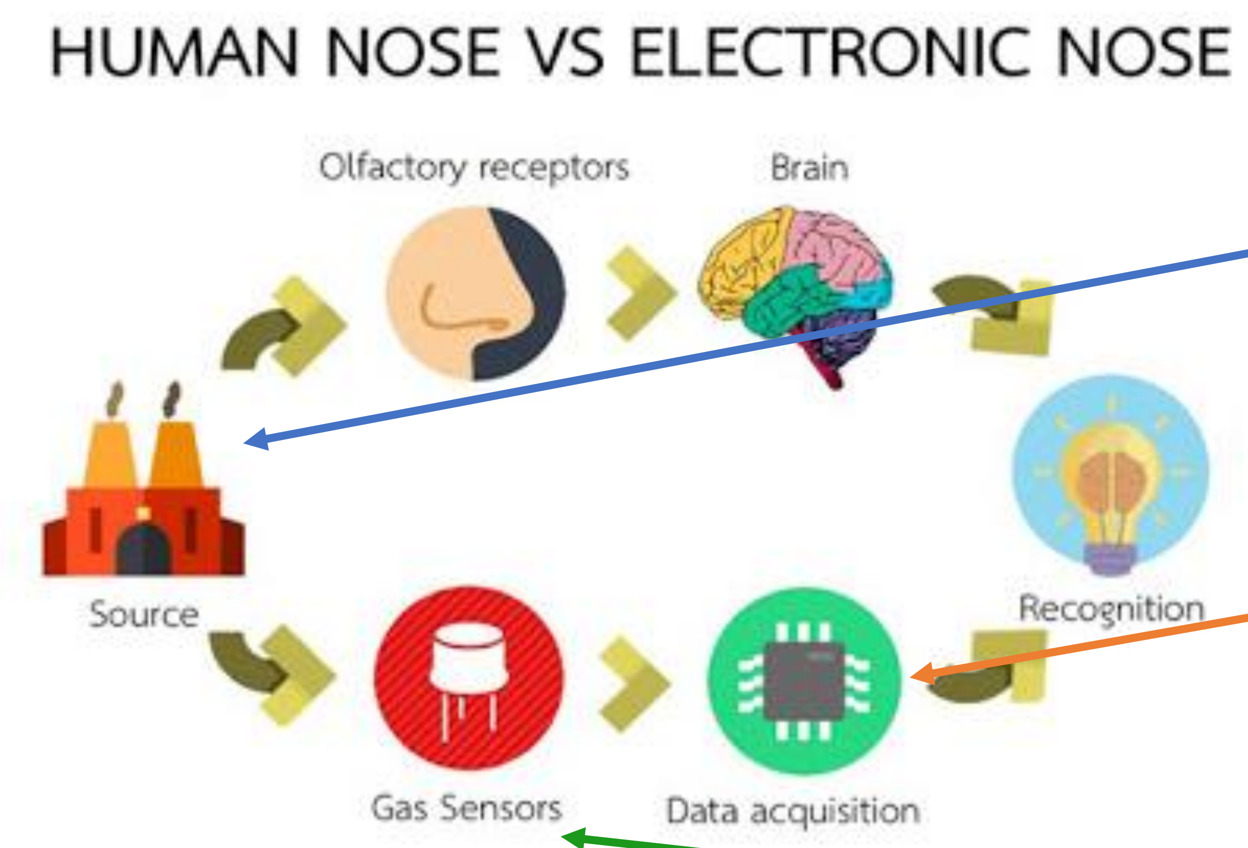
- Accurate
- Low Detection limit

- Expensive
- Large
- Power consumption
- Difficult to use

Oluwasola Lawal et al., Metabolomics, 2017, 13, 110.

E-nose

PathaCov:



Sampling:
ULiège, Ulille
(data processing)
All hospitals

Signal processing:
KULeuven +
sensor makers

Sensors:
IMT Douai,
Materia Nova,
UReims
UMONS

Metal oxide gas sensor

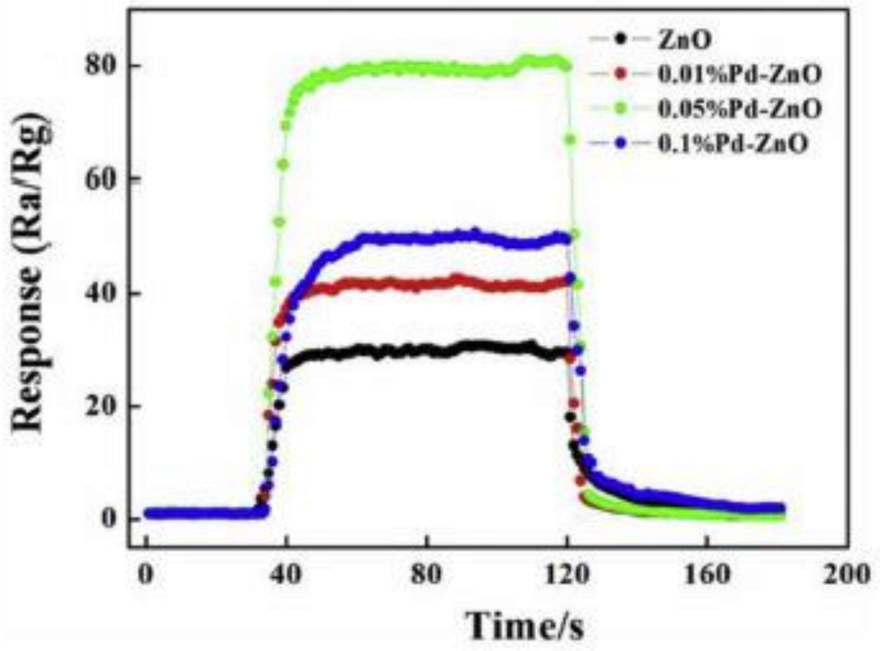
Zinc Oxide (ZnO), Tin Oxide (SnO_2), Tungsten oxide (WO_3), Titanium dioxide (TiO_2)……

Advantage

- Good response
- Easy to prepare
- Easy to modify

Disadvantage

- High working temperature
- Poor selectivity
- Possible humidity effect



Response-recovery curves of a 2D nanosheet-assembled Pd-ZnO microflowers to 200 ppm acetone at 370 °C. [1]

[1] Zhang et al. Journal of Physics and Chemistry of Solids 124 (2019) 330–335

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Strategy and methods

Improvement of the sensing performance

Adsorption model

$$\theta = \frac{k_{ads} \bullet p_A}{k_{ads} \bullet p_A + k_{des}} \bullet [1 - \exp(\frac{-t}{\tau})]$$

p_A: Pressure in the system;

t : Reaction time;

k_{ads}: Adsorption coefficient;

k_{des}: Desorption coefficient;

θ: Surface coverage

$$k_{ads} = k^0_{ads} \bullet \exp(\frac{-E_{ads}}{k_B T})$$

$$k_{des} = k^0_{des} \bullet \exp(\frac{-E_{des}}{k_B T})$$

$$\tau = \frac{1}{k_{ads} \bullet p_A + k_{des}}$$ → Response time

$$\theta^\infty = \frac{p_A}{pA + \frac{k_{des}}{kads}}$$ → Sensitivity

Reducing adsorption and desorption energy

↓

High aspect ratio
(Nanoneedles or wires)

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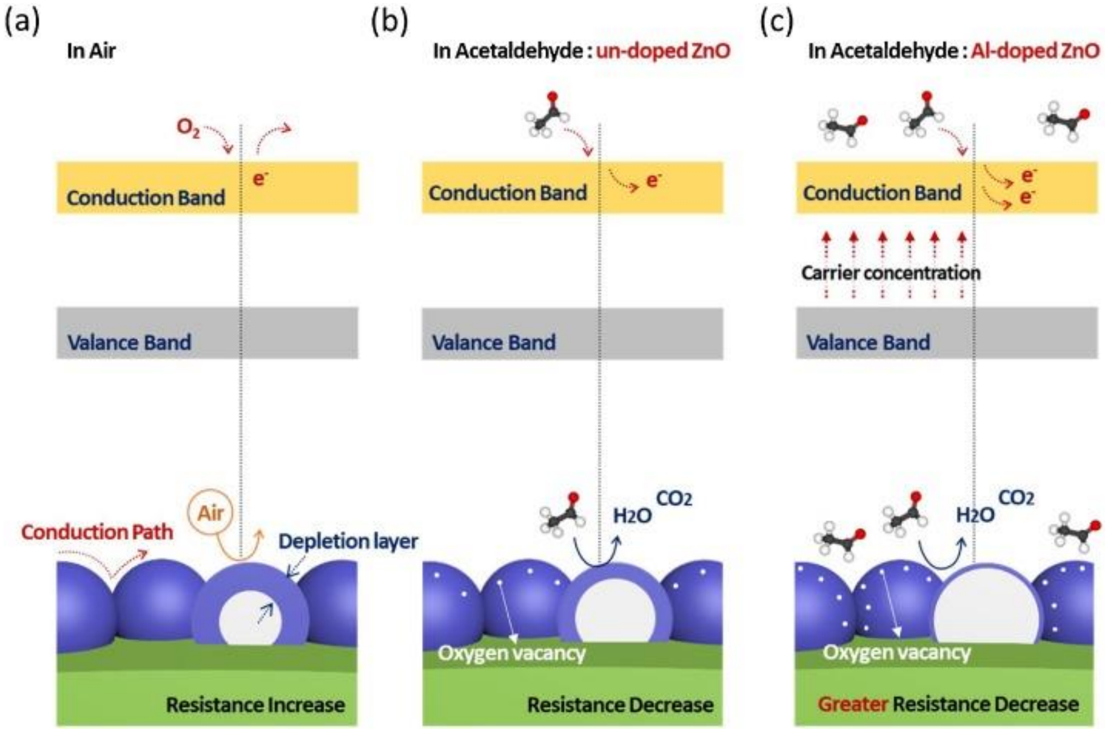
Improvement of the sensing performance

N-type doping

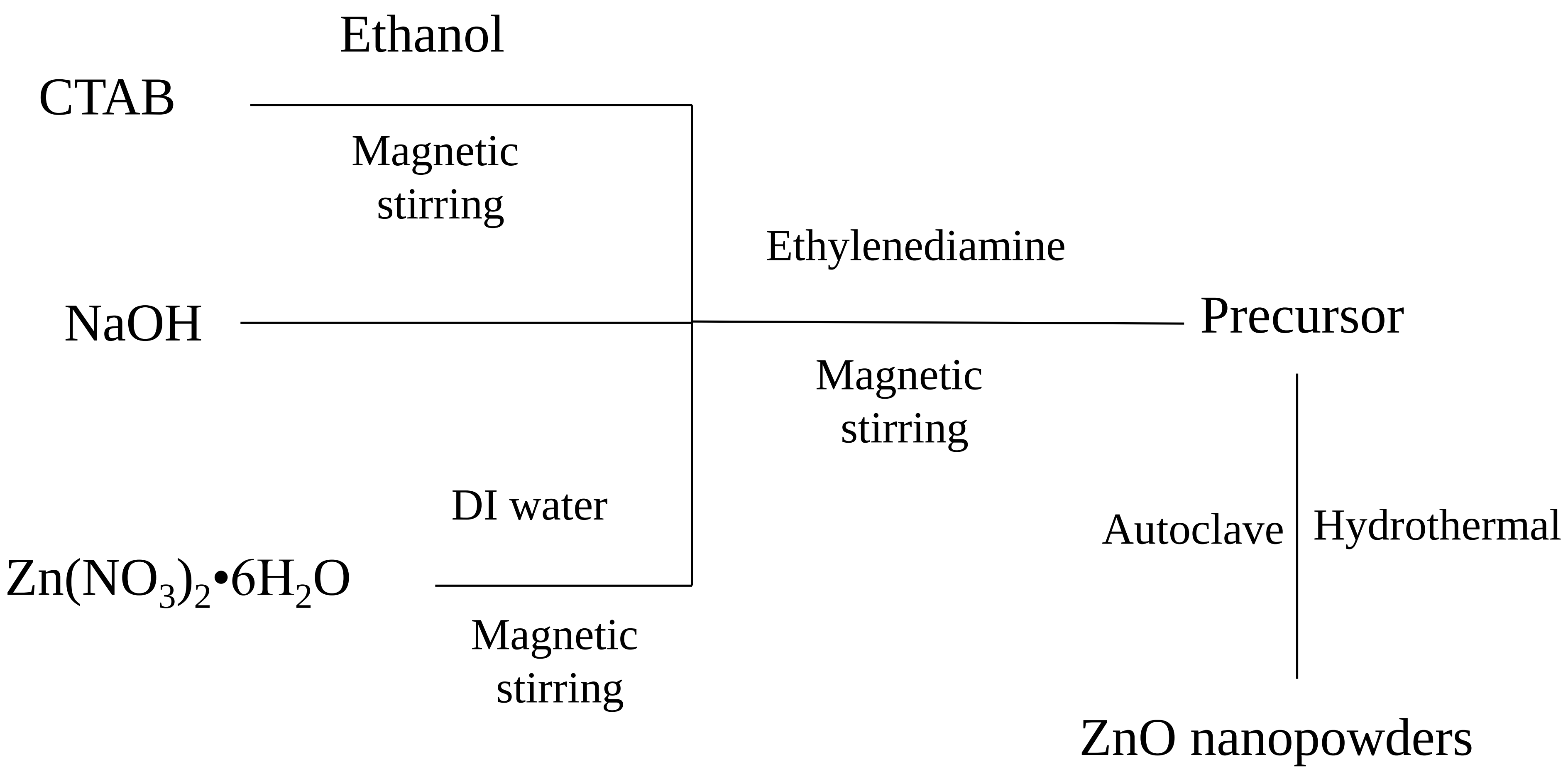
High valent metal ions → Acceptors → Reduce the bandgap width / Lattice structure change



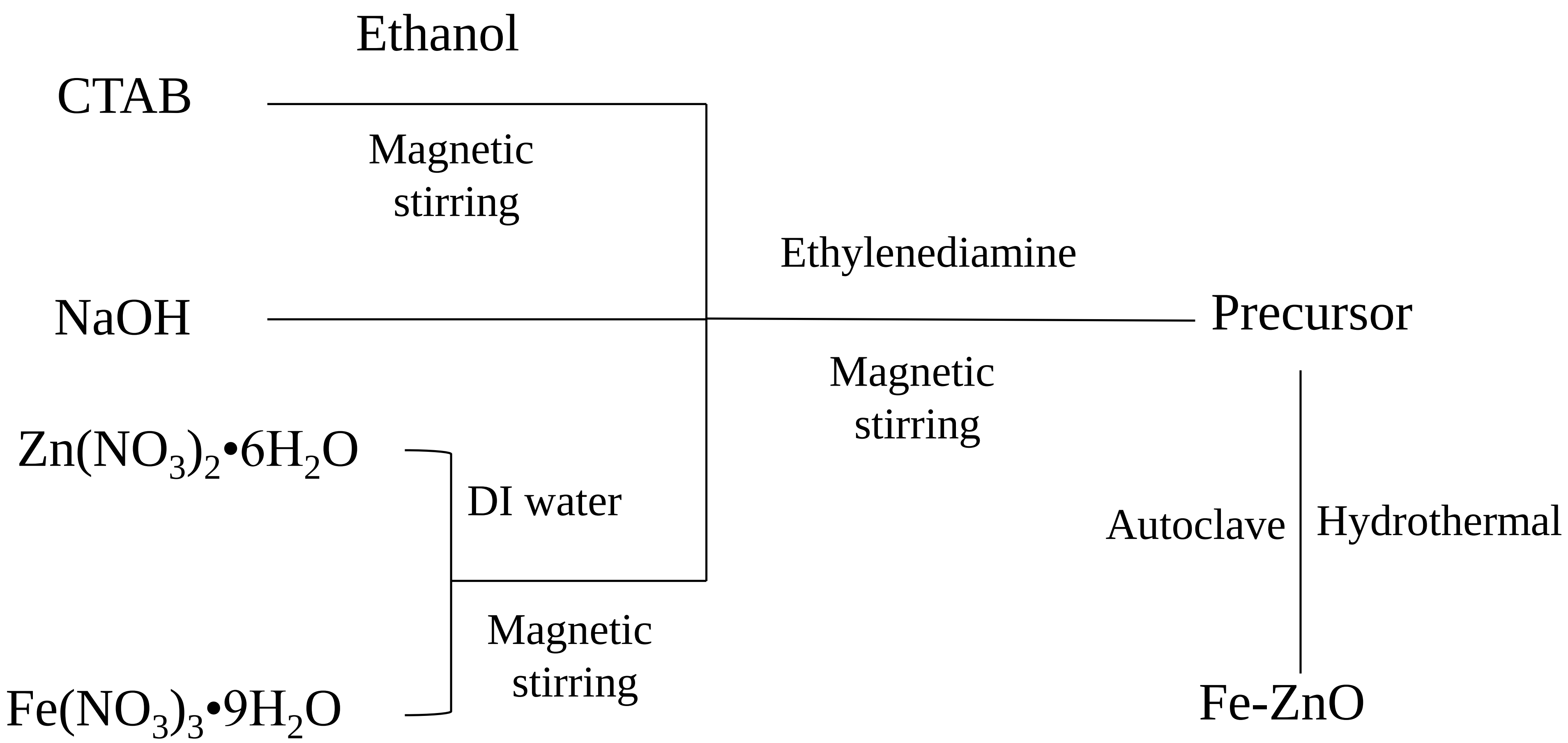
A schematic of the sensing mechanism of the (a) un-doped or Al-doped ZnO NPs in air, (b) un-doped ZnO NPs in acetaldehyde, and (c) Al-doped ZnO NPs in acetaldehyde. [1]

[1] R. Yoo et al. Sensors and Actuators B: Chemical, 266, 2018, 883-888,

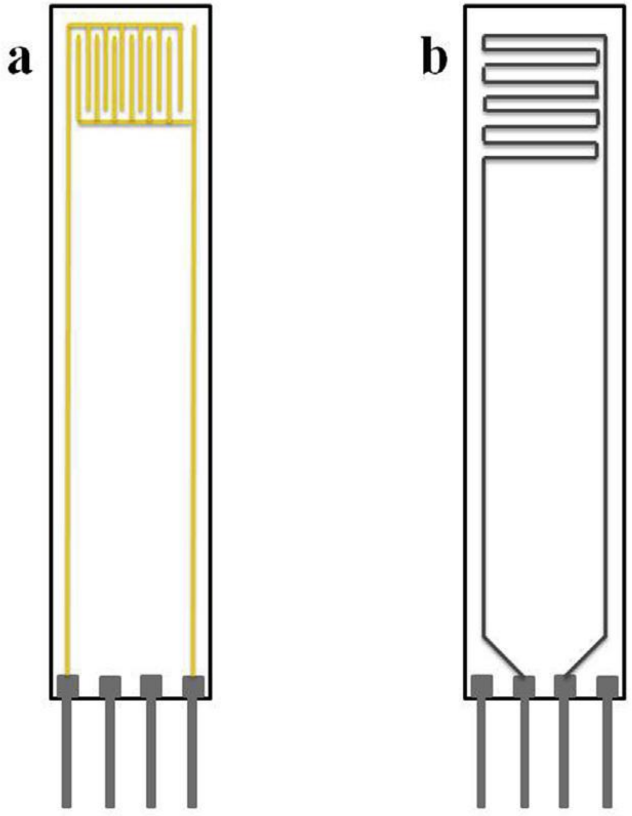
Preparation of ZnO nanoneedles



Preparation of Fe-doped ZnO nanoneedles



Preparation of sensors

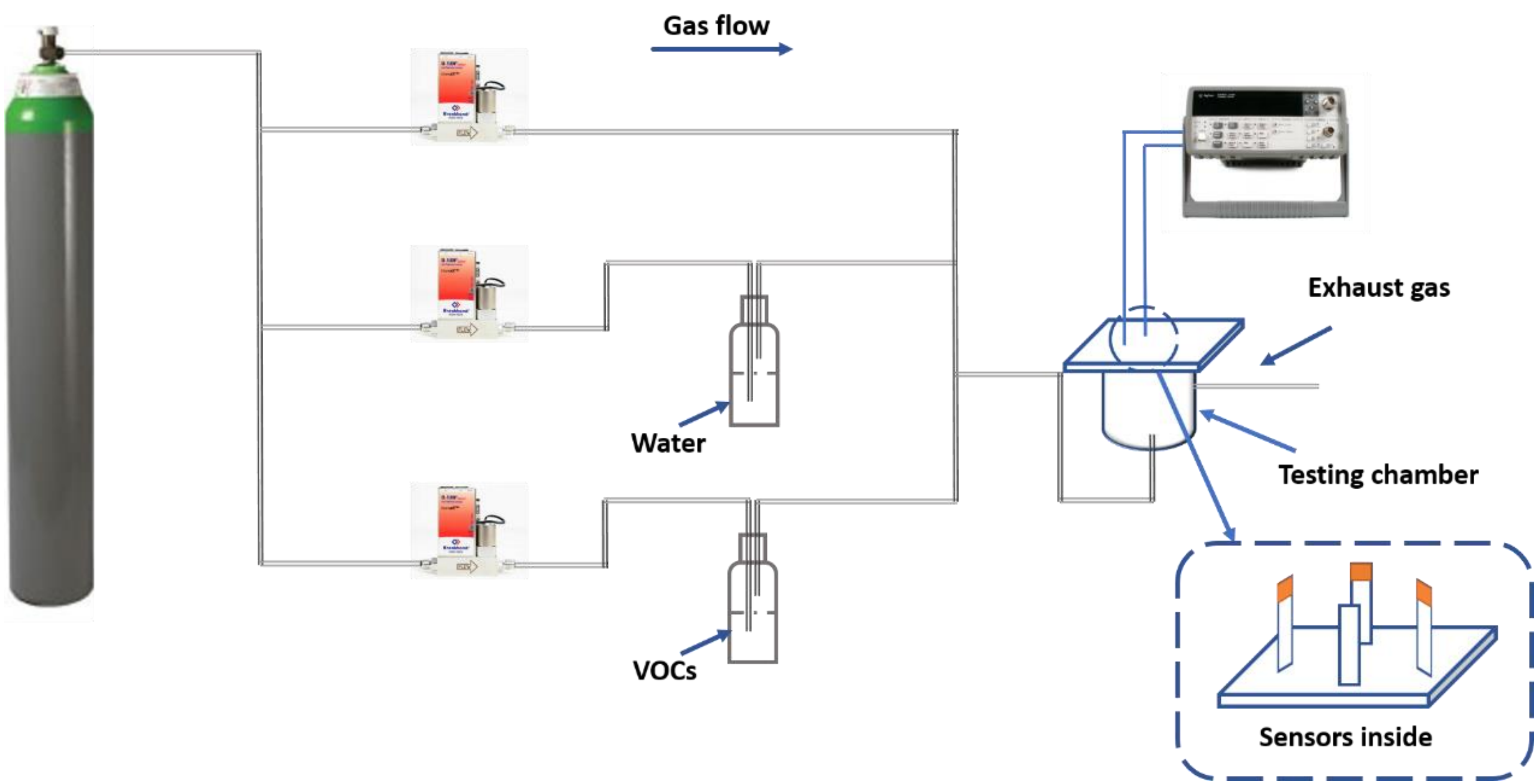


Schematic diagram of the sensor substrate

Methods of making sensors:
Spray coating

Treatment:
Pre-heating at 350^{o}C before gas sensing test.

Sensing test



Schematic of the gas sensing system

$S=(R_a-R_g)/R_g$ (n-type)

S: Response

R_a: resistance in air

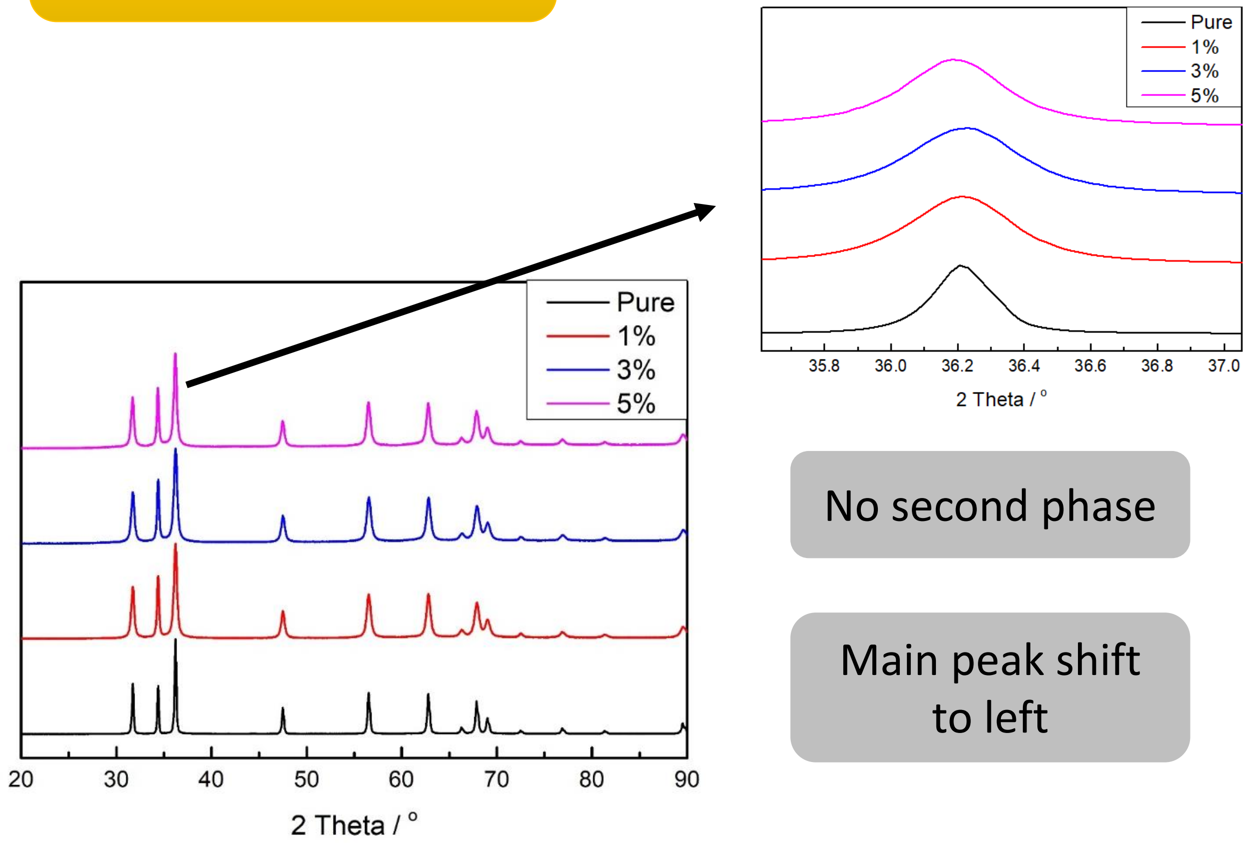
R_g: resistance in target gas

Response time: time to reach 90% of the response

Recovery time: time to recover to 110% of the baseline

Characterization of Fe-doped ZnO nanoneedles

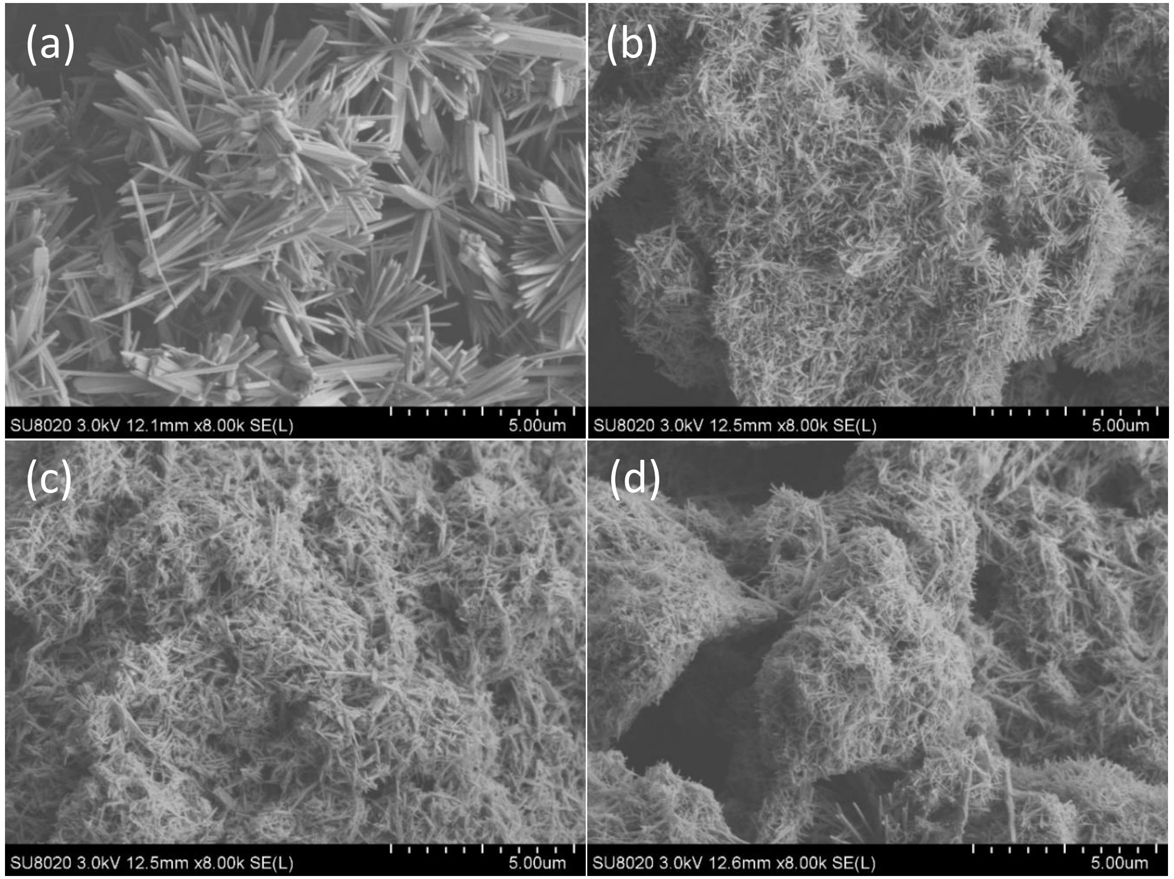
XRD and SEM



No second phase

Main peak shift to left

XRD patterns of pure and Fe-doped ZnO nanoneedles



SEM image of (a)ZnO (b) 1 at% (c) 3 at% (d) 5 at% Fe-doped ZnO on the surface of sensor substrates

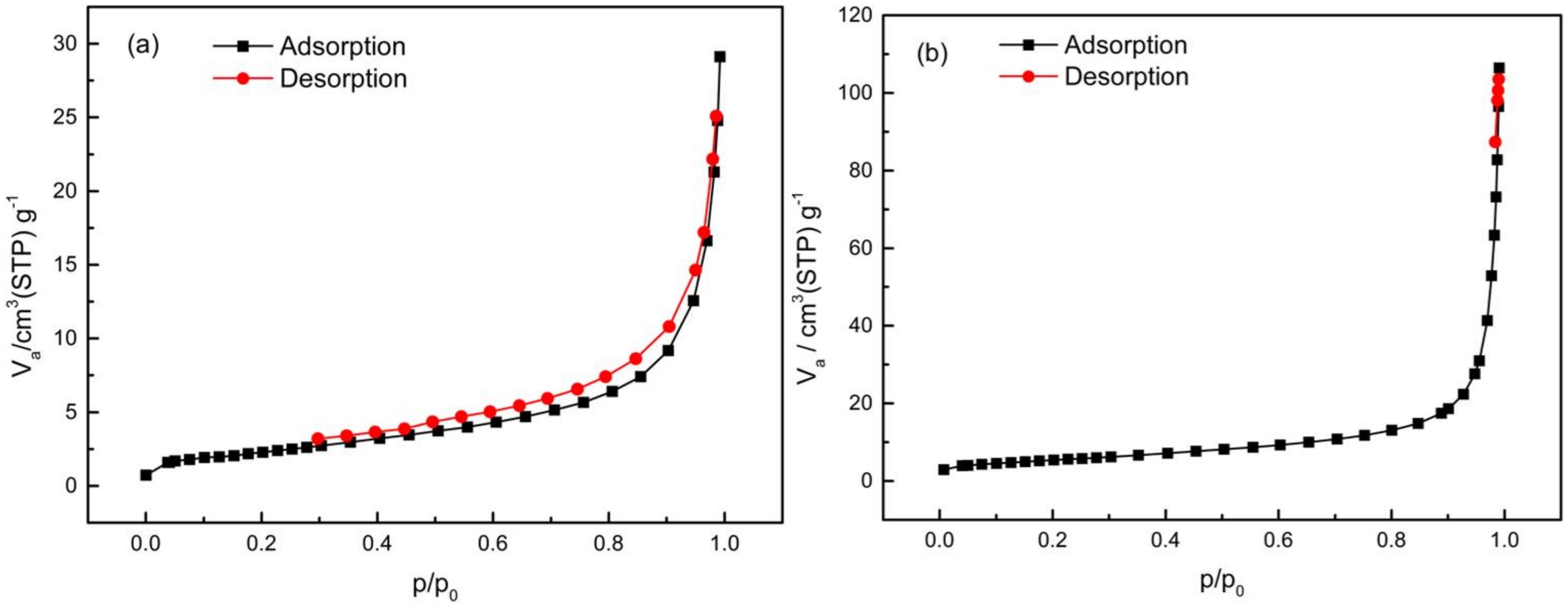
Characterization of Fe-doped ZnO nanoneedles

BET

Specific surface area:

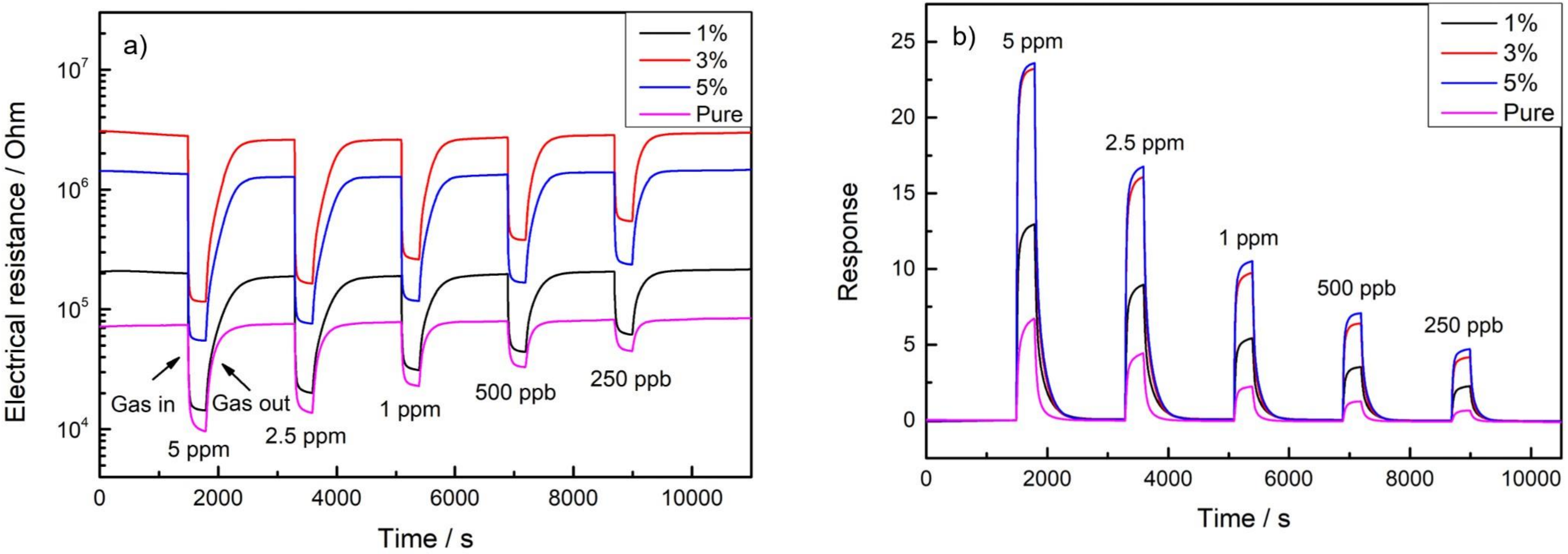
Pure: 8.6422 m^2/g

1 at%: 18.974 m^2/g



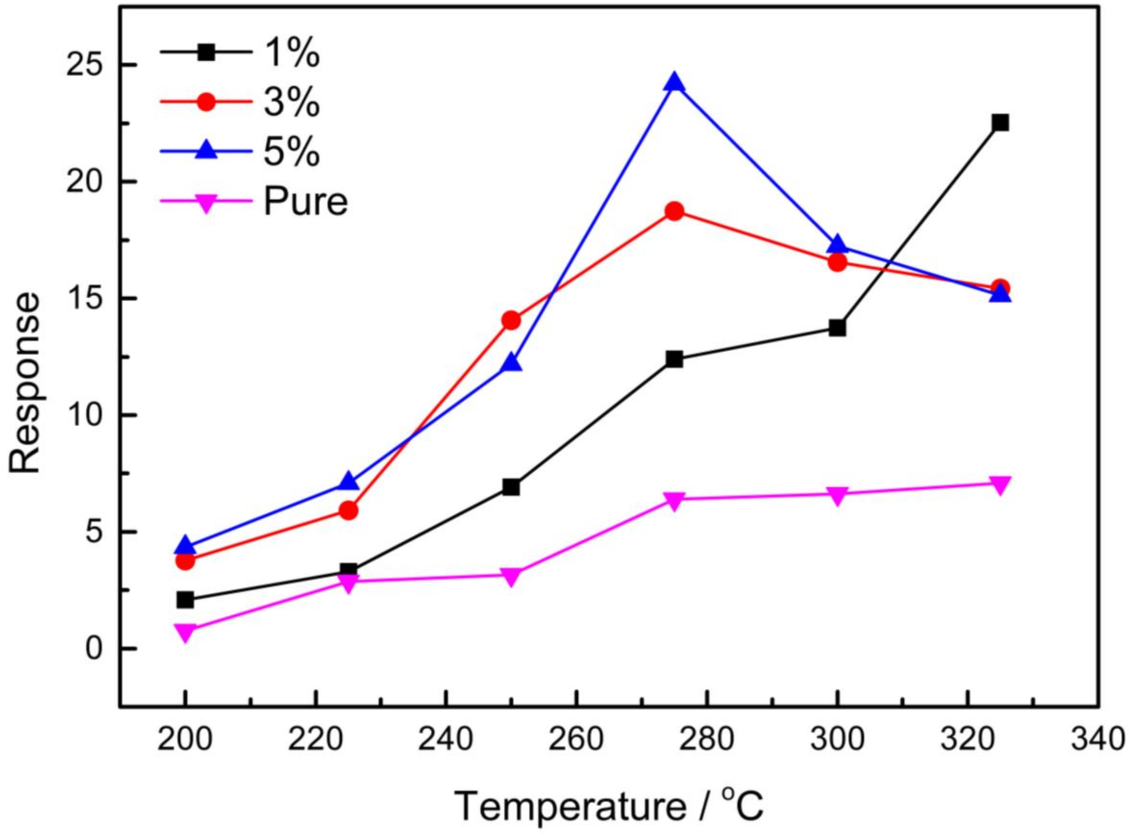
N_2 adsorption/desprotion curve of the (a) pure and (b) 1 at% Fe-doped ZnO.

Sensing performance of Fe-doped ZnO nanoneedles



(a) Electrical resistance change and (b) response of pure and Fe doped ZnO nanoneedles to isopropanol with 50% of humidity at 275^{o}C

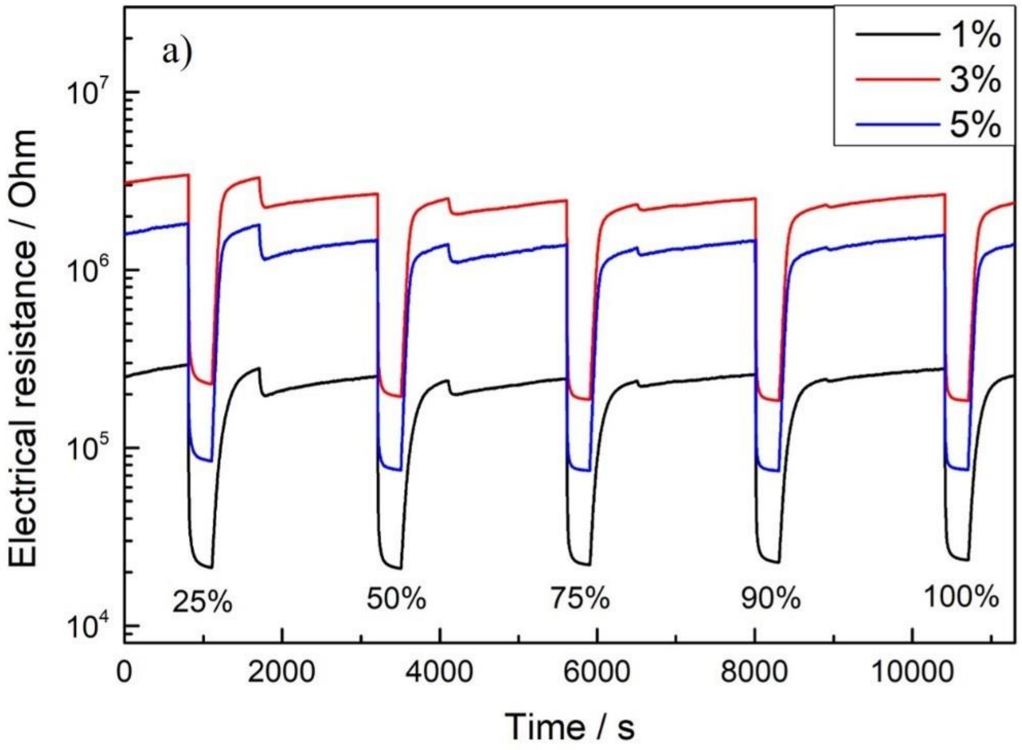
Temperature effect on the sensors

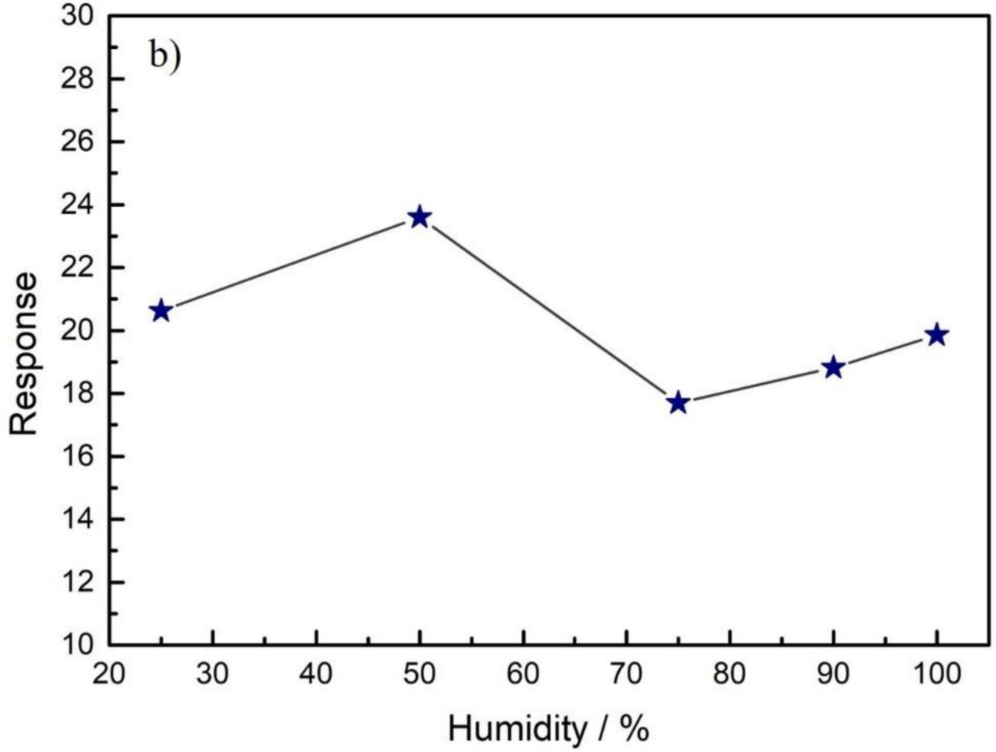


Response to 5 ppm isopropanol of different Fe-doped ZnO under different operating temperature

- Optimal temperature at 275°C;
- Fe doping decreases the temperature

Humidity effect of Fe-doped ZnO nanoneedles

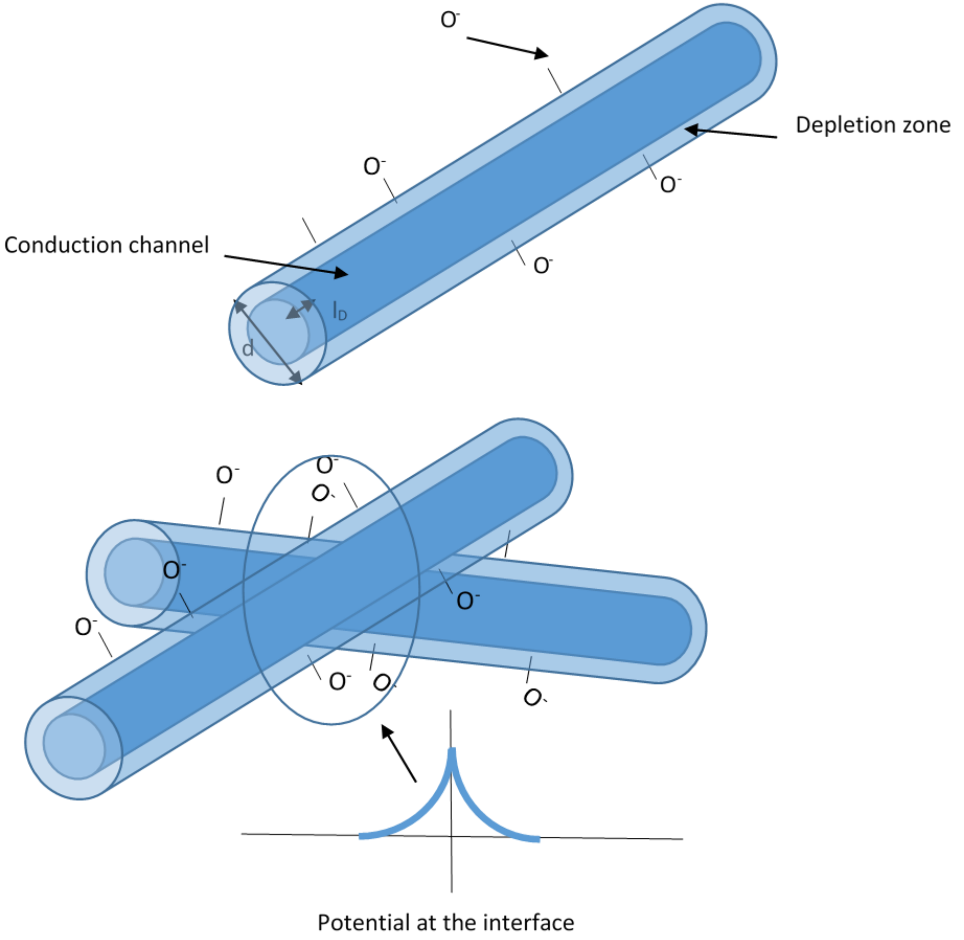




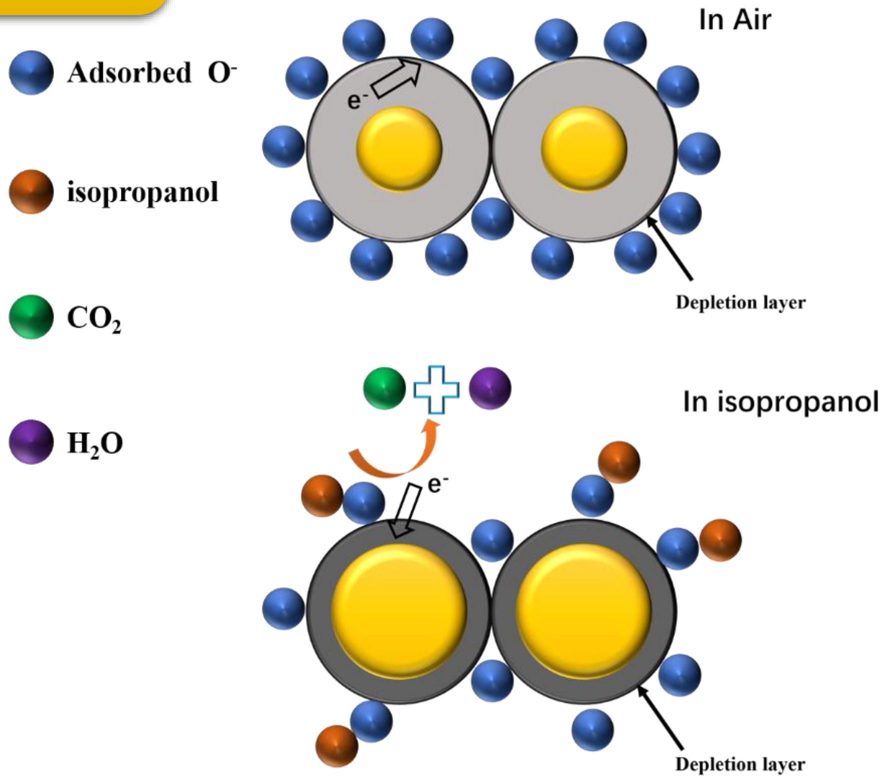
- Relatively stable with the humidity change
- Resistance decreased with the increase of humidity

(a) electrical resistance change of different Fe-doped ZnO. (b) Response of 5 at% Fe-doped ZnO under different RH% to 5 ppm isopropanol at 275°C

Sensing mechanism of Fe-doped ZnO nanoneedles



Representation of the contact between the needles and the potential barrier between different needles



Schematic figure for the isopropanol sensing process

$$CH_3CH(OH)CH_3 \ + \ 9O^- \ \rightarrow 3CO_2 + 4H_2O + 9e^-$$

Conclusion for this presentation

- The ZnO nanoneedles were successfully doped with Fe by slowly adding $Fe(NO_3)_3$ into the precursor.

- Fe doping change the morphology of ZnO needles and increase the specific surface area.

- The 5 at% Fe-doped ZnO showed the best sensing performance to isopropanol at 275^{o}C.

- The improvement of sensing properties is considered as the adjustment of the band structure by the doping of Fe and the increase of specific surface area.

- More works like DFT calculation can be done to further study the mechanism.

Thank you!