Metal Oxide based Heterostructured Nanowire Arrays for Ultra-Sensitive and Selective Multi-Mode High Temperature Gas Detection

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March 20, 2017
DoE Crosscutting Research &
Rare Earth Elements Portfolios Review Meeting

INSTITUTE OF MATERIALS SCIENCE

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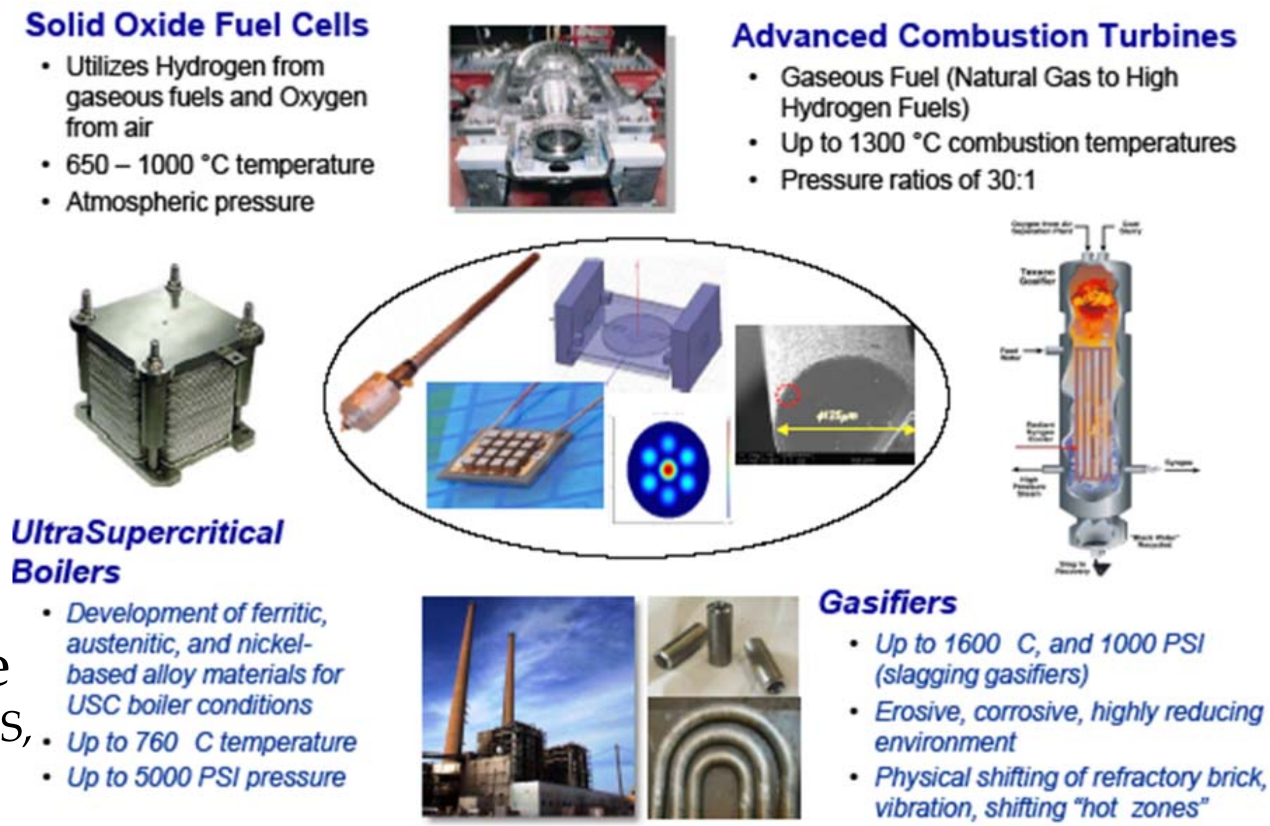
Harsh Environment in Power Systems: Sensing/monitoring Challenges

- Harsh environment
  - Pressure (-1000psi)
  - Temperature (-1600^{o}C)
  - Atmosphere (erosive, corrosive, highly reducing)
- Materials challenge
  - Physical stability
  - Chemical stability
  - Functional stability
- Sensitivity and selectivity challenge
  - Multiple species (H_2, H_2S, CO, CO_2, CH_4, O_2, SO_x, NO_x, NH_3, etc.)
  - Cross-talk



R. Romansky, US DoE/National Energy Technology Lab, 2012

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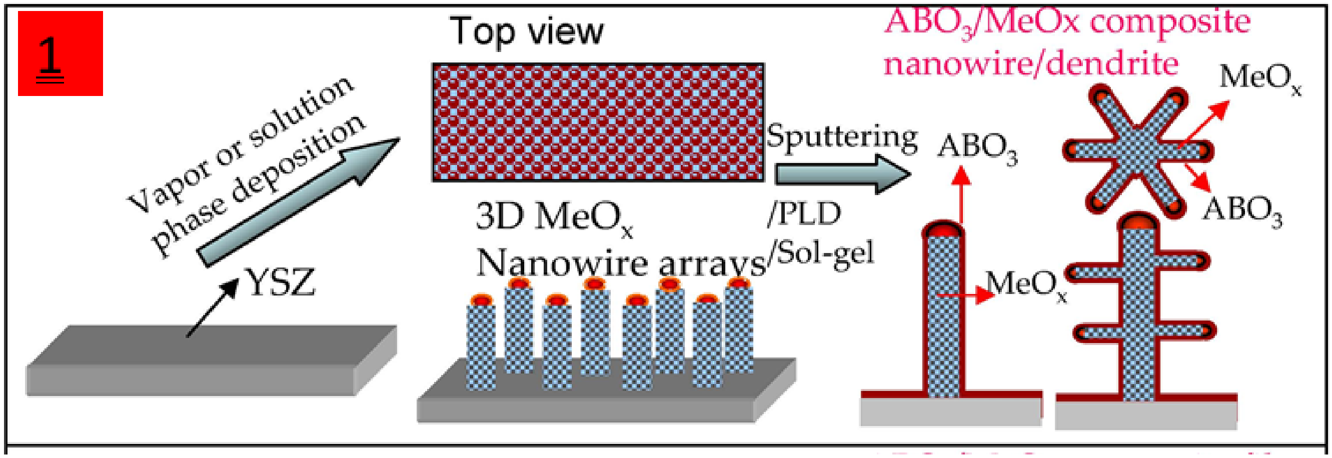
Technical Approach:
Sensor Nanomaterials Design & Integration



a) MeO_x: metal oxide semiconductor, ZnO, Ga_2O_3, CeO_2, etc. → demonstrated in industry sensing up to 700°C. → can we improve the temperature range and functionality?

b) ABO_3: perovskite, (La,Sr)CoO_3(LSCO); La,Sr)MnO_3(LSMO);(La,Sr)FeO_3(LSFO), etc.→ high stability, mixed ionic/electronic transport conductivity, catalytic filtering, A/B site doping flexibility

c) Metal: Pt, Au, Pd, etc.→ catalytic sensing effect, metallic conduction, optical/plasmonic effect, Shottcky junction, selectivity

Materials Advantages: 1) Ultrahigh surface area; 2) High thermal stability; 3) Strong adherence; 4) Low cost; 5) High tailoring ability

Gao et al., *DoE/NETL Sensors & Control Program Meeting*, **2009**.
Gao et al., ., *Proc. SPIE*, **2011**.
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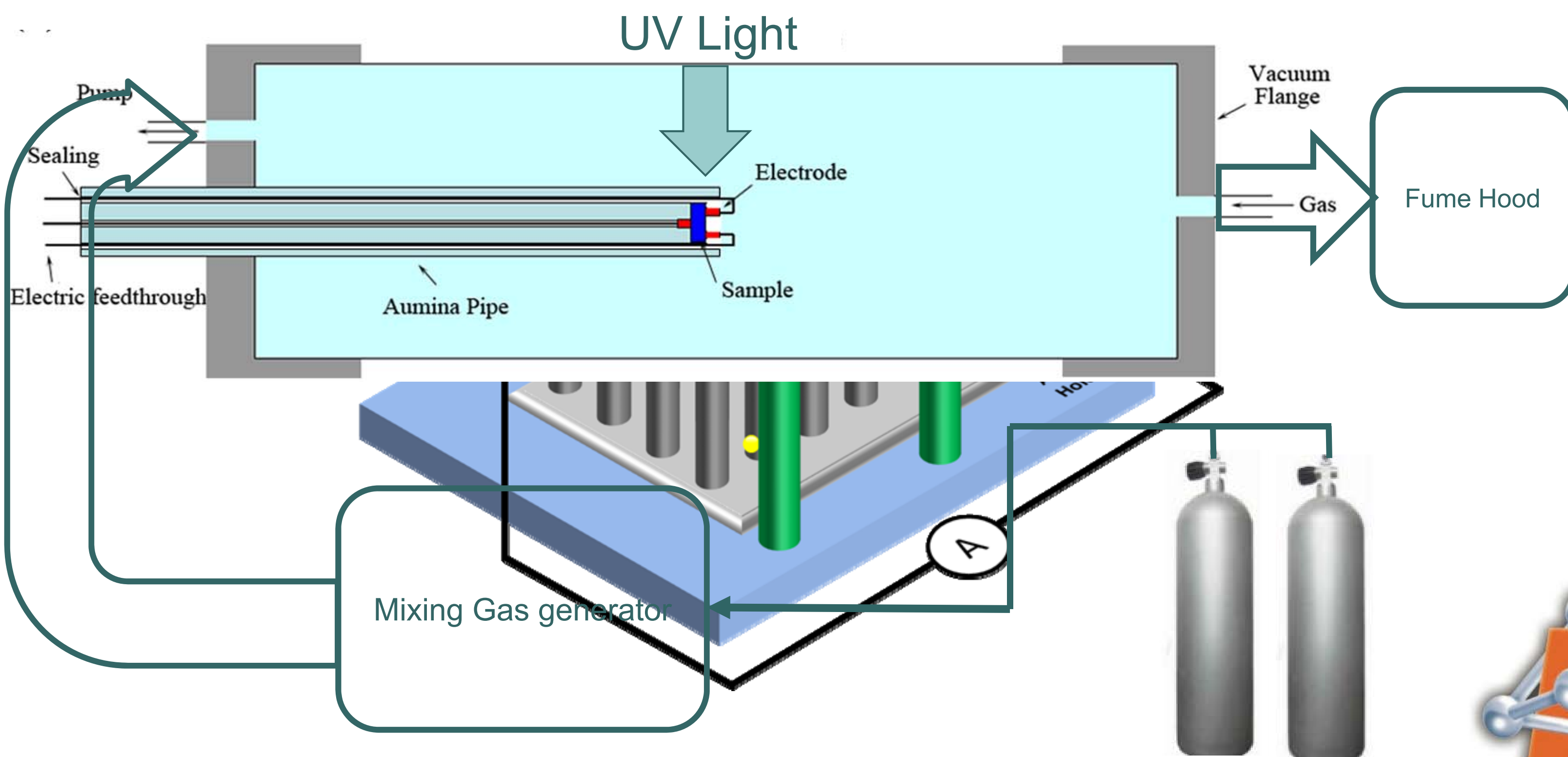
Technical Approach:
Multi-mode Sensor Testing Setup



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Liu, et al., *RSC Advance*, **2012**. Sun, et al., *Frontier Chem.*, **2014**.

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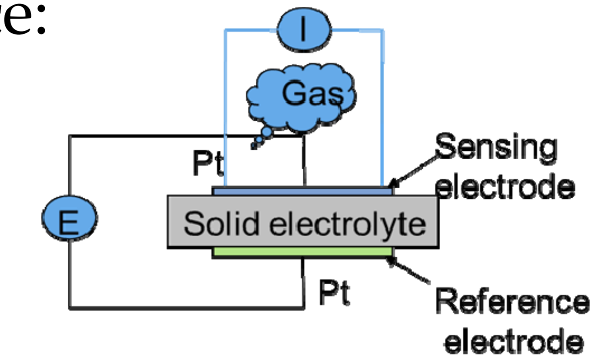
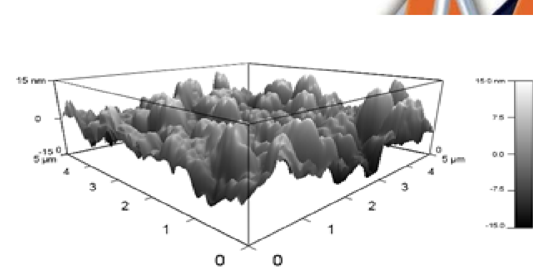
Technical Approach: Multiple Detection Modes in Nanowire Array Sensor

- Multiple sensing signals in one device:
  - Electrical resistance
  - Impedancemetric
  - Photocurrent mode
  - Potentiometric



- Advantages: multiple signals correlation with respect to selective species → accuracy; selectivity (PCA data processing); sensitivity; → add new sensing capability such as physical sensing (T, P, etc.)



Gao et al., *DoE/NETL Sensors & Control Program Meeting*, **2009**.
Zhang, Gao, et al., *J. Mater. Chem.*, **2012**.
Sun, Gao, et al., *Frontier Chem.*, **2014**.

Accomplishments

(Project period: 5/2016-3/2017)

1) Synergy material design in Ga_2O_3 and ZnO based heterostructured nanowire sensors.
    a) Perovskite LSFO LSCO and Pt sensitized Ga_2O_3 Nanowire CO Sensors (500^oC)
    b) Au, Fe_2O_3, Au/Fe_2O_3 hybrid nanoparticles on ZnO nanowire arrays

2) Sensitivity and selectivity enhancement toward CO and NO_2 detection using ZnO and Ga_2O_3 based multi-mode sensors.
    a) Electrical
    b) Photo- illumination
    c) Surface impedance

3) Selectivity enhancement through multi-mode sensing at high temperature.

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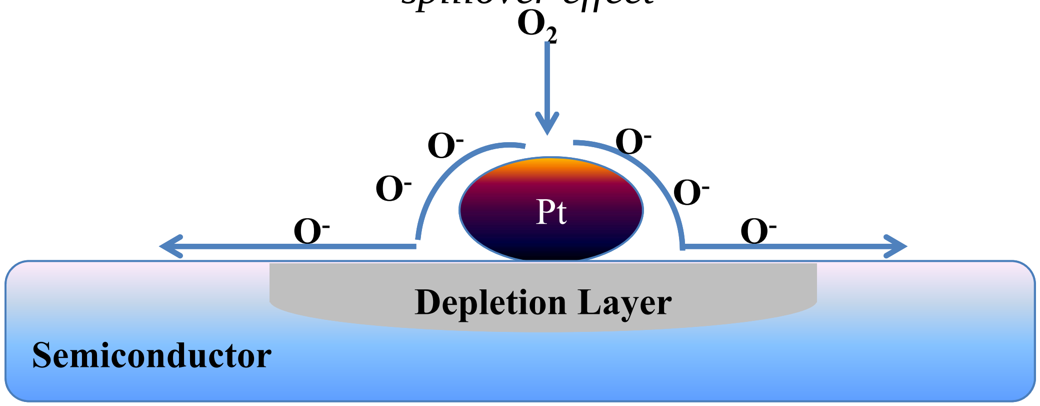
1) Synergy Materials Design at High Temperature

- Noble metal nanoparticles widely used for sensitizing metal oxide chemical sensors through the catalytic spillover mechanism.
- However, the significantly decreased melting points of noble metal nanoparticles limit their applications in harsh environments due to a size effect coupled with inherent chemical instabilities.
- Limited resources in noble metals on earth → alternatives?

Pt nanoparticle: spillover effect



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1a) Perovskite-type LSFO Nanoparticles Sensitizing Effect for CO Detection

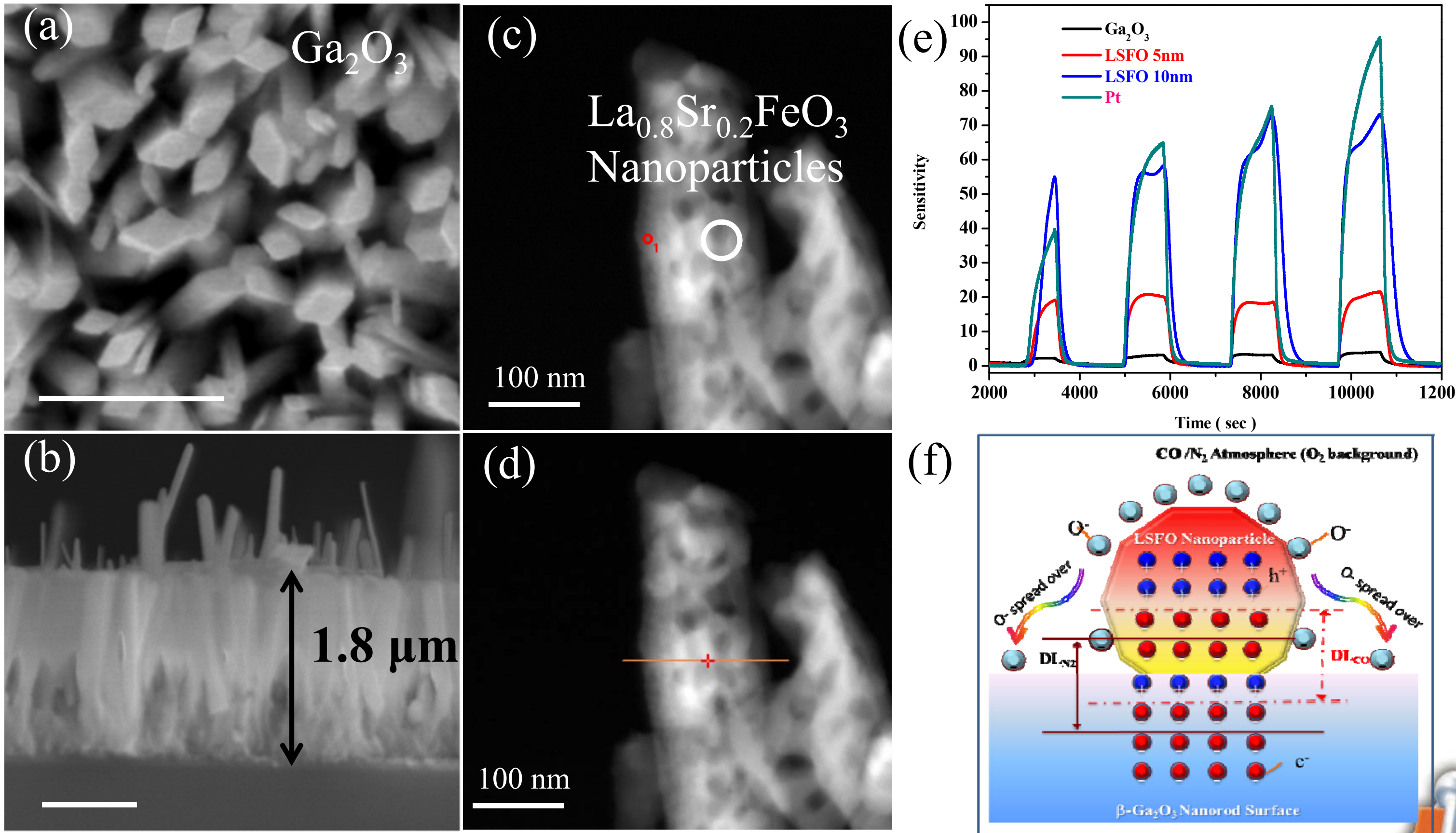

Figure 1: Top view (a) and (b) cross-sectional view SEM image of Ga_2O_3 nanorods array.(c) (e) STEM images of a LSFO decorated β-Ga_2O_3 nanorod showing its porous structure;the corresponding EDX spectrum of (d) point scanning, (f) line scanning revealing the existence and distribution of LSFO composition on β-Ga_2O_3

Lin, Gao, Ohodnicki, et al. *ACS Appl. Mater. Int.* **2016**

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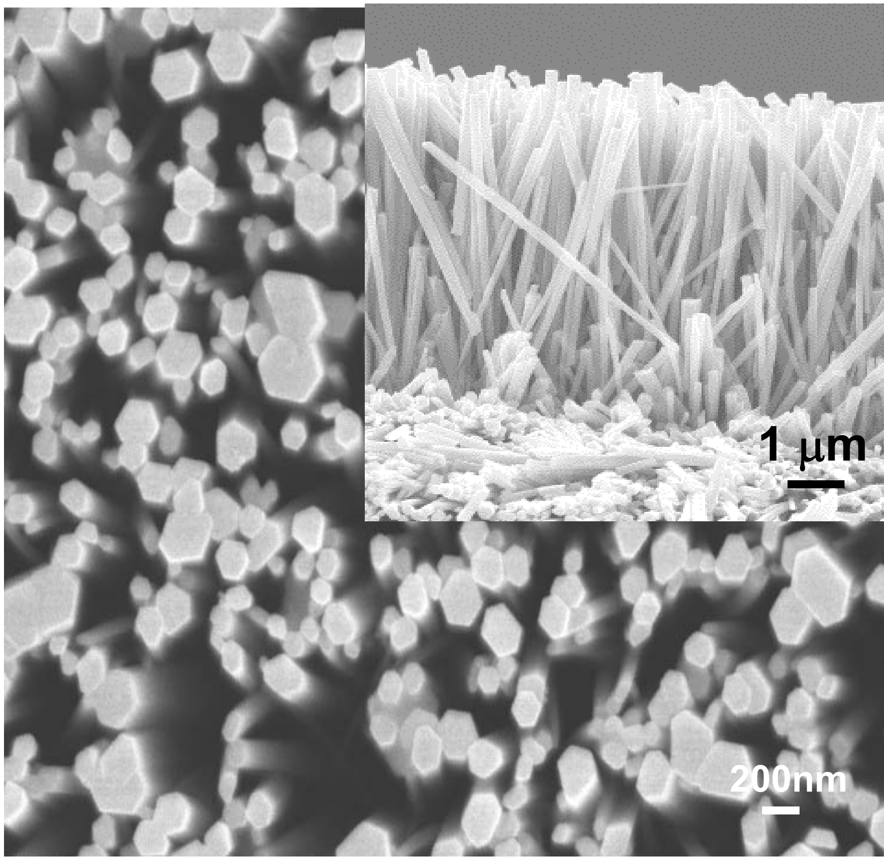
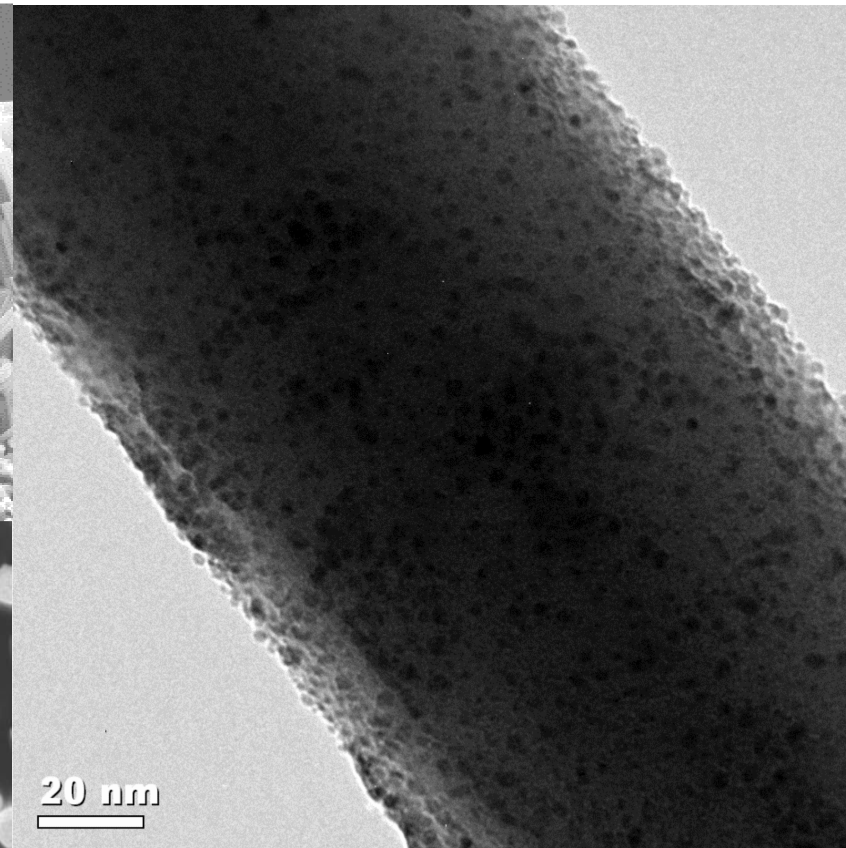
1b) Au/ZnO based Nanowire Array Sensors: Au nanoparticle decoration





- Diameter of Au nanoparticles (NPs): 2nm
- AuNPs dip-coated on the ZnO nanowires
- Uniformly distributed AuNPs on the surface of ZnO nanowires

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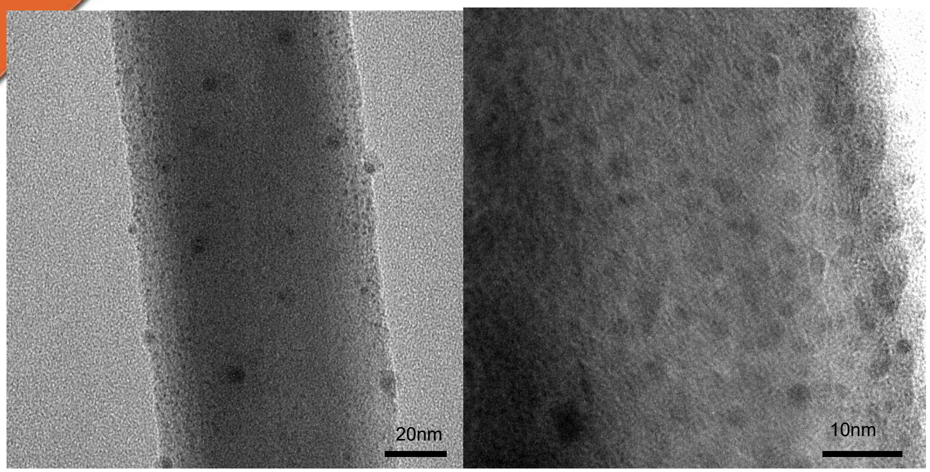
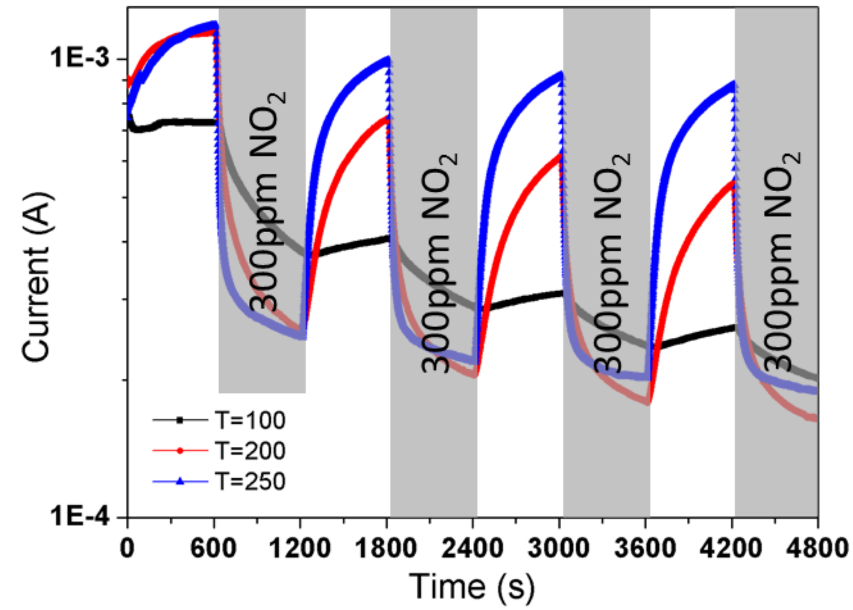
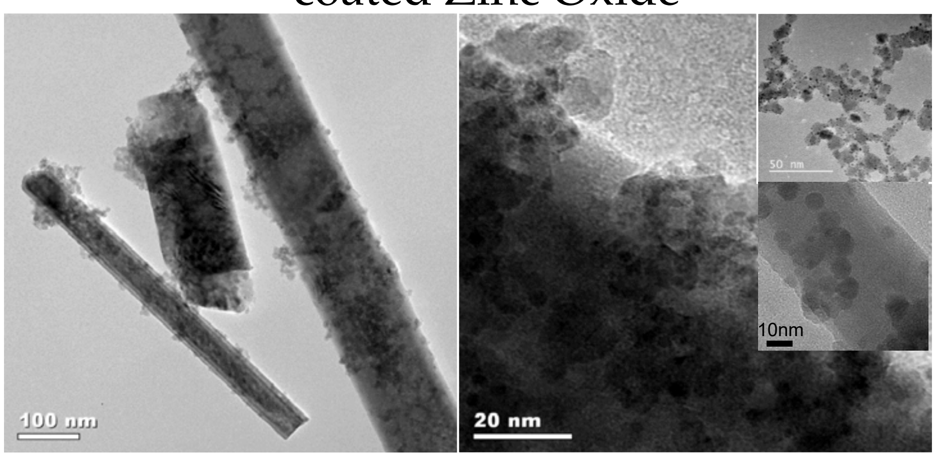
1b) Au/ZnO based Nanowire Array Sensors: Au/Fe_2O_3 nanoparticles decoration

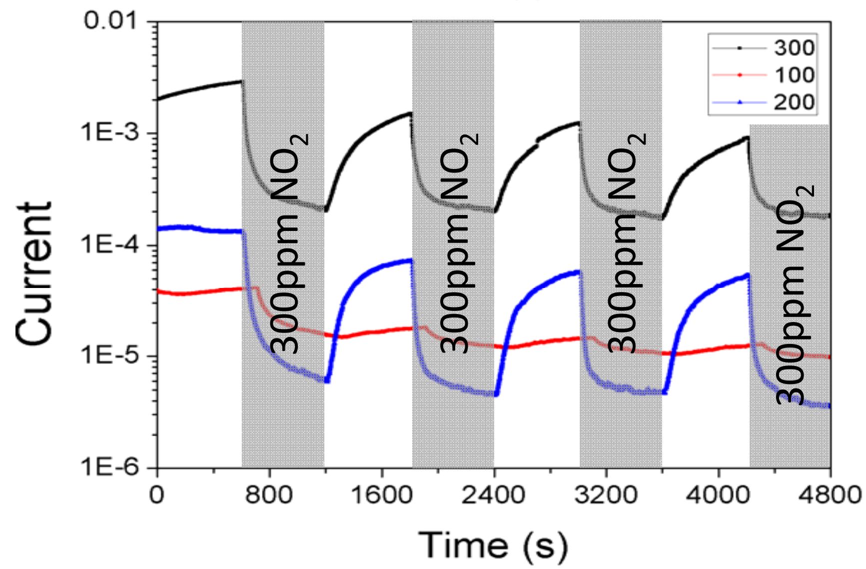


Single Crystalline AuNPs coated Zinc Oxide





Hybrid (Integrated Fe_2O_3 and Au nanoparticles) AuNPs coated ZnO nanowires



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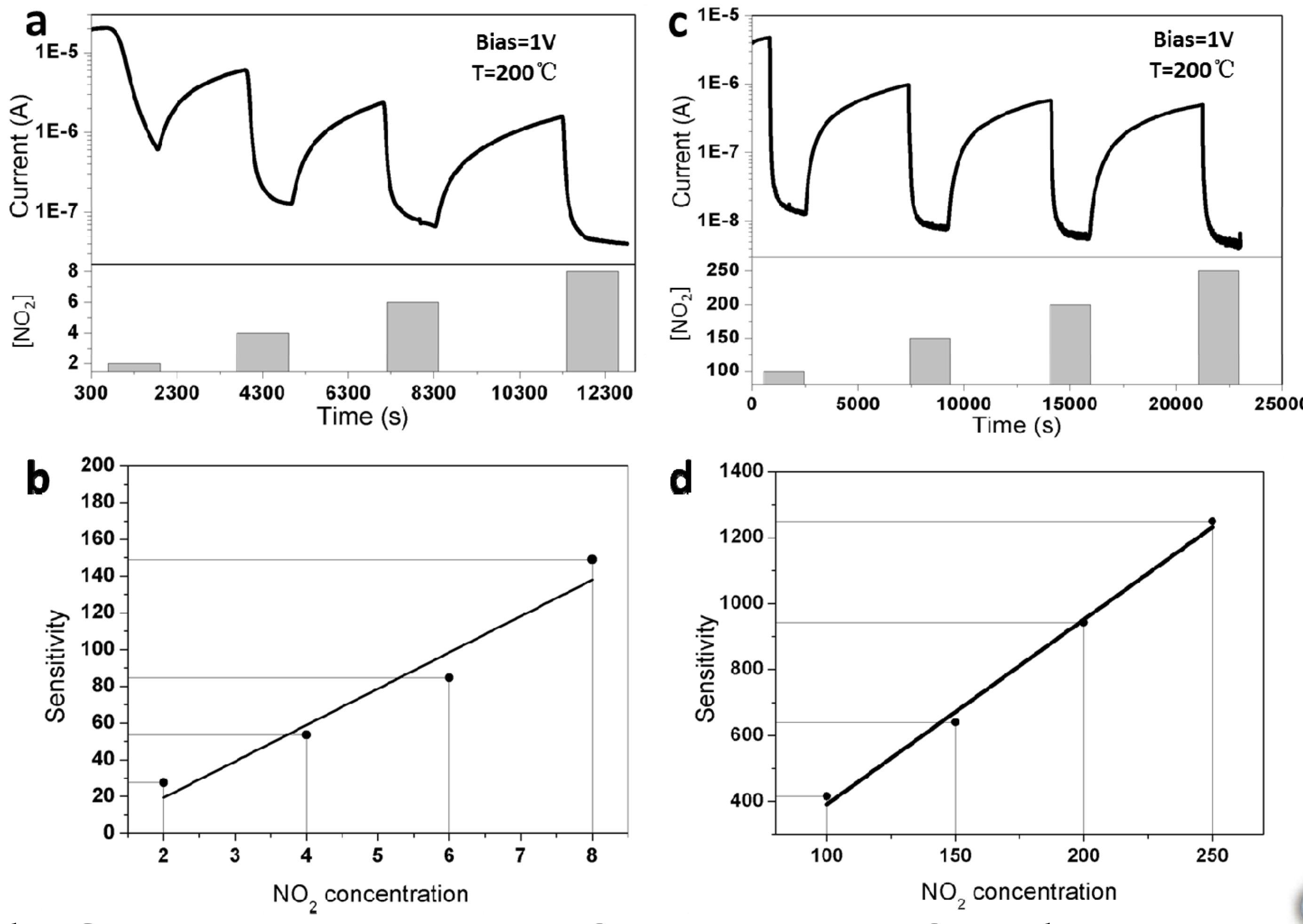
2a) Au/ZnO based Nanowire Array Sensors: Sensitivity and Calibration line



- The Gas parameter is 2ppm NO_2 to 250 ppm NO_2 and Nitrogen as the balance gas. The flow rate is 1500 sccm.
- The relationship between sensitivity and NO_2 concentration could be fitted to a linear function.

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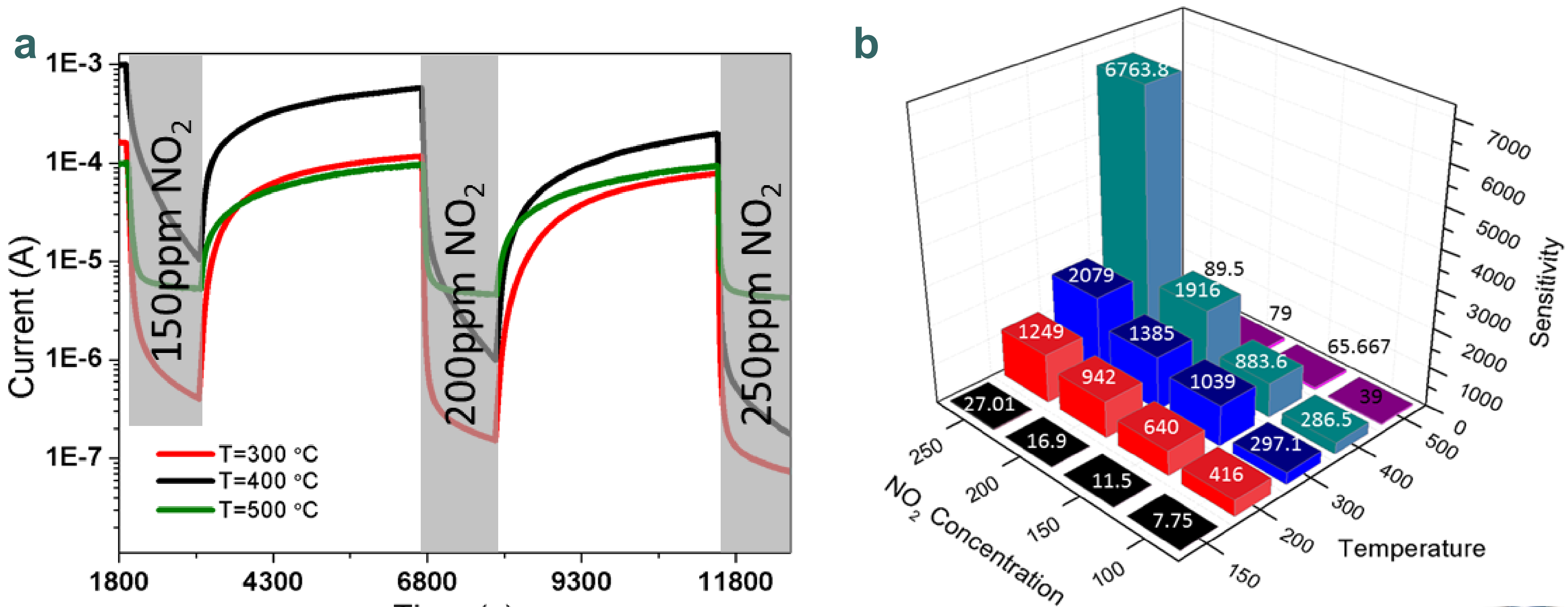
2a) Au/ZnO based Nanowire Array Sensors: Enhanced electrical sensing performance at elevated temperature



- Optimal sensing performance is obtained under 400 °C, in which up to a ultra-high sensitivity of 6000 upon 250ppm NO_2 can be achieved.
- When temperature is above 500°C, the sensing performance will decrease dramatically due to the obvious agglomeration of Au nanoparticles.

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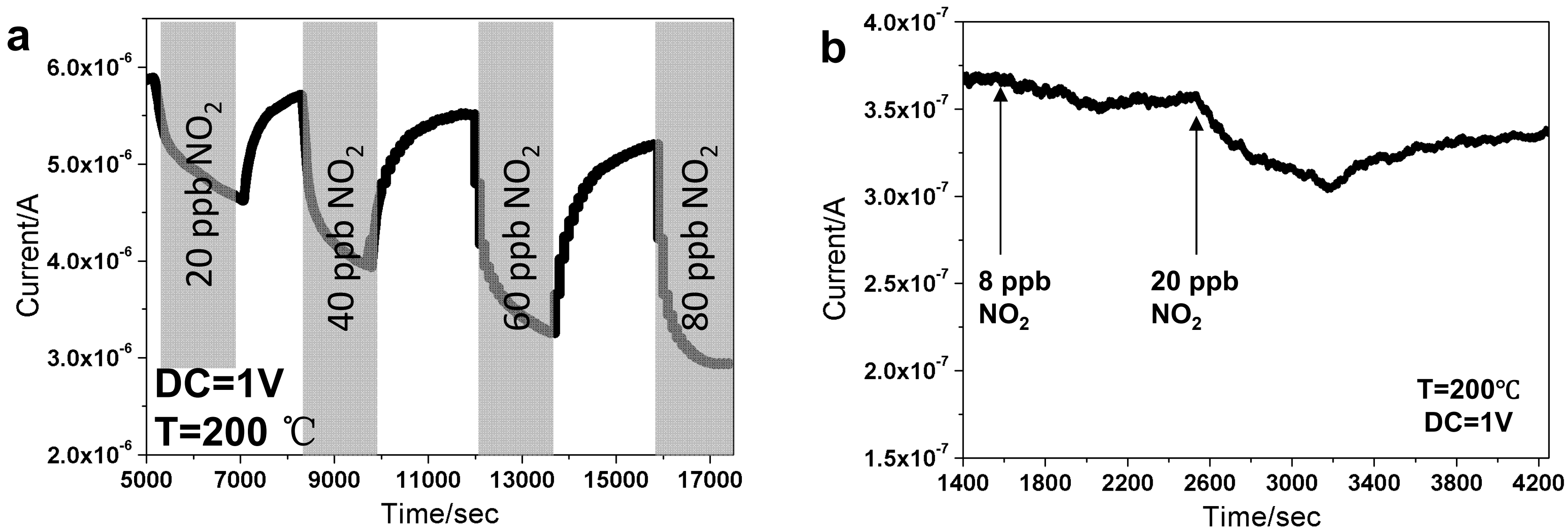
2a) Au/ZnO Nanowire Array NO_2 Sensors: Excellent sensing performance towards ppb level NO_2



- The distinguishable response should be at least 3 times larger than the background noise fluctuation
- The decoration of polycrystalline Au Nanoparticles result into the remarkable detection limit down to 8 ppb.

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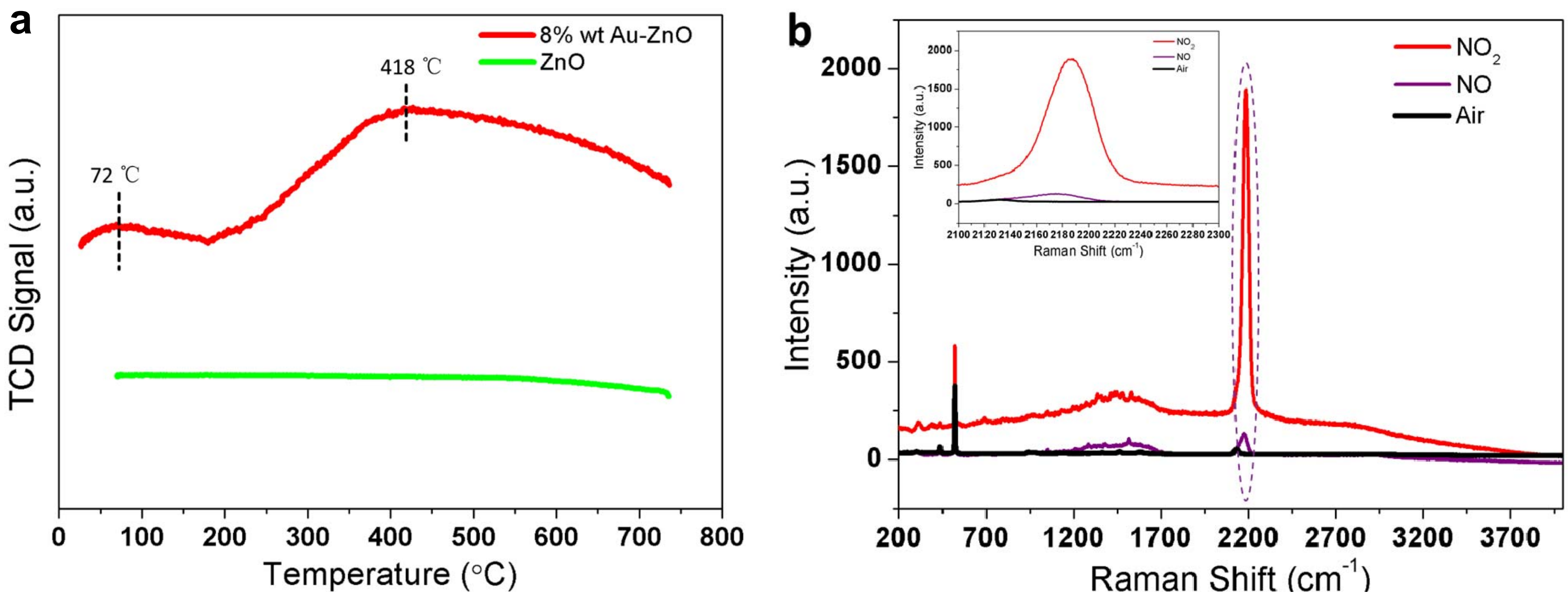
2a) Au Nanoparticles sensitizing effect: TPD spectra and Raman spectra



- Two peaks indicating the physical desorption and chemical desorption of NO_2 molecules are observed in the Au/ZnO curve.
- The obvious Raman peak (2186 cm^{-1}) is believed to be assigned to adsorption of NO_2 molecules while the sample sealed in NO only display a small peak of NO adsorption

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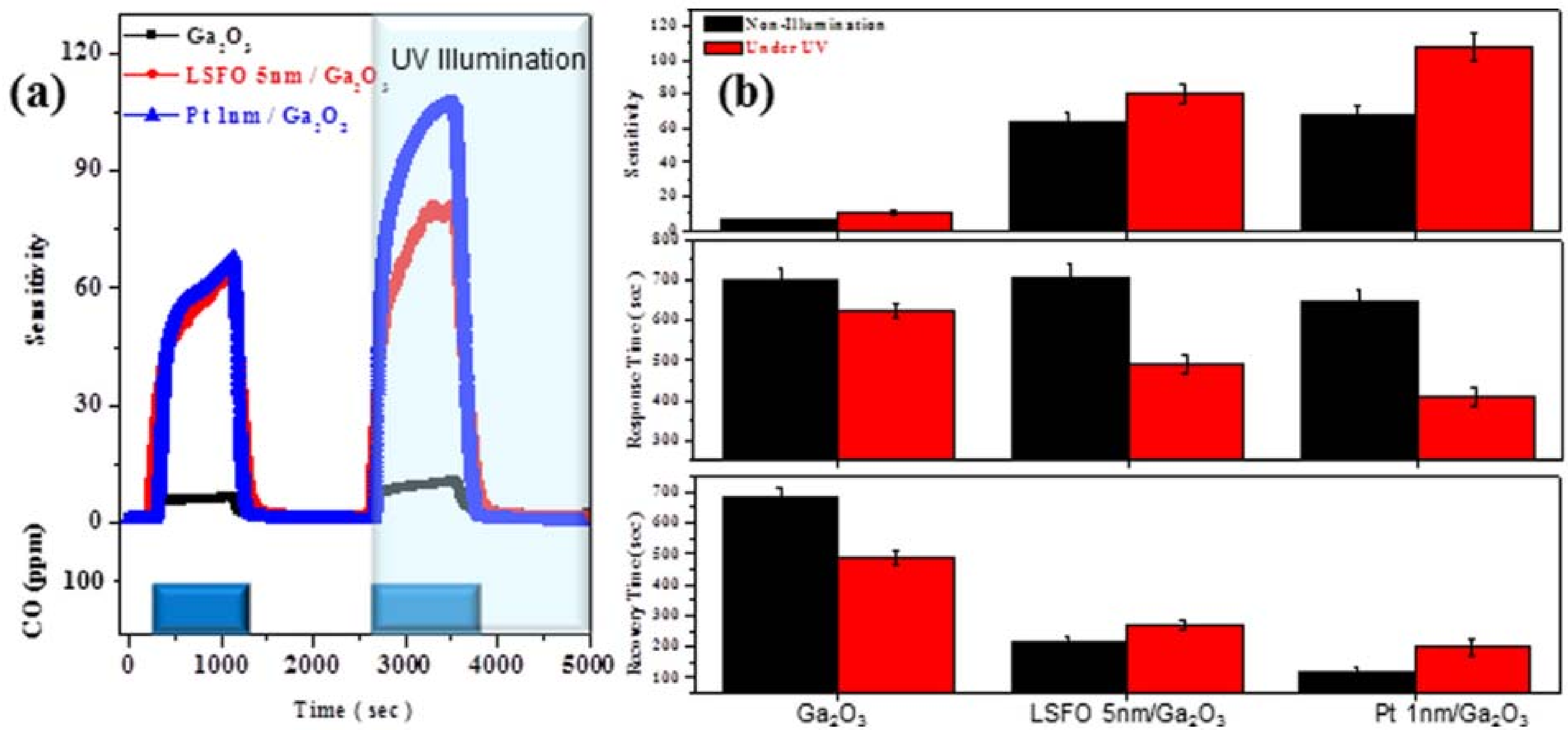
2b) UV-assisted CO sensing using Ga_2O_3-based nanorod arrays at elevated temperature



- The pristine Ga_2O_3 sensor under UV illumination shows about 30% higher sensitivity and faster response time over the non-UV condition at 500°C.
- Upon LSFO surface decoration, the sensitivity was enhanced by ~10 times compared to pure Ga_2O_3 nanorod array. With UV illumination, the sensitivity was further improved to 80 times, another 20% enhancement.

Lin, Gao, et al. *Appl. Phys. Letts.*, **2016**

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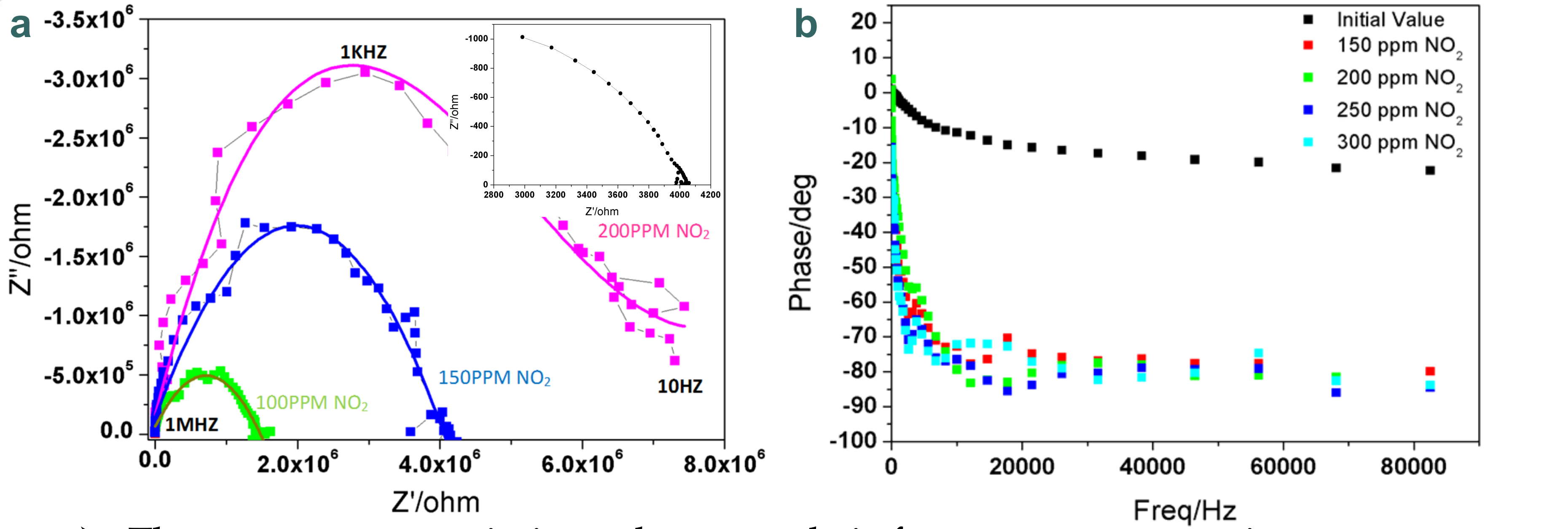
2c) Au/ZnO Nanowire Array NO_2 Sensors: Surface impedance mode



- The response curve in impedance mode is frequency parametric response. The real part is plotted on X axis and the imaginary part is plotted on the Y axis.
- In difference frequency, the response towards NO_2 are significantly different and the response decrease with the increase of frequency.
- Unlike the impedance value, the phase is independent on the gas concentration, the phase degree is an approximated constant under certain frequency.

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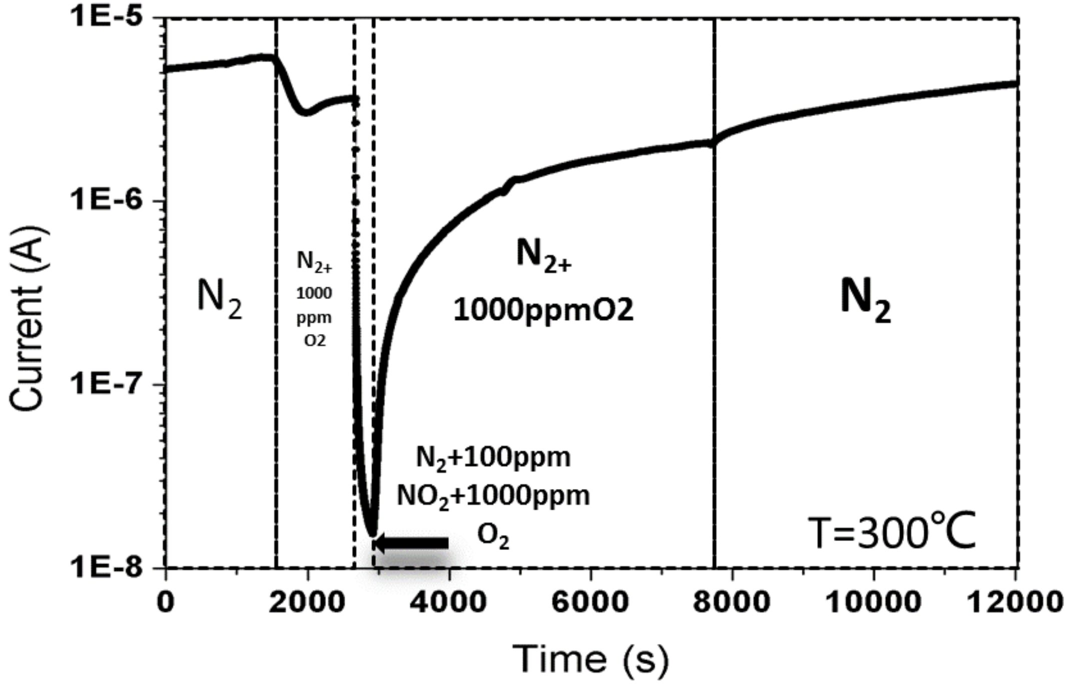
3) Au/ZnO Nanowire Array NO_2 Sensors:
Selectivity of gas sensor in mixture gases based on resistance mode



$$\textit{Selectivity} = \frac{\text{Sensitivity of the sensor towards target gas}}{\text{Sensitivity of the sensor towards interference gas}}$$

- The remarkable selectivity is due to the preferential chemiresistive sensing towards NO_2 in the presence of O_2, CO, N_2.

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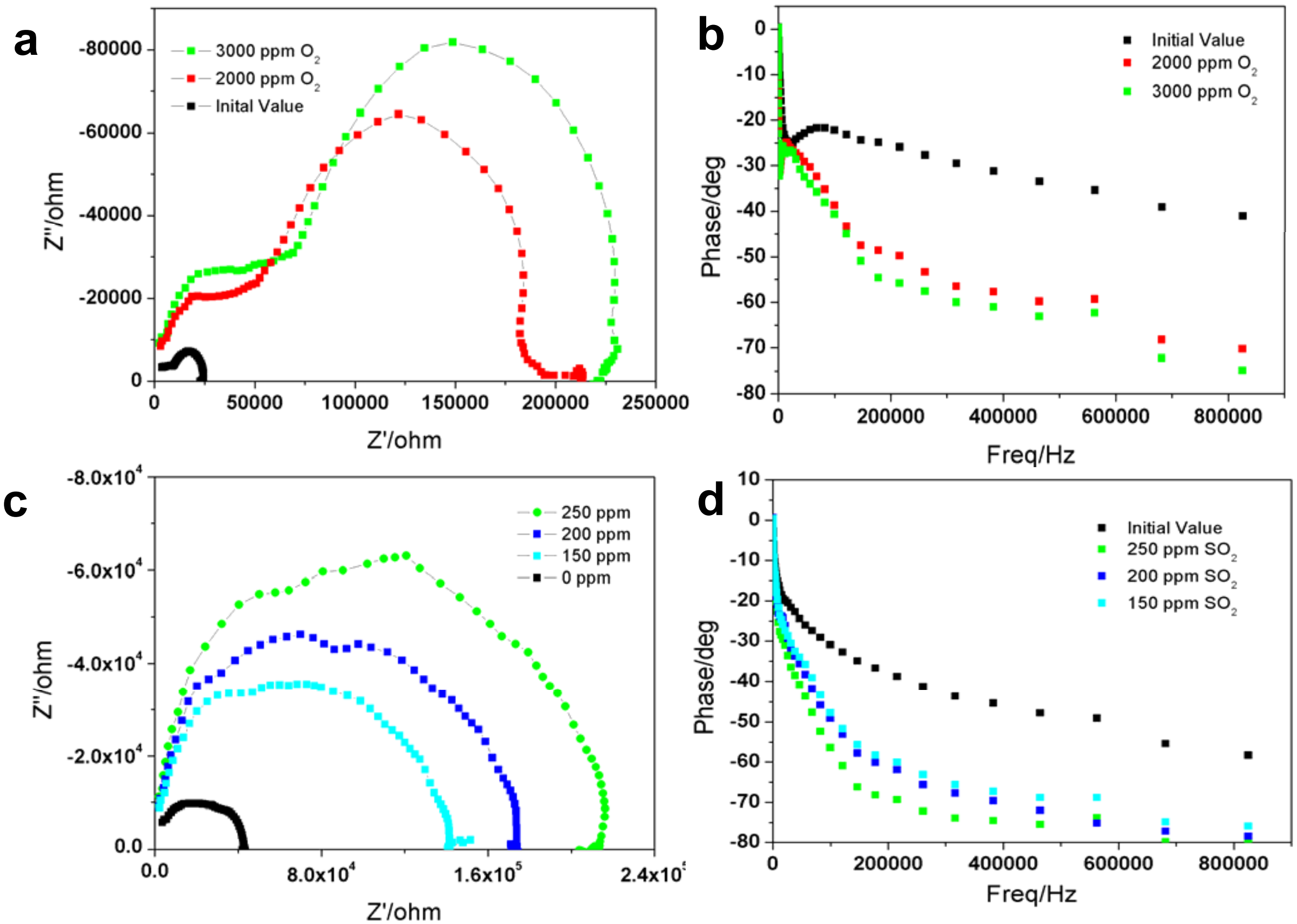
3) Au/ZnO Nanowire Array Sensors towards interfering gas based on Surface impedance mode



- Similar as NO_2, the phase is also independent on the O_2 and SO_2 concentration, their phase value fluctuate around an approximated constant.
- Different gas has different characteristic phase degree under a certain frequency.

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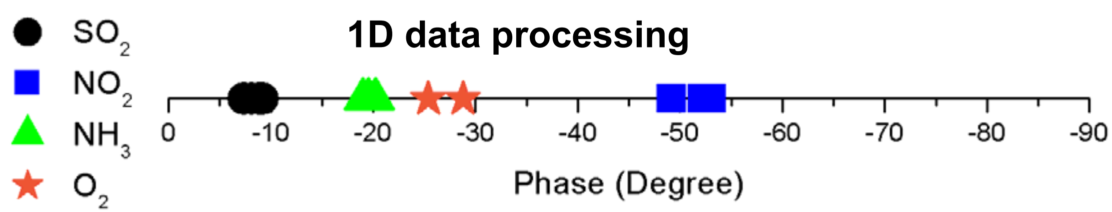
3) Correlation between the Surface impedance mode and Resistance mode

(SO_2, 150 ppm, -9.2)	**(SO_2, 200 ppm, -8.8)**	**(SO_2, 250 ppm, -8.1)**	**(SO_2, 300 ppm, -7.4)**
(NO_2, 150 ppm, -49.1)	(NO_2, 200 ppm, -49.9)	(NO_2, 250 ppm, -52.2)	(NO_2, 300 ppm, -53.1)
(NH_3, 150 ppm, -20.2)	(NH_3, 200 ppm, -19.5)	(NH_3, 250 ppm, -19.0)	
(O_2, 2000 ppm, -25.4)	(O_2, 3000 ppm, -28.8)		



- The impedance mode enable us to distinguish the gas species based on the phase degree variation.

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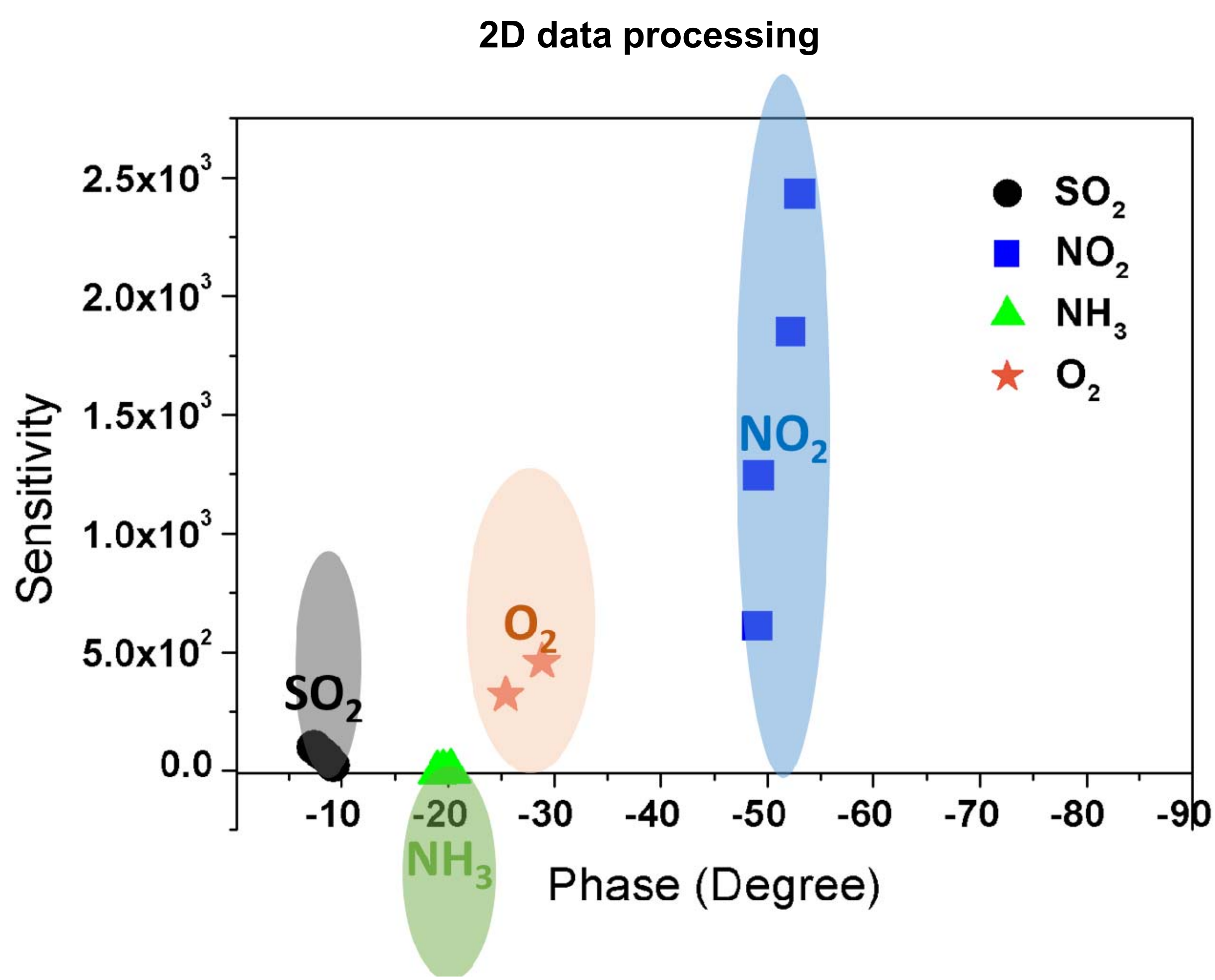
3) Correlation between the Surface impedance mode and Resistance mode



- In addition to the single resistance mode, the correlation based on the double working mode enable the target gas recognition and quantitative analysis.

Conclusions and Future work

1) Using solution and vapor phase deposition methods, Ga_2O_3 and ZnO based heterostructured nanowire arrays have been fabricated.
2) Synergy effect was unraveled in materials selections, highlighted by the discovery of heterojunction effect of Au/Fe_2O_3 hybrid and electrical sensitizing effect of $LaSrFeO_3$ or $LaSrCoO_3$ nanoparticle over ZnO and Ga_2O_3 nanowire array sensors, respectively.
3) Enhanced sensor performance includes the excellent sensitivity, selectivity and detection limit was achieved through applying three modes including resistance, photocurrent and surface impedance on ZnO/Au as well as Ga_2O_3 based nanowire sensors.
4) Finally, the correlation based on the electrical resistance and impedance mode enable the target gas recognition and quantitative analysis.

5) **Future work:**

a) Further study of nanoparticle enhancement effect over metal oxide nanowire array based sensors in terms of sensitivity, selectivity and stability.
b) Data collection and analysis of nanowire sensors to establish 3-mode selectivity and sensitivity correlations;
a) Further study of nanowire sensors with multiple sensing modes upon mixture gas stream at high temperature.

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Acknowledgement

- Postdoc and students: Dr. Haiyong Gao, Sibo Wang, Xingxu Lu, Qiuchen Dong, Rodrigo Vinluan (UT Dallas), Yingyu Huang (UT Dallas)
- Collaborators: Dr. Yu Lei (Co-PI, UConn), Drs. Paul Ohodnicki, John Baltrus (NETL); Dr. Chang-Yong Nam (BNL), Dr. Jie Zheng (UT Dallas), Dr. Yong Ding (Georgia Tech)
- DoE/NETL project manager: Rick Dunst
- Funding sources:

  UConn – Research Foundation

  US Department of Energy (DOE/NETL)

  US National Science Foundation (NSF)

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Collaborations

- National Laboratories:

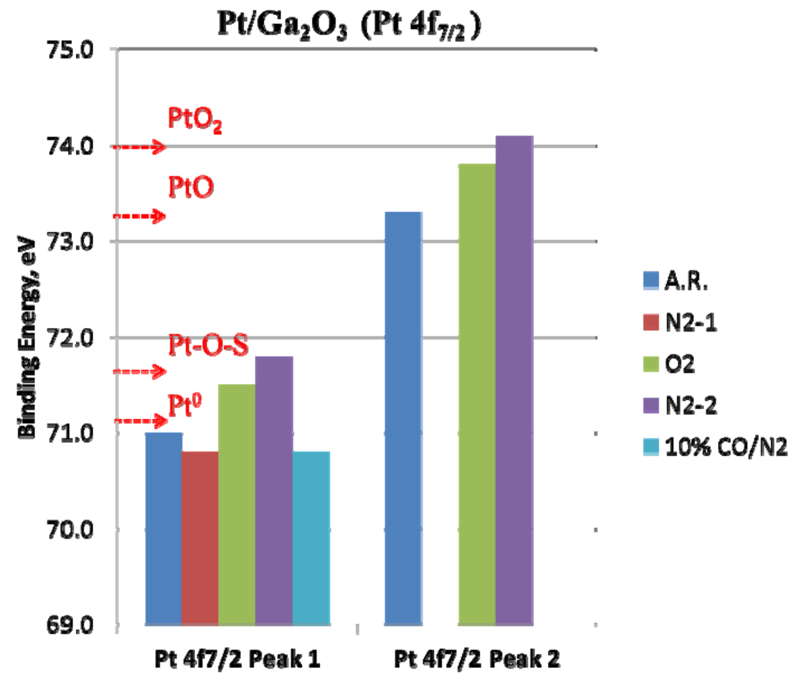
National Energy Technology Lab: In-situ XPS and optical sensor studies of nanowires with Drs. John Baltrus and Paul Ohodnicki.

Brookhaven National Lab: electronic transport study of oxide/perovskite nanowires with Dr. Chang-Yong Nam through Center for Functional Nanomaterials (CFN).

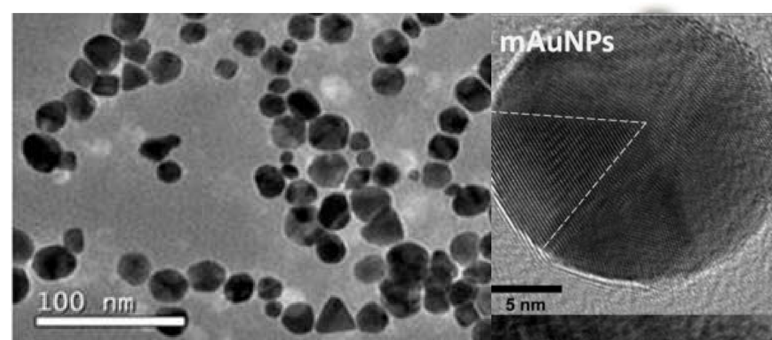
- Universities:

UT Dallas: synthesis of well-defined metal and oxide/metal nanoparticles as sensitizers for nanowire sensors, with Dr. Jie Zheng.

Georgia Tech: STEM and 3D hollography study on oxide/perovskite nanowires, with Dr. Yong Ding.



Lin, Baltrus, Ding, Ohodnicki, Gao et al., *ACS Appl. Mater. Interfaces*, **2016**.



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