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

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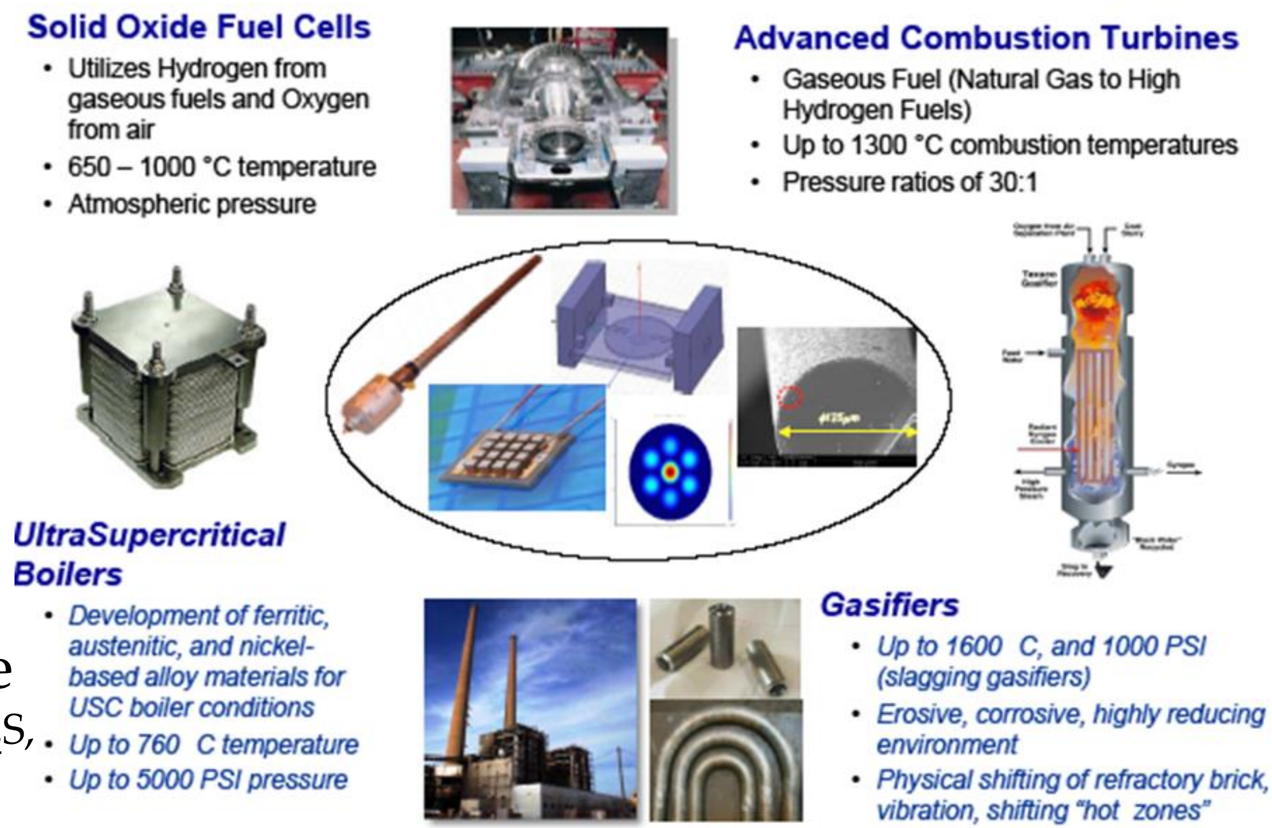
Harsh Environment in Power Systems: Sensing/monitoring Challenges

- 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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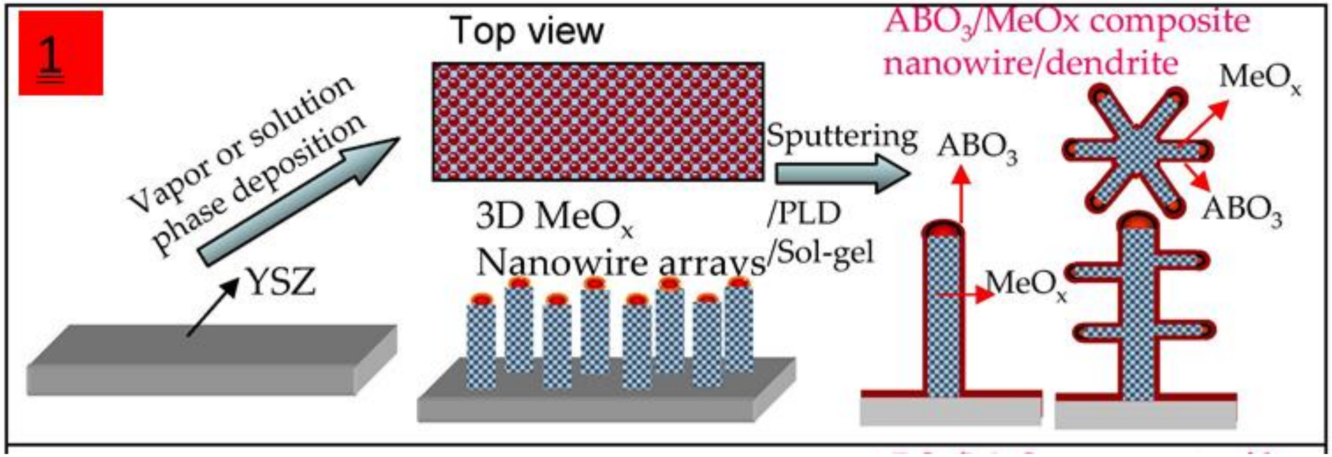
Technical Approach: Sensor Nanomaterials Design & Integration



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: Au, Pd, Pt, etc.→ High physical and chemical stability, electronic charge transfer 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**.
Gao et al., *J. Phys. D.*, **2010**.
Zhang et al., J. Mater. Chem., **2012**.
Gao, et al., *Int. J. Mol. Sci.*, **2012**.
Ren, et al., Frontier Chem. **2014**.
Gao et al., UConn invention disclosure filed, **2012**.

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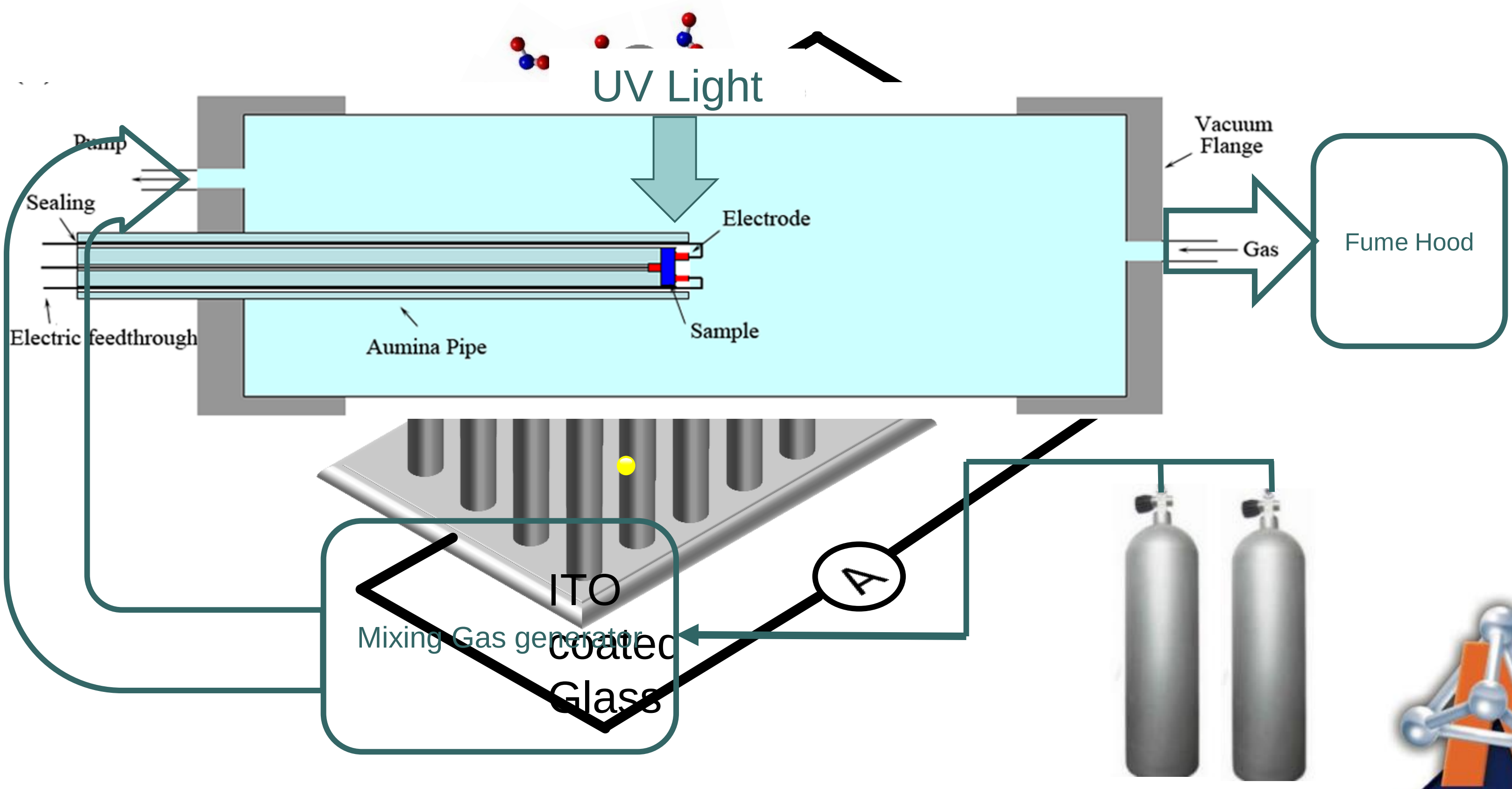
Technical Approach:
Multi-mode Sensor Testing Setup



Gao et al., *DoE/NETL Sensors & Control Program Meeting*, **2011**.
Liu, et al., *RSC Advance*, **2012**. Sun, et al., *Frontier Chem.*, **2014**.

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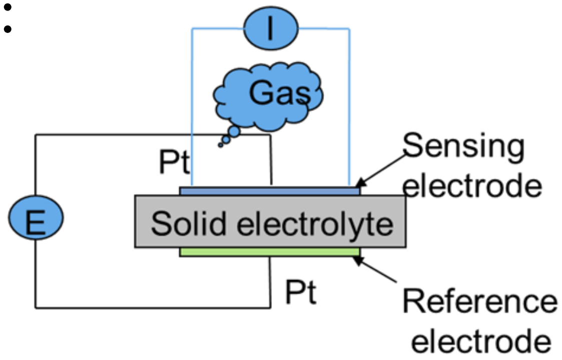
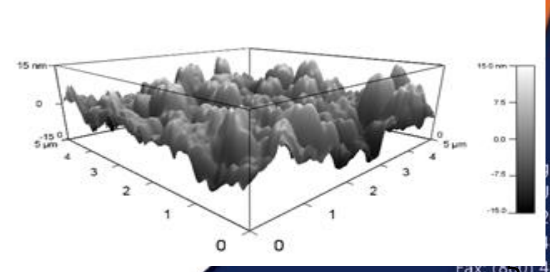
Technical Approach: Multiple Detection Modes in Nanowire Array Sensor

- 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: 5/2015-4/2016)

1) Synergy material design in Ga_2O_3 and ZnO based heterostructured nanowire sensors.
   a) Perovkiste sensitized Ga_2O_3 Nanowire Array CO Sensors (500°C)
   b) Perovskite sensitized Ga_2O_3 Nanowire Array NO_2 Sensors (800°C)
   c) Nanoparticle and hybrid nanoparticles on ZnO nanowire arrays

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

3) Selectivity enhancement in mixing gas at high temperature.

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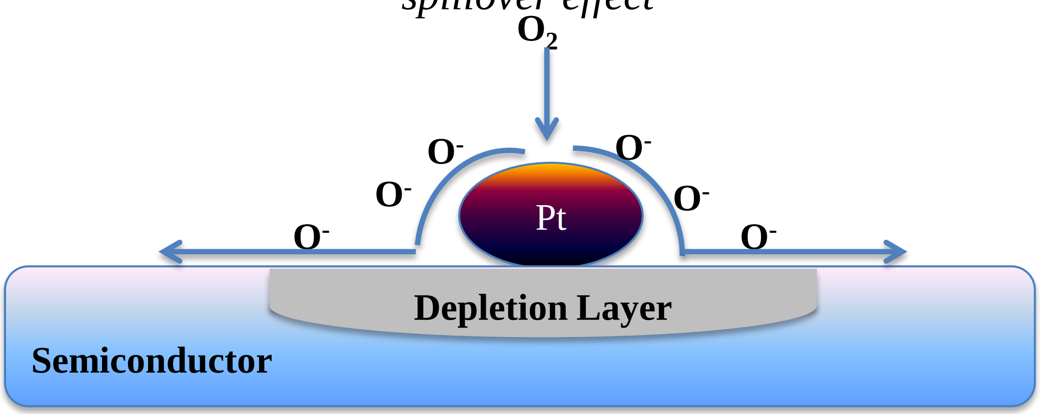
1) Synergy Materials Design at High Temperature

- 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



Yamazoe, N., *Catal. Surv. Asia*, **2003**, **7**,63–75

Gao et al., *DoE/NETL Sensors & Control Program Meeting*, **2009**. Gao et al., *Proc. SPIE*, **2011**. Gao et al., *J. Phys. D*, **2010**. Zhang et al., *J. Mater. Chem.*, **2012**. Gao, et al., *Int. J. Mol. Sci.*, **2012**. Gao et al., *UConn invention disclosure filed*, **2012**.

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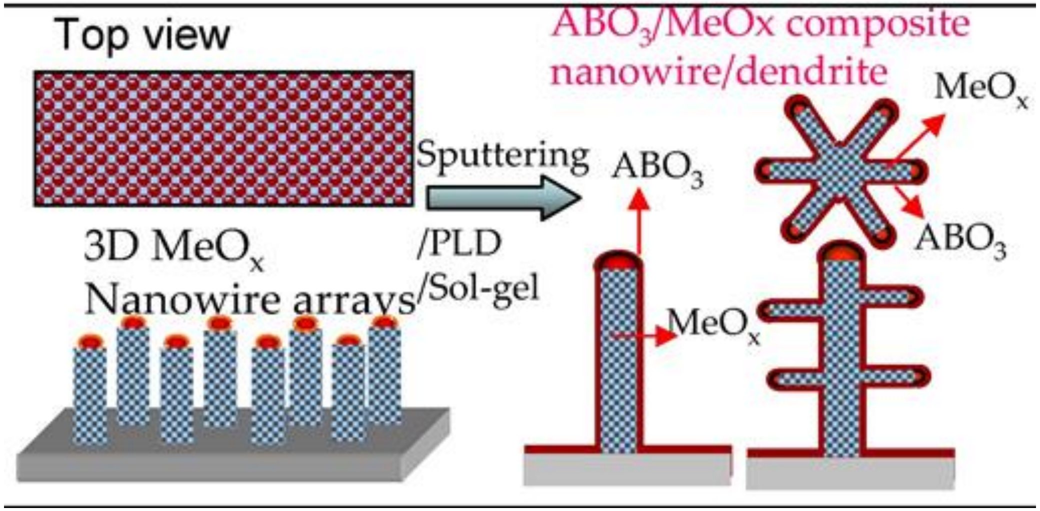

- ❖ MeO_x: metal oxide, ZnO, SnO_2, ZrO_2, Ga_2O_3, CeO_2, etc. → demonstrated in industry sensing up to 500°C robustly. → improve the temperature range and functionality?
- ❖ ABO_3: perovskite, $(La,Sr)CoO_3$, $(La,Sr)FeO_3$, etc.→ high stability, mixed ionic/electronic transport conductivity, catalytic effect, A/B site doping flexibility
- ❖ Metal: Pt, Au, Pd, etc.◎ catalytic sensing effect, metallic conduction, optical/plasmonic effect, Shottcky junction, selectivity

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

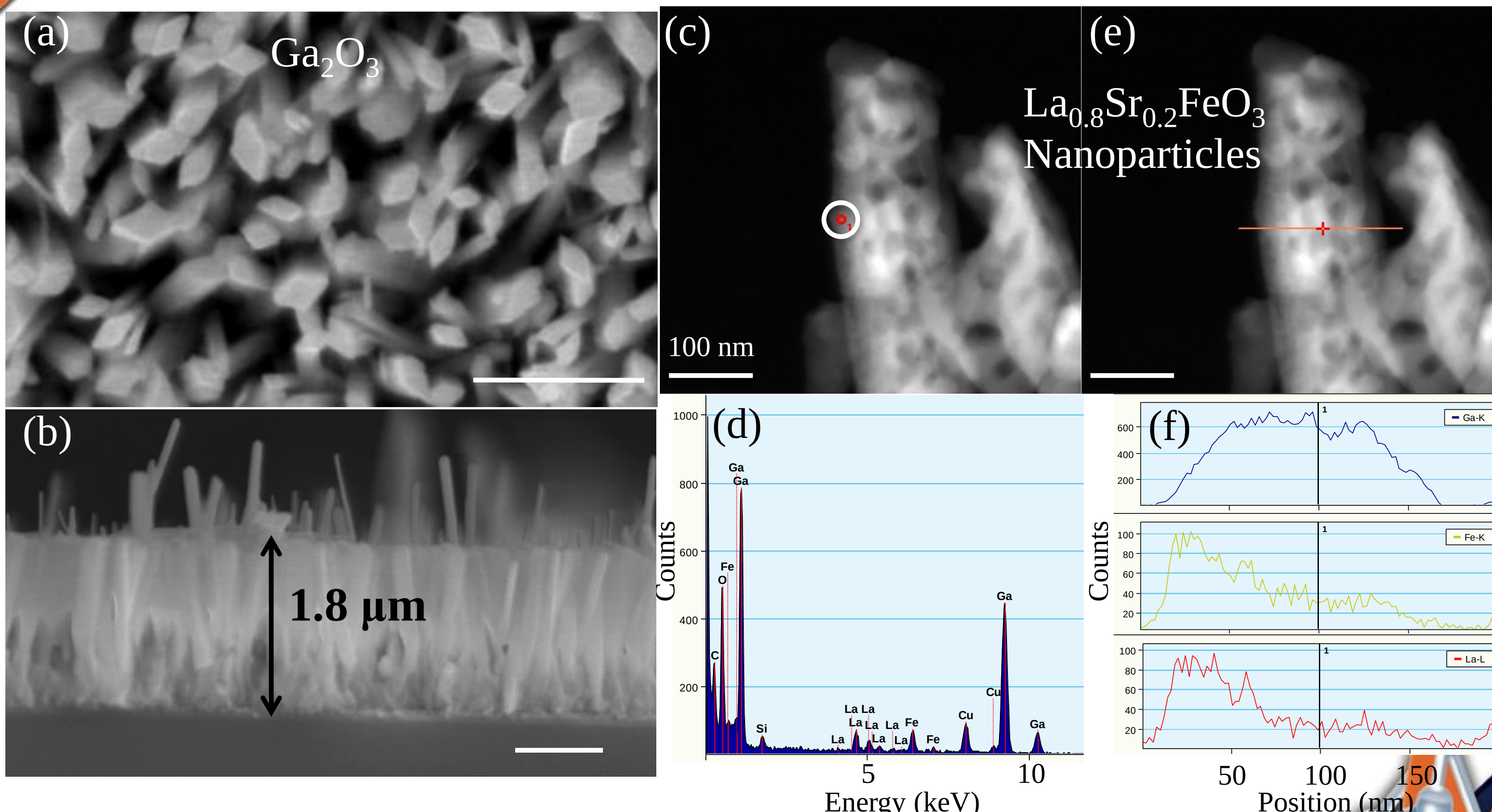

Figure 1: Top view (a) and (b) cross-sectional view SEM image of Ga_2O_3 nanorods array.(c) (e) STEM images of a LSFO decorated β-Ga_2O_3 nanorod showing its porous structure;the corresponding EDX spectrum of (d) point scanning, (f) line scanning revealing the existence and distribution of LSFO composition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

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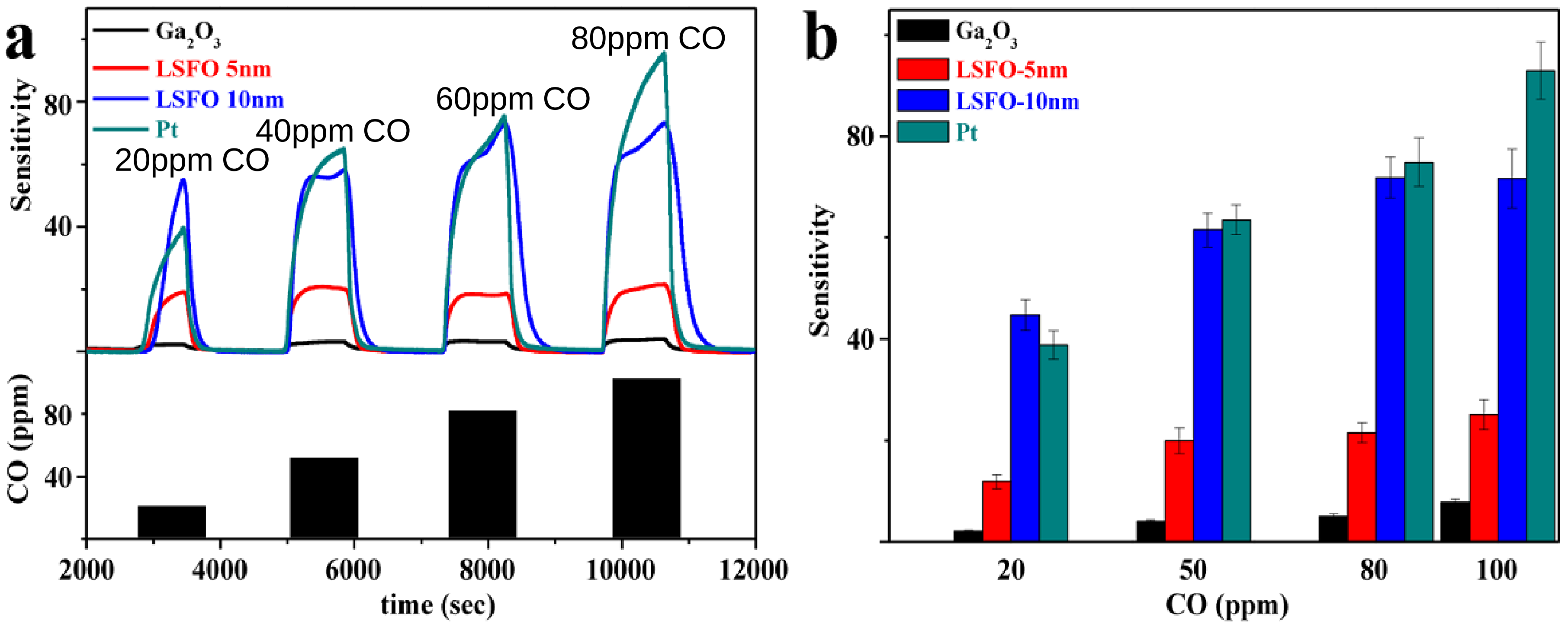
1a) LSFO Nanoparticle Sensitizing Effect for CO Detection at 500ºC



- The LSFO is found to have an excellent gas sensing catalytic performance on Ga_2O_3 nanorods.
- The sensitivity is dramatically increased by the LSFO decoration and the enhancement approach the noble metal decoration

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

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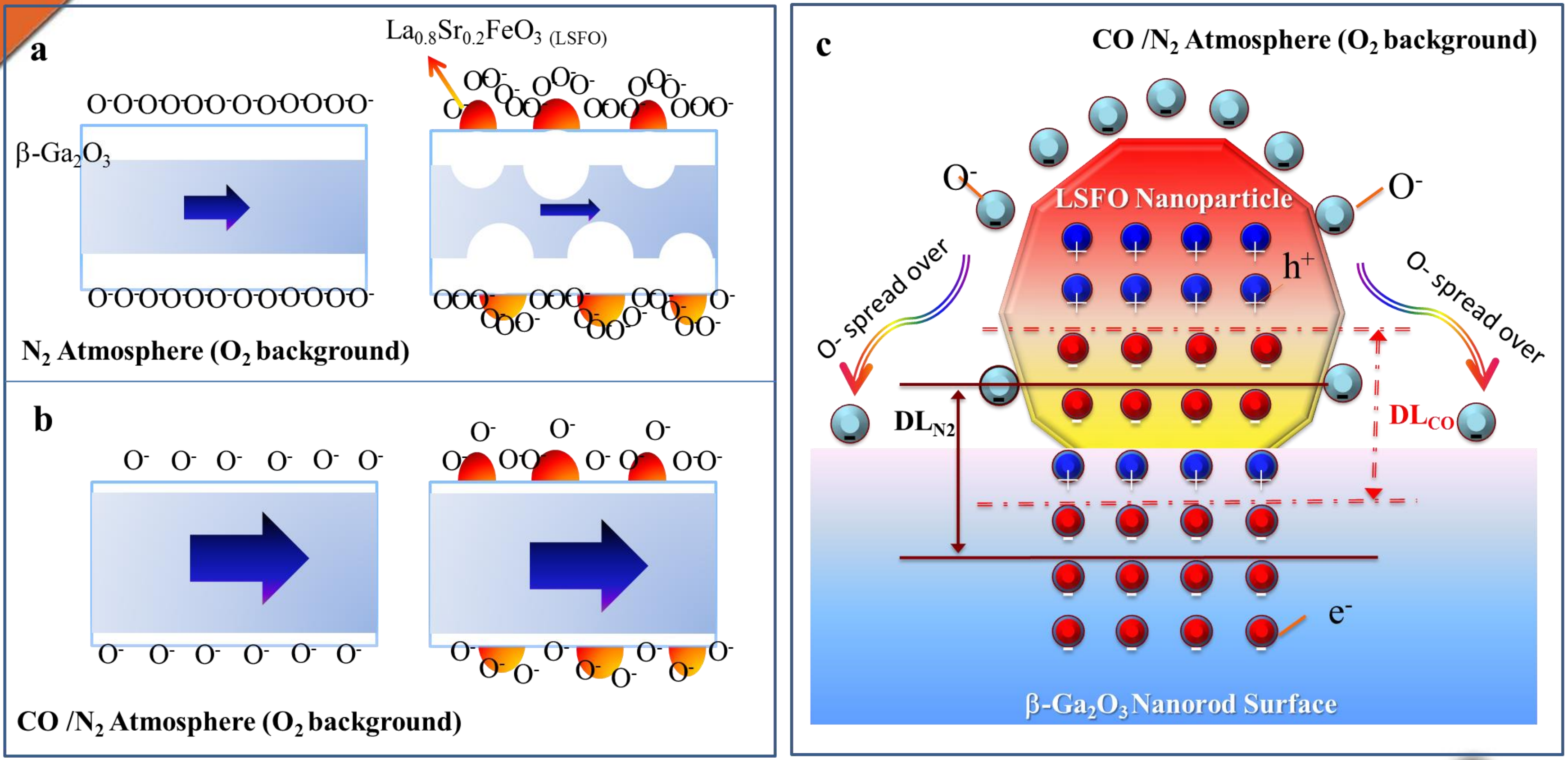
1a) LSFO Nanoparticle Sensitizing Effect: CO Detection Mechanism at 500 ºC



- LSFO induced charge depletion layer on the Ga_2O_3 surface, resulting in spontaneous charge transfer.
- Depletion layer thinner upon CO introduced
- Gas-LSFO- Ga_2O_3 triple-interface as a sink to attract O-, causing it to spread over to Ga_2O_3 nanorod surface

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

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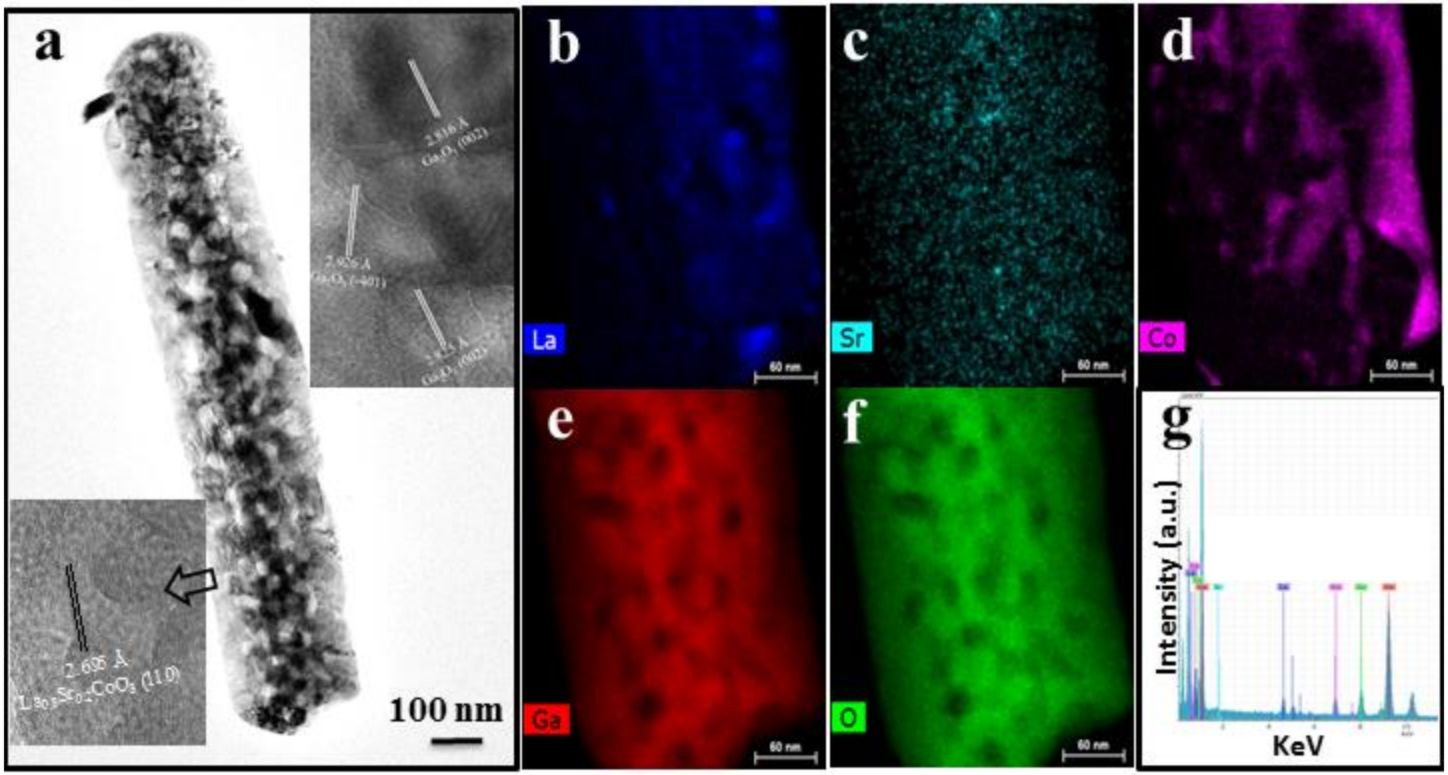
1b) Nanoparticle Decoration for Selective NO_2 Detection at 800°C



- A typical nanorod of rough surface coated with nanoparticles is revealed.
- The elemental mapping display strong uniform intensities of Ga and O signals through the whole nanorod.

Lin, Gao et al., *submitted*, **2016**.

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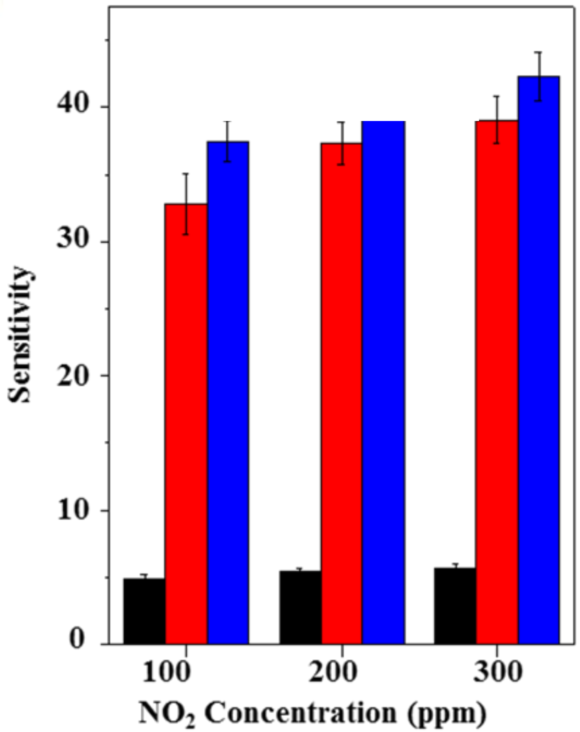
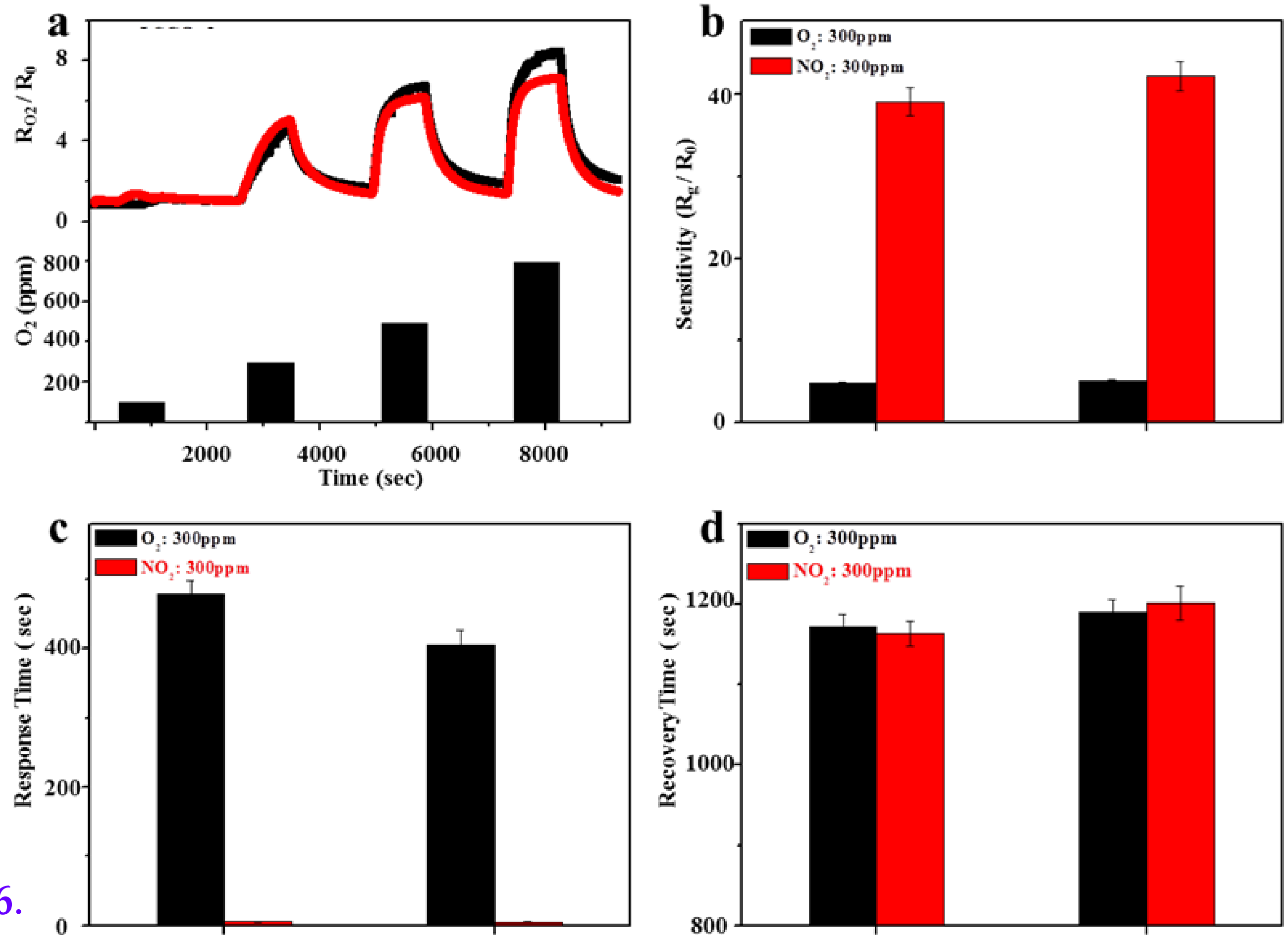
1b) Oxide Nanoparticle Decoration for Selective NO_2 Detection at 800°C





Lin, Gao et al., *submitted*, **2016**.

- Nanoparticles greatly enhances selective NO_2 sensing performance .
- Thicker nanoparticles decoration increase the sensitivity resulted from an improved nanoparticle surface coverage.

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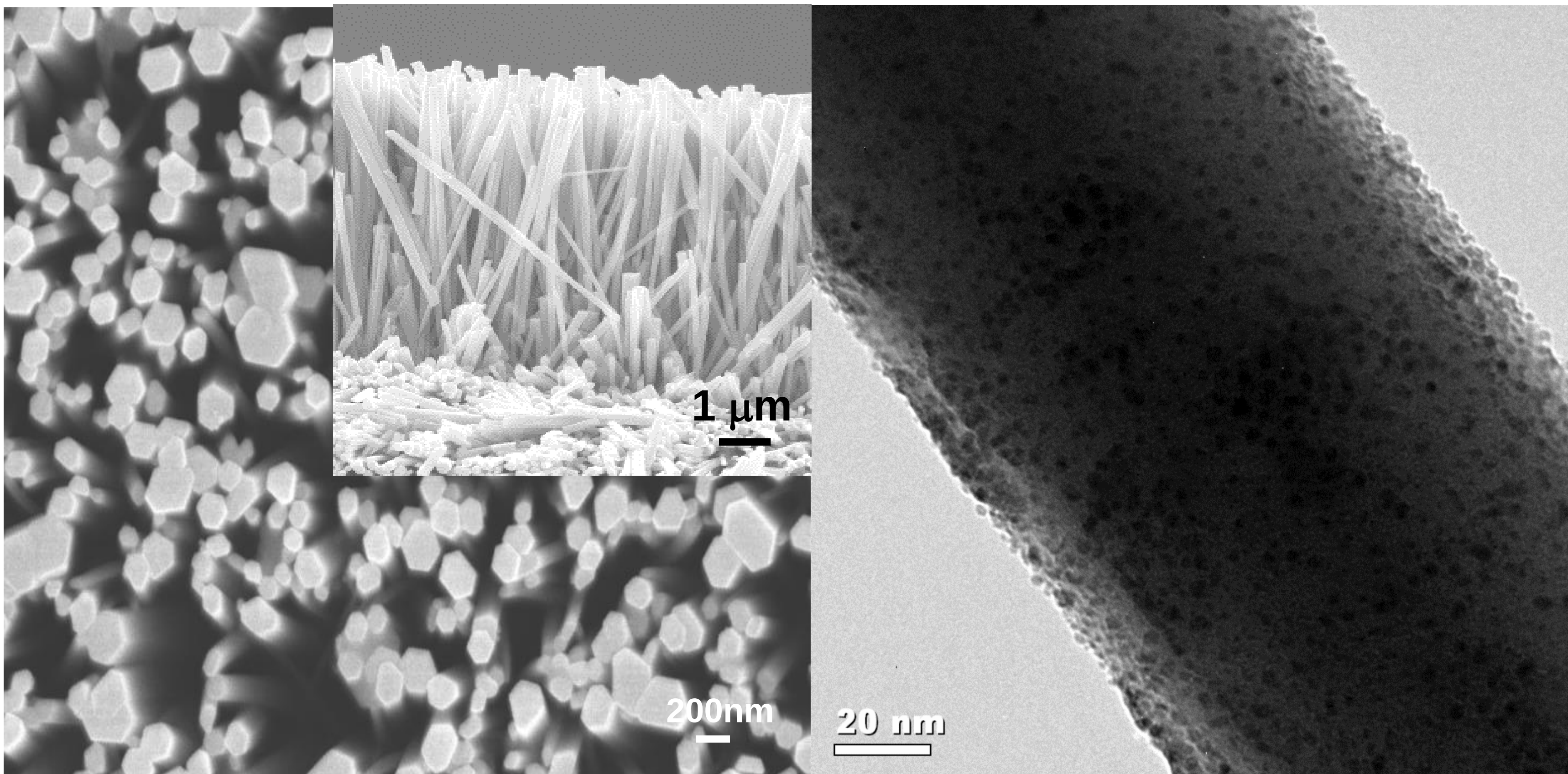
1c) Nanowire Array Sensors: nanoparticle decoration



- Nanoparticles dip-coated on the nanowires
- Uniformly distributed NPs on the surface of nanowires

Zhang, Gao et al., *in preparation*.

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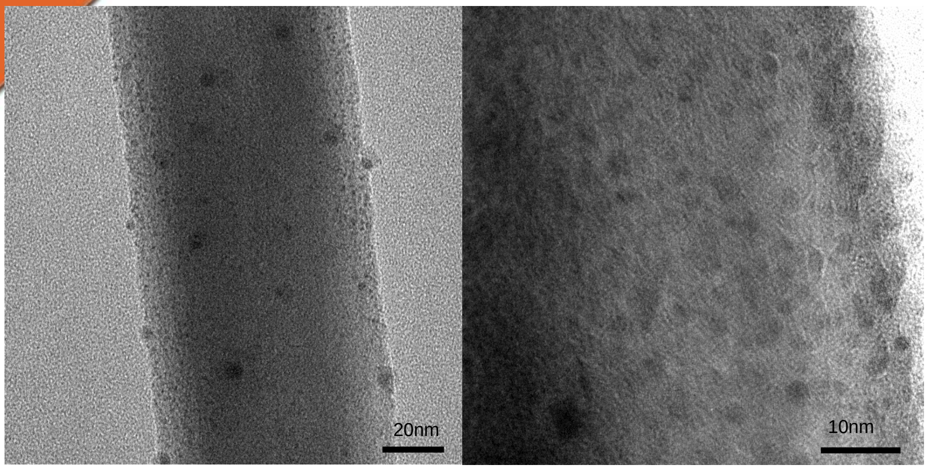
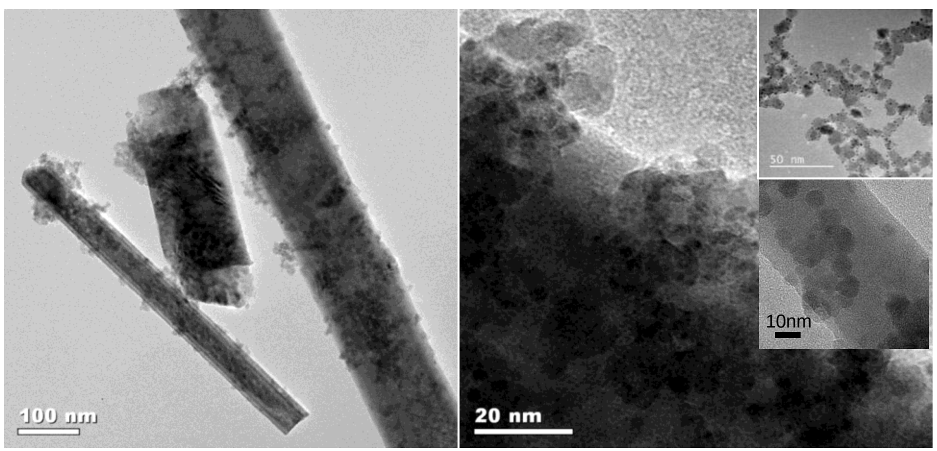
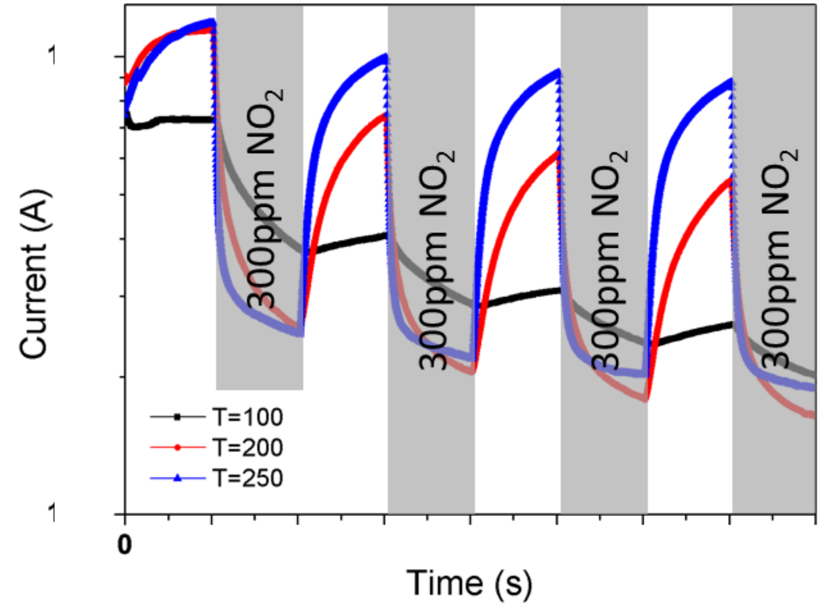
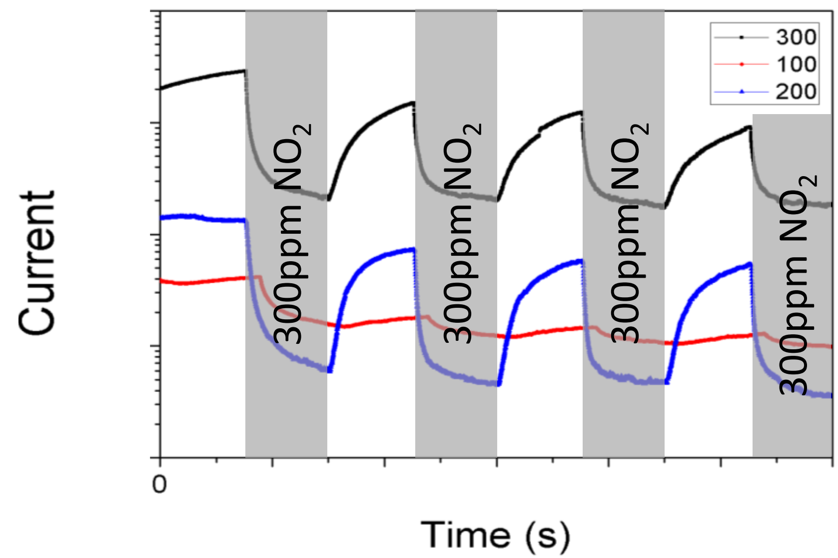


Nanoparticles on nanowire



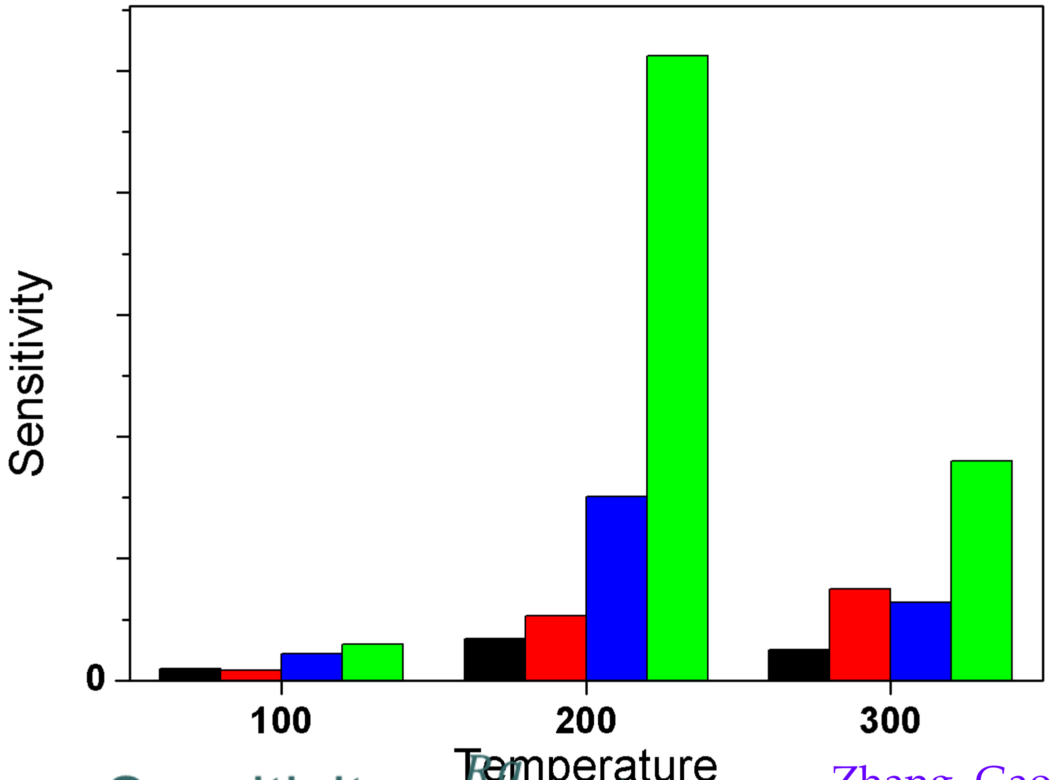
Hybrid nanoparticles on nanowires





Zhang, Gao et al., *in preparation*.

1c) Nanowire Array Sensors: Sensitivity and Response Time



Zhang, Gao et al., *in preparation*.

$$\text{Sensitivity} = \frac{Rg}{Ra} - 1$$

R_{ag} = resistance after the target gas is introduced

R_a = initial resistance

- hybrid nanoparticles enhanced sensitivity while the NPs improve d response time.
- Hybrid nanoparticles integrate the advantages of NPs and hybrids

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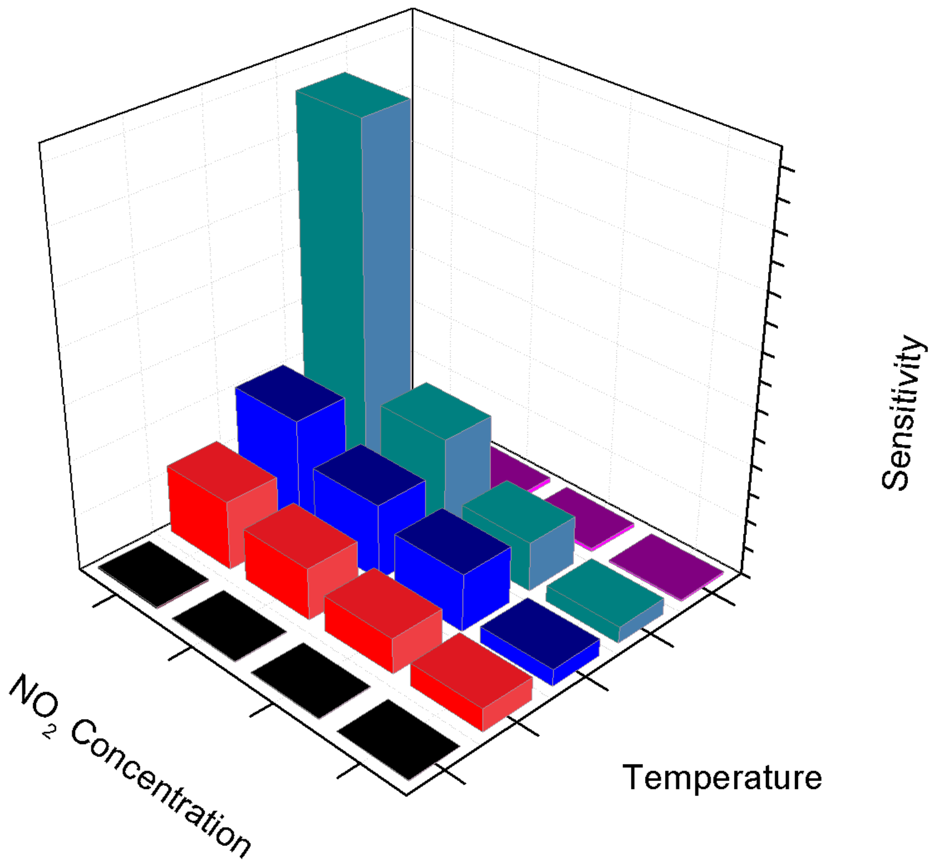
2a) Nanowire Array Sensors: Enhanced electrical sensing over NO_2



Temperature dependent sensing performance.

- Optimal sensing performance is obtained.
- When temperature is high, the sensing performance will decrease dramatically due to the obvious agglomeration of nanoparticles.

Zhang, Gao et al., *in preparation*.

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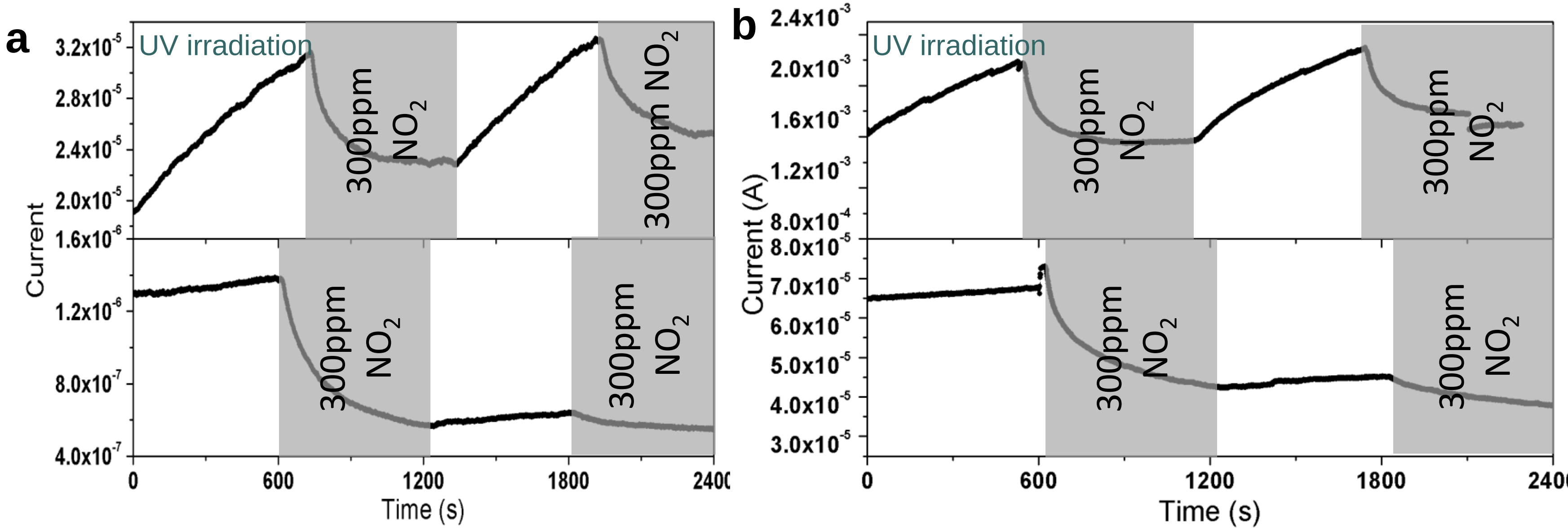
2b) Nanowire Array NO_2 Sensors: Photo-illumination enhancement



300ppm NO_2 and N_2 balance, room temperature, 1500sccm

- At room temperature, the resistive mode nearly has no recovery.
- UV irradiation mode enable the device to detect target gas repeatedly.
- UV irradiation mode decrease the response time greatly compared to the resistive mode.

Zhang, Gao et al., *in preparation*.

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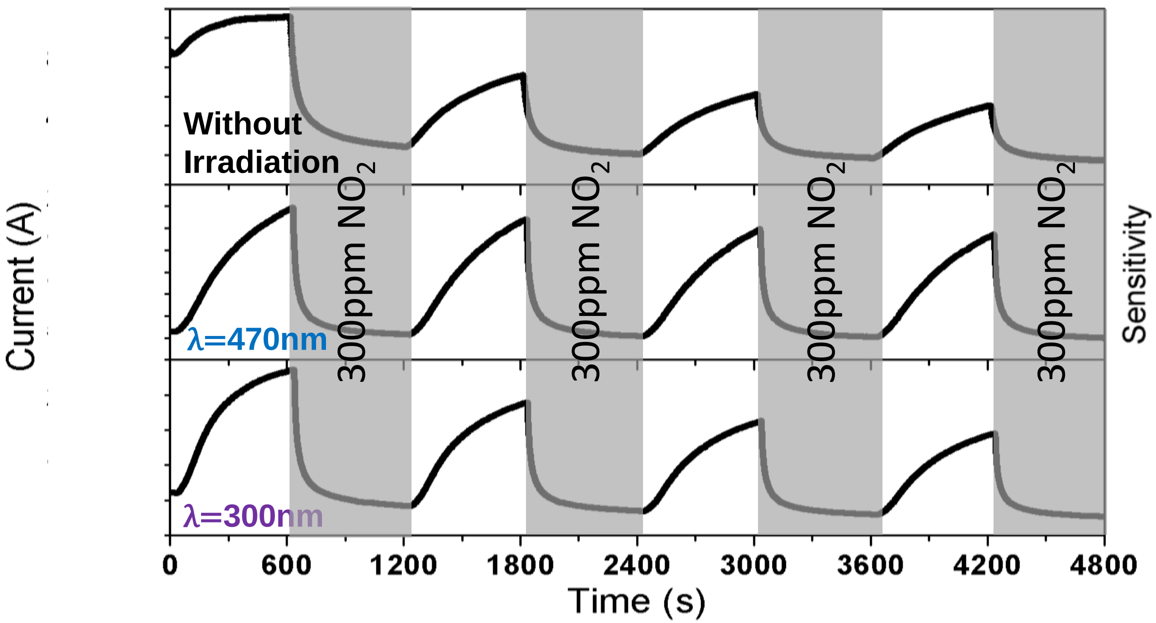
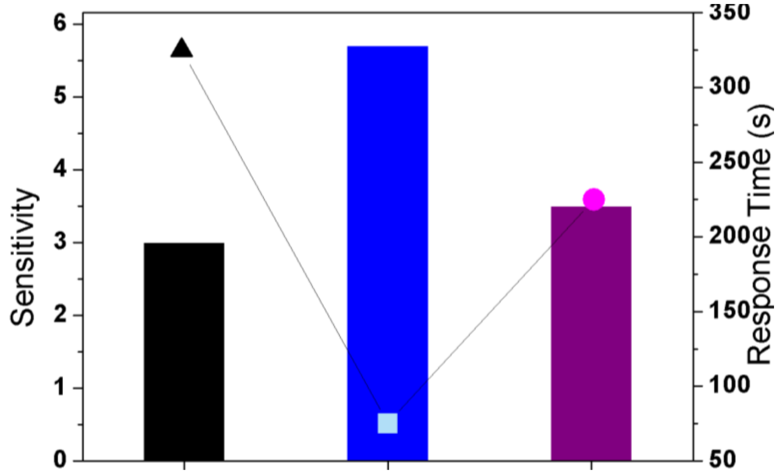
2b) Nanowire Array NO_2 Sensors: Mono-wavelength photo-illumination mode





- Ultraviolet light and blue light can enhance the recovery and response rate obviously.
- 100% Larger response was observed in Blue light mode in the subsequent cycles.

Zhang, Gao et al., *in preparation*.

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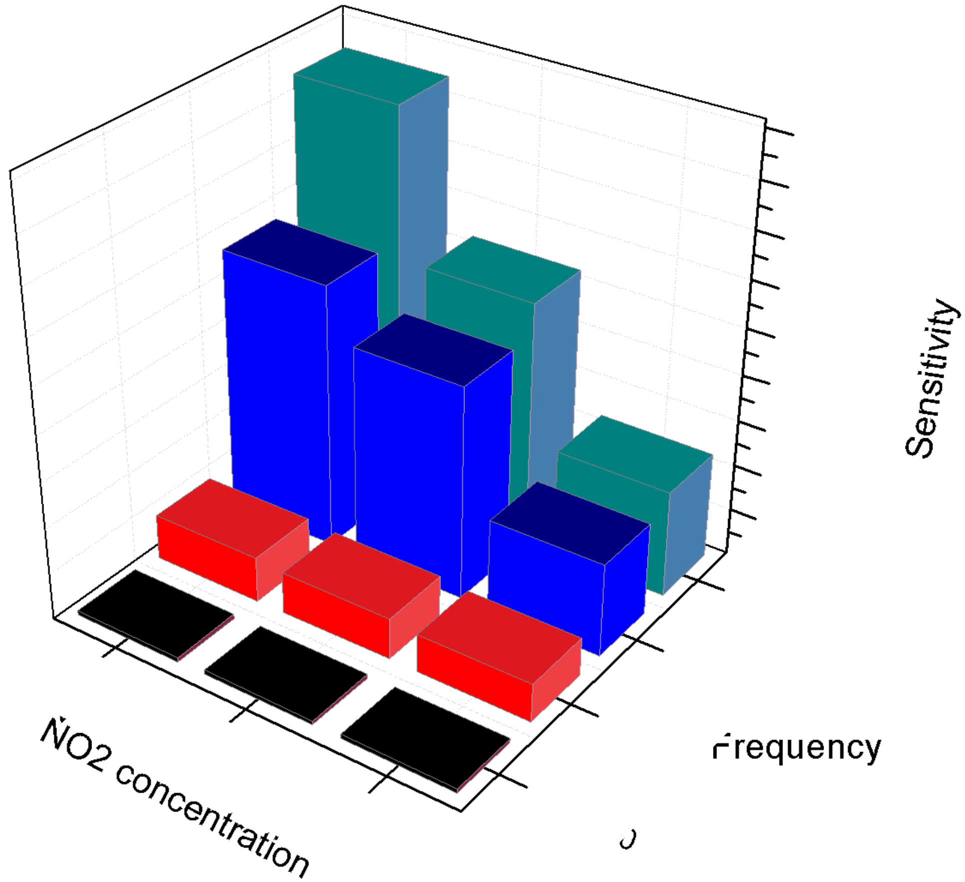
2c) Nanowire Array NO_2 Sensors: Surface impedance mode



- In difference frequency, the response towards NO_2 are significantly different and the response decrease with the increase of frequency.

Zhang, Gao et al., *in preparation*.

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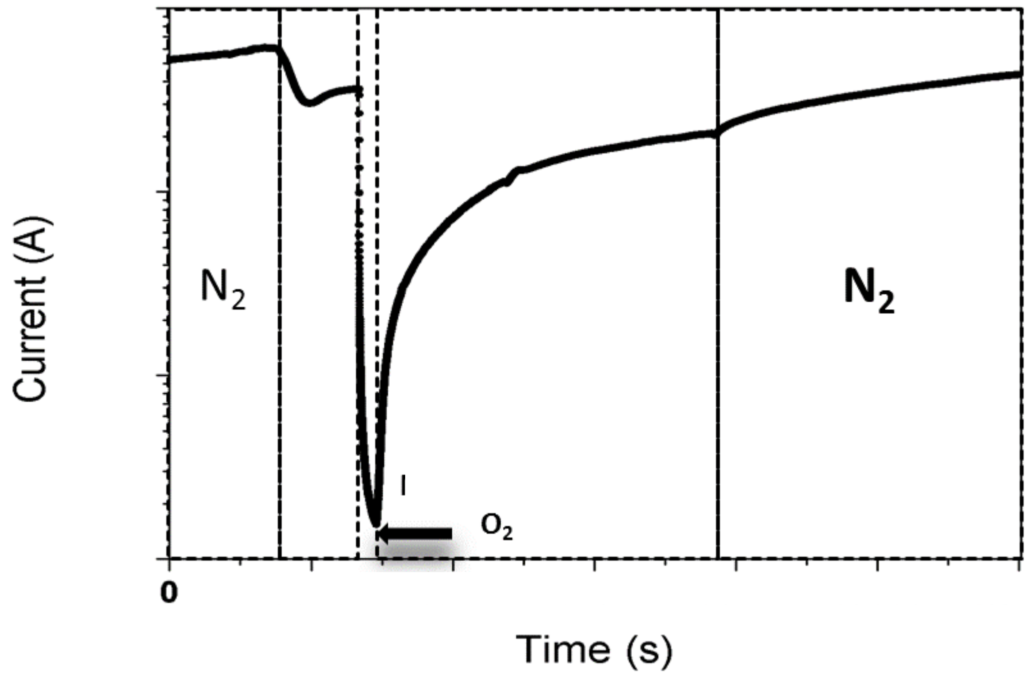
3) Nanowire Array NO_2 Sensors: Selectivity of gas sensor in mixture gases



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

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

Zhang, Gao et al., *in preparation*.

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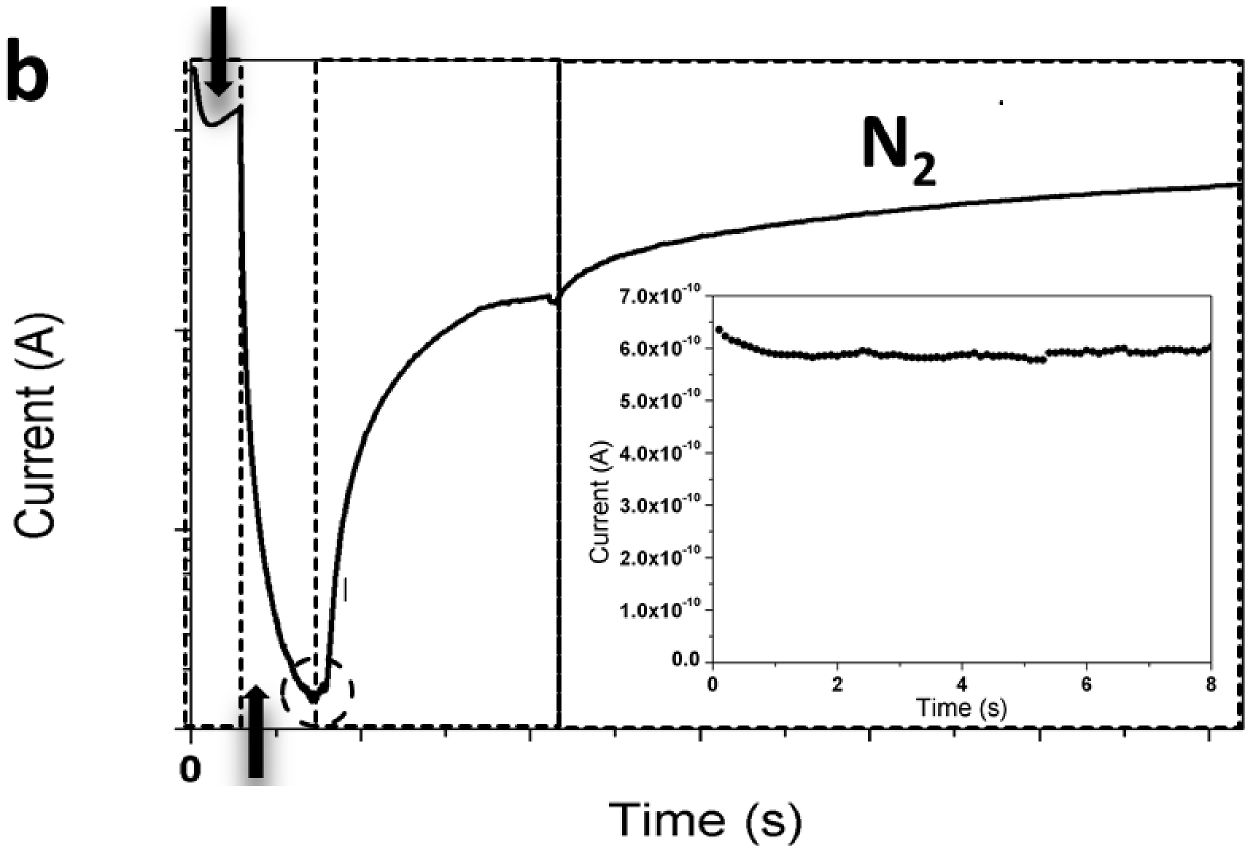

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Conclusions and Future work

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 hybrid and electrical sensitizing effect of perovsksite nanoparticle over nanowire array sensors, respectively.
3) Enhanced sensor performance was achieved through applying three modes including resistance, photocurrent and surface impedance on nanowire sensors.
4) Finally, mixture gas stream was applied to nanowire array sensors, which revealed a good selectivity of NO_2 over CO and O_2.

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;
c) Further study of nanowire sensors with multiple sensing modes upon mixture gas stream at high temperature.

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Thank you !

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