3D printing and laser curing of Al/α-Fe_2O_3 nanothermites for gas and strain sensing

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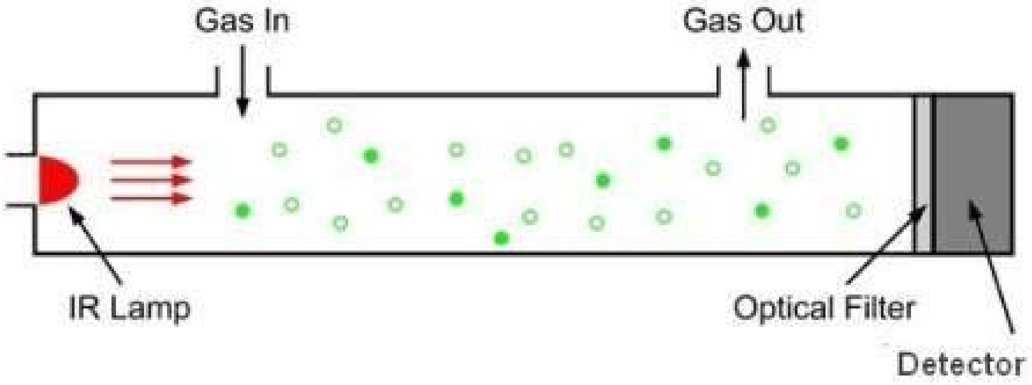
THE UNIVERSITY OF TENNESSEE KNOXVILLE

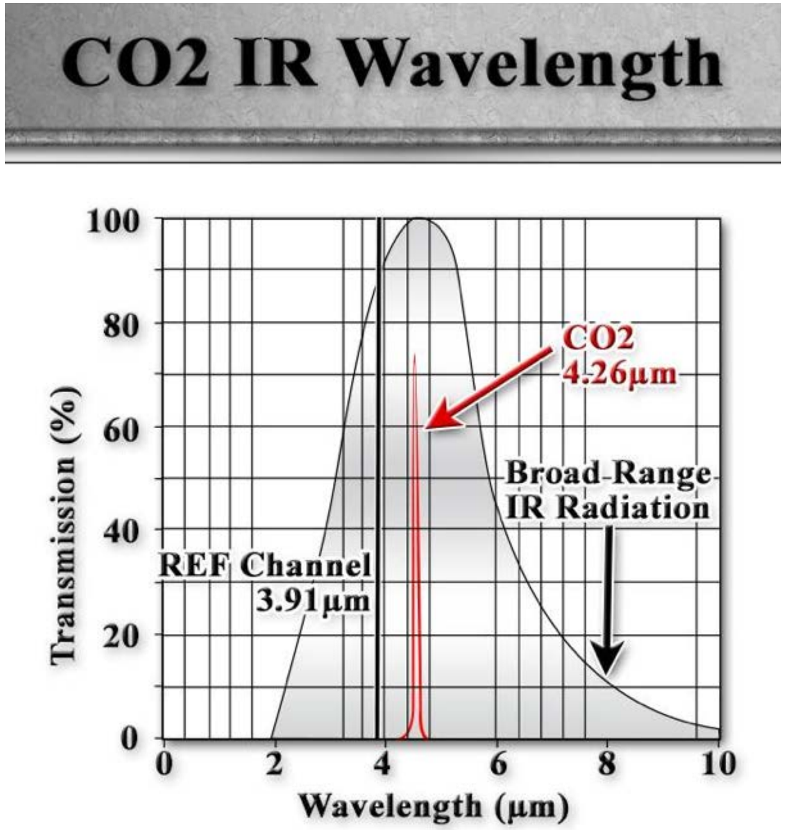
HENDERSON, NV 24 – 27 JUNE
NSMMS CRASTE 2019
NATIONAL SPACE & MISSILE MATERIALS SYMPOSIUM
COMMERCIAL AND GOVERNMENT RESPONSIVE ACCESS TO SPACE TECHNOLOGY EXCHANGE

Outline

1. Introduction
2. State of-the-art
3. Sensor synthesis and measurement
4. Results and Discussion
5. Conclusion

Commercial CO2 Sensors





- An infrared (IR) lamp directs waves of light through a tube filled with a sample of air
- An IR light detector and measures the amount of IR light that hits it.
- IR spectrum of each molecule is unique, it can serve as a signature or "fingerprint" to identify the CO2 molecule.

https://www.co2meter.com/blogs/news/6010192-how-does-an-ndir-co2-sensor-work
https://www.dwyer inst.com/articles/?Action=View&ArticleID=49

Commercial CO2 Sensors

NDIR CO2 Sensor

97 x 20 x 17 mm (LxWxH)
400ppm-10000ppm
Accuracy ± 50ppm+ 5% reading value

Gravity Analog Infrared CO2 Sensor

37mm x 69mm
0 ~ 5000ppm
Accuracy: ± (50ppm + 3% reading)

- **Large size**
- **non-flexible due to working principal**
- **large measurement error （±5ppm + 5%）**

https://sandboxelectronics.com/?product=100000ppm-mh-z16-ndir-co2-sensor-with-i2cuart-5v3-3v-interface-for-arduinoraspeberry-pi
https://www.robotshop.com/en/gravity-analog-infrared-co2-sensor-arduino.html

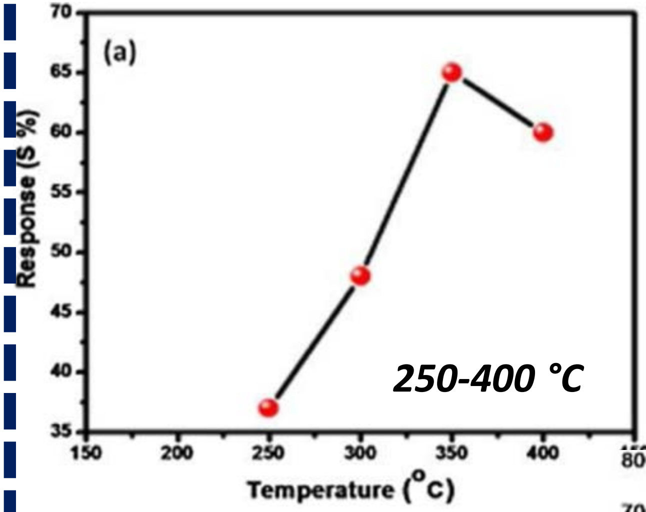
Electrochemical CO2 sensors

- **Metallic oxide CO_2 sensor**
  - ZnO Thin Film sensor
  - Zinc Oxide Nanoflakes
- **Composite Material CO_2 sensor**
  - $MgFe_2O_4$
  - $Li_7La_3Zr_2O_{12}$
- **Hybrid Material CO_2 sensor**
  - π-Conjugated Amine (NBA)−ZnO
  - TiO_2–PANI Nanocomposite Thin Film

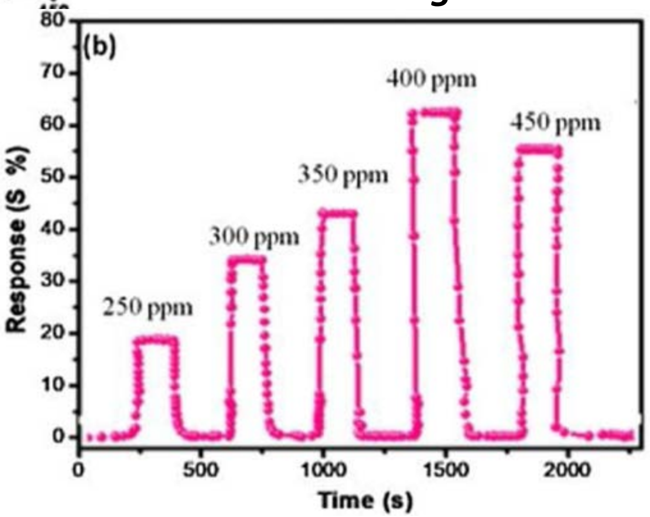
Metallic oxide CO_2 sensor

ZnO Thin Film sensor

Operation Temperature



Detection Range

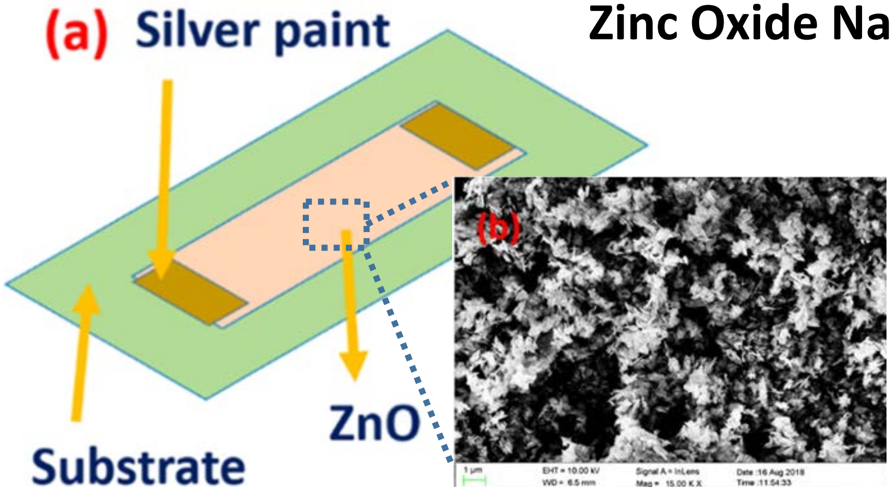


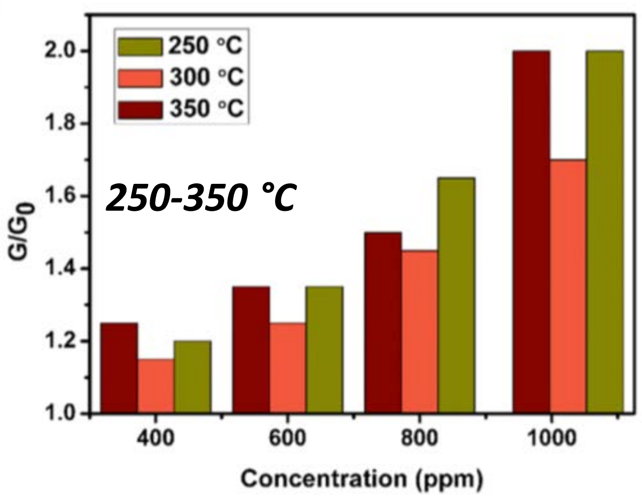
SEM images of ZnO thin films

Actuators B: Chemical 274 (2018): 1-9.

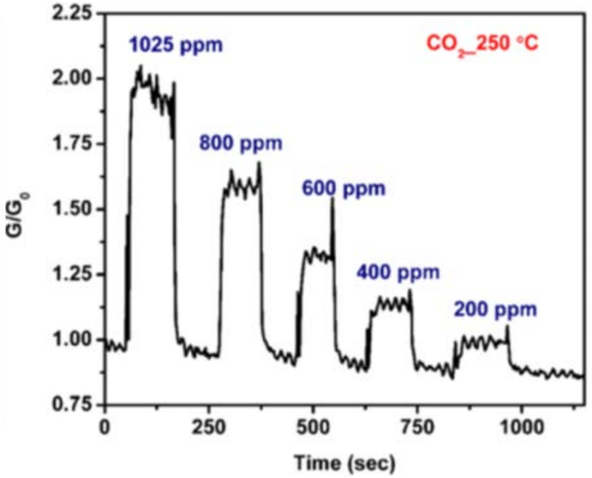
ACS Applied Nano Materials 2.2 (2019): 700-706

Zinc Oxide Nanoflakes





Operation Temperature



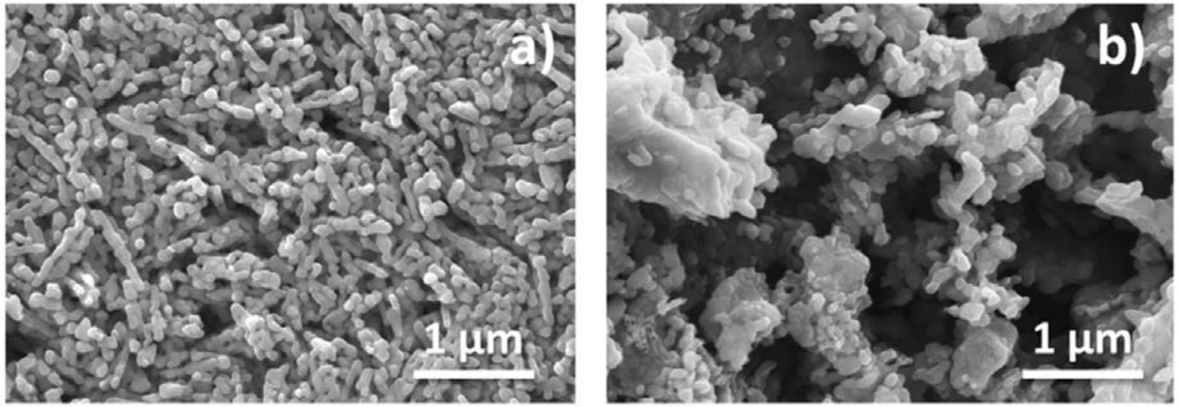
Detection Range

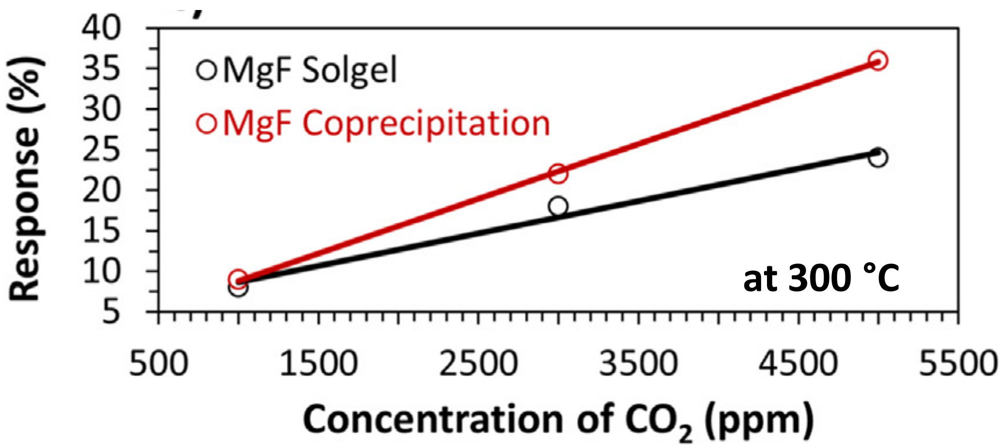
Composite Material CO_2 sensor

$MgFe_2O_4$

MgF Coprecipitation

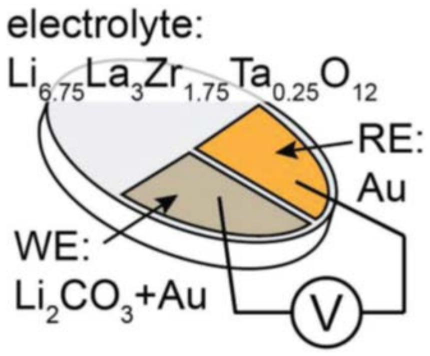
MgF Solgel

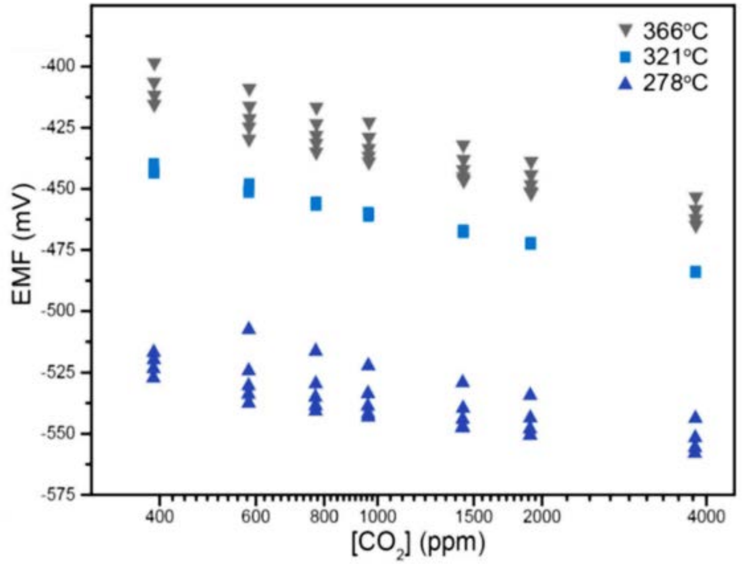


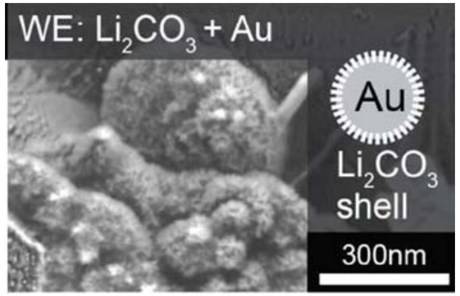


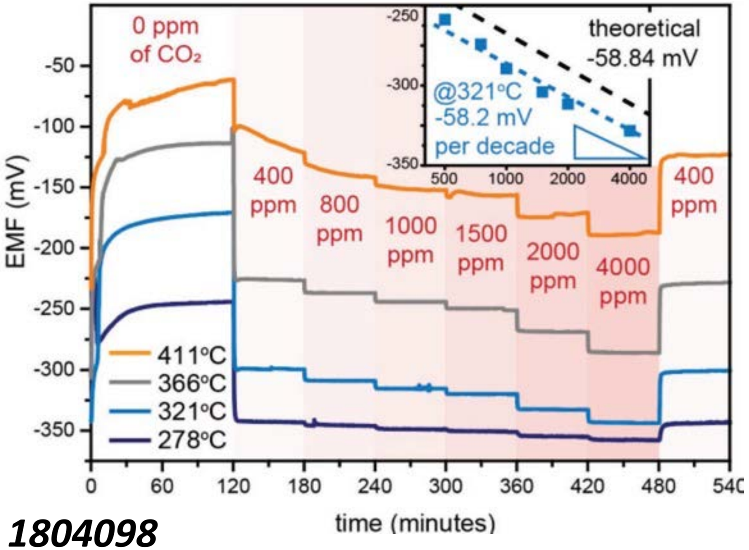
Ceramics International 44.15 (2018): 18578-18584

$Li_7La_3Zr_2O_{12}$









Adv.Materials 30.44 (2018): 1804098

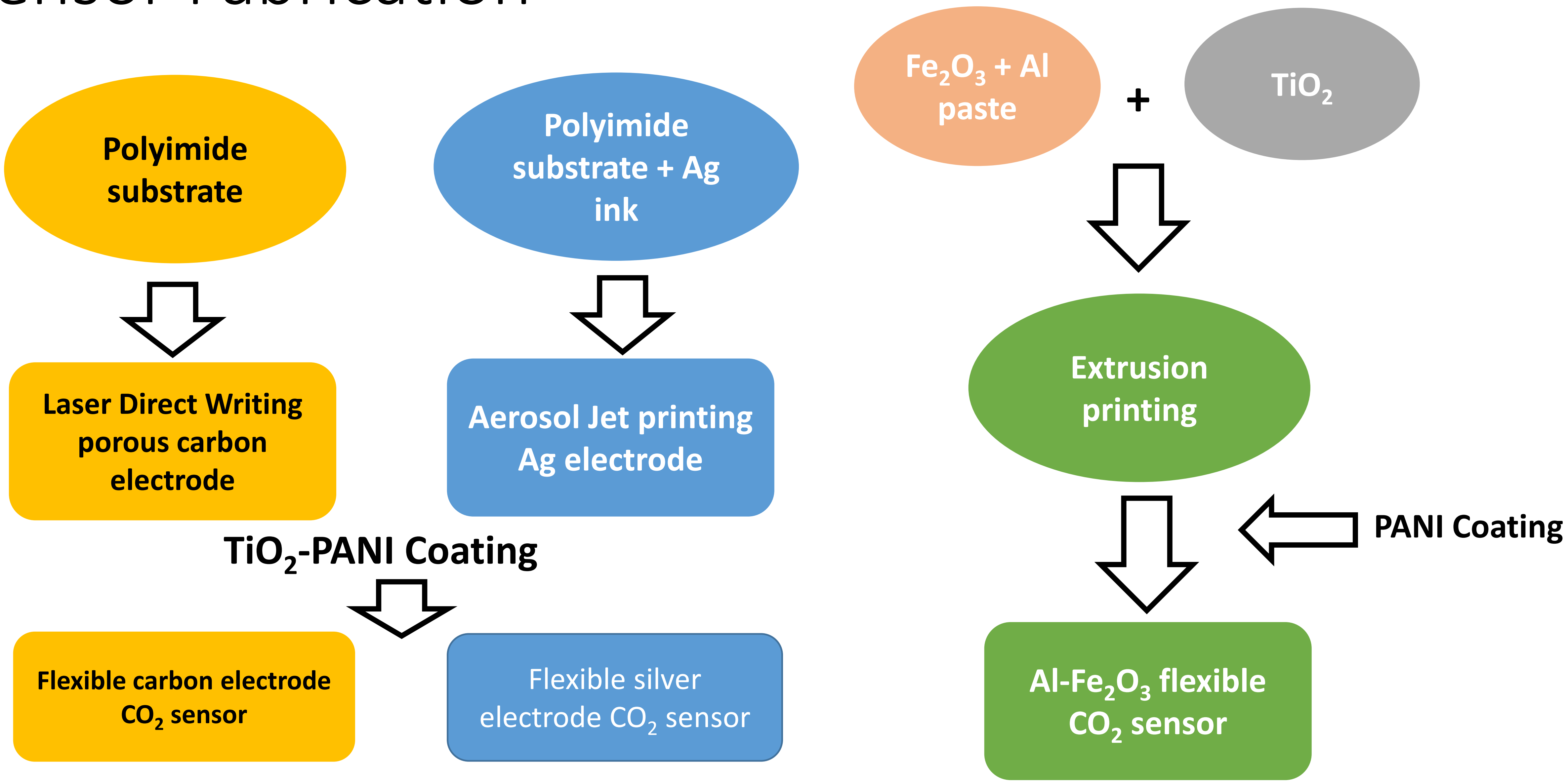
State of-the-art sensor types

Material	Operating temp (°C)	CO_2 detection range（ppm）	Response (%)	Reference
ZnO base	250-450	200-1500	65	[1,2]
MgFe2O4	300	1000-5000	35	[3]
NASICON	200-400	100-2000	>90	[4,5]
Li7La3Zr2O12	270-360	350-4000	>90	[6]
(NBA)−ZnO	Room temperature	500-10000	9-39	[7]
TiO2-PANI	**Room temperature**	**1000**	**53**	**[8]**

[1] Actuators B: Chemical 274 (2018): 1-9.
[2] ACS Appl. Nano Mater 2.2 (2019): 700 706.
[3] Ceramics International 44.15 (2018) 18578-18584
[4] Sens. Actuators, B 2000, 64, 102.
[5] Electrochem. Soc. 2008, 155, J117.
[6] Adv.Materials 30.44 (2018): 1804098
[7] ACS Appl. Nano Mater 1.12 (2018): 6912 6921
[8] J. Mater. Sci. Mater. Electron. 27.1 (2016): 11726-11732

- **Low operation temperature**
- **High response show a potential for high sensitivity and large detection range**

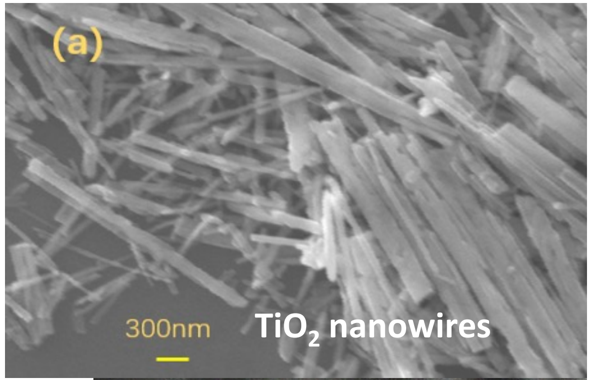
Sensor Fabrication

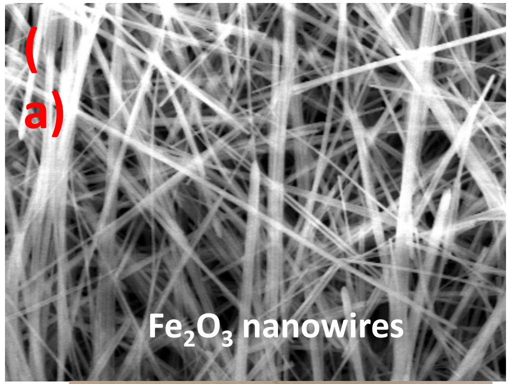


Nanomaterial fabrication

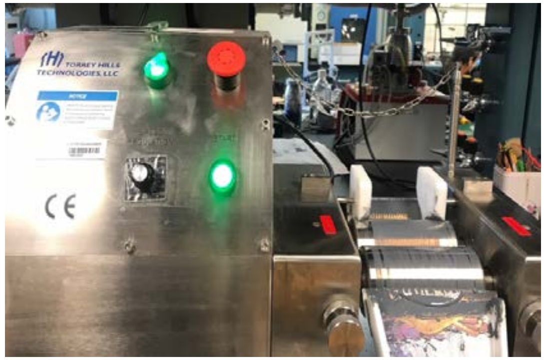
Material fabrication:

- TiO_2 nanowire
- Fe_2O_3 nanowire
- Graphene
- Al-Fe_2O_3 paste





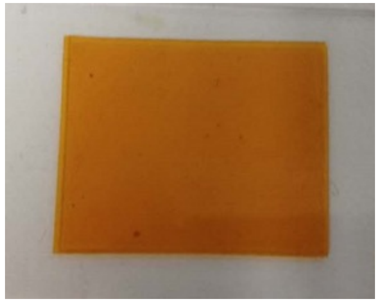
Pre-mixing Al paste & Fe2O3 nanowires

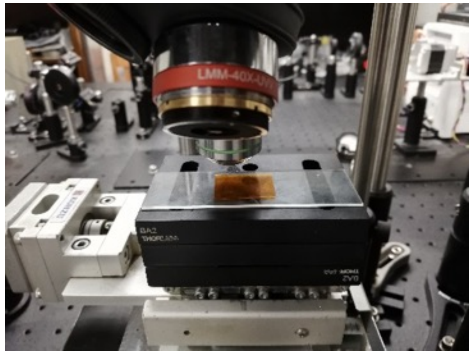


Three-roll milling paste

Al-Fe_2O_3 paste

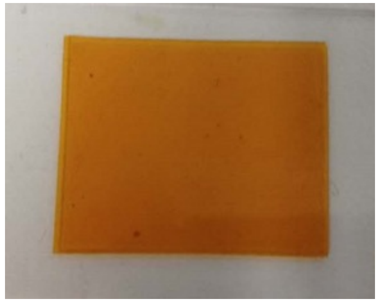
Sensor Deposition





Laser direct writing

Carbon electrode CO_2 sensor



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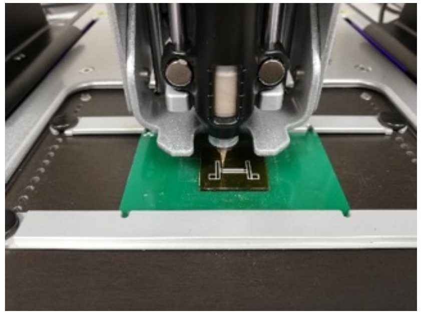
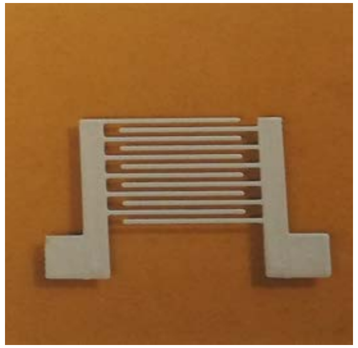
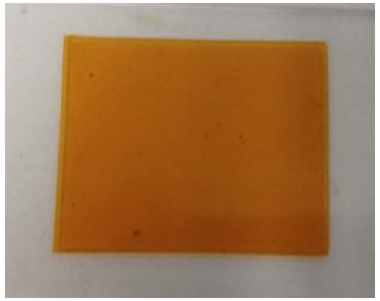


voltera printing



Silver electrode CO_2 sensor



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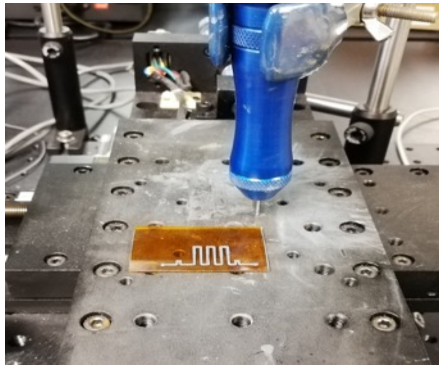
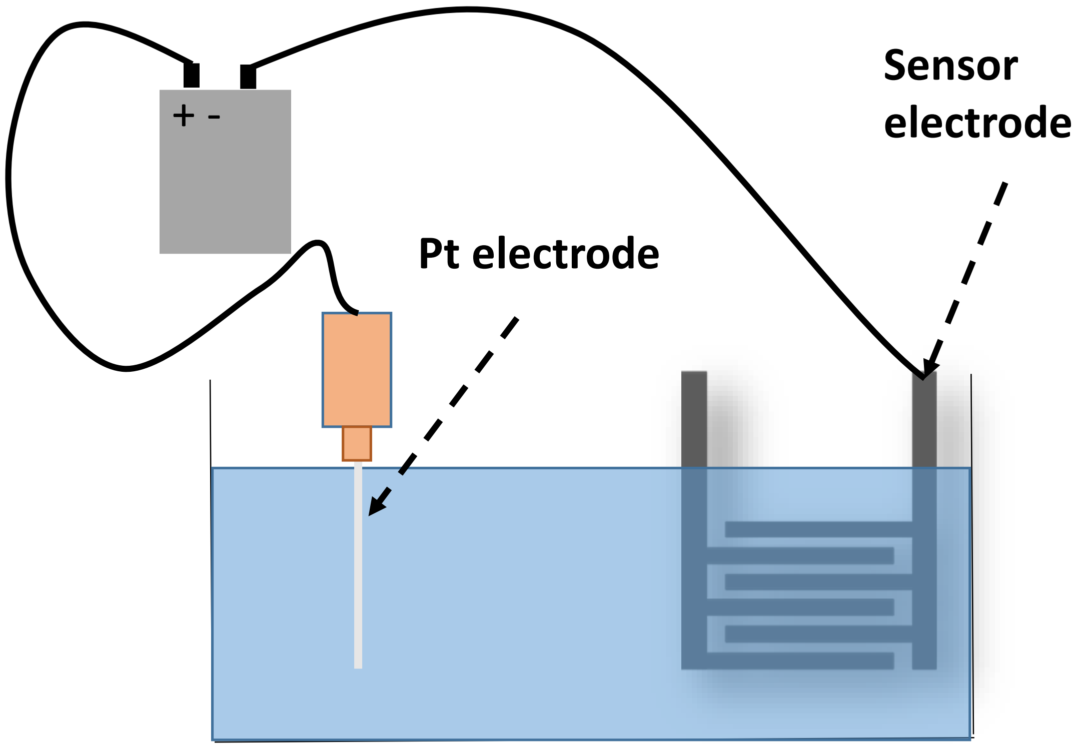


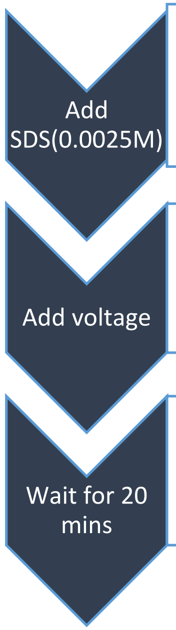
extrusion printing

Al-Fe_2O_3 electrode CO_2 sensor

Surface activation

Coating techniques: ***electro-deposition***





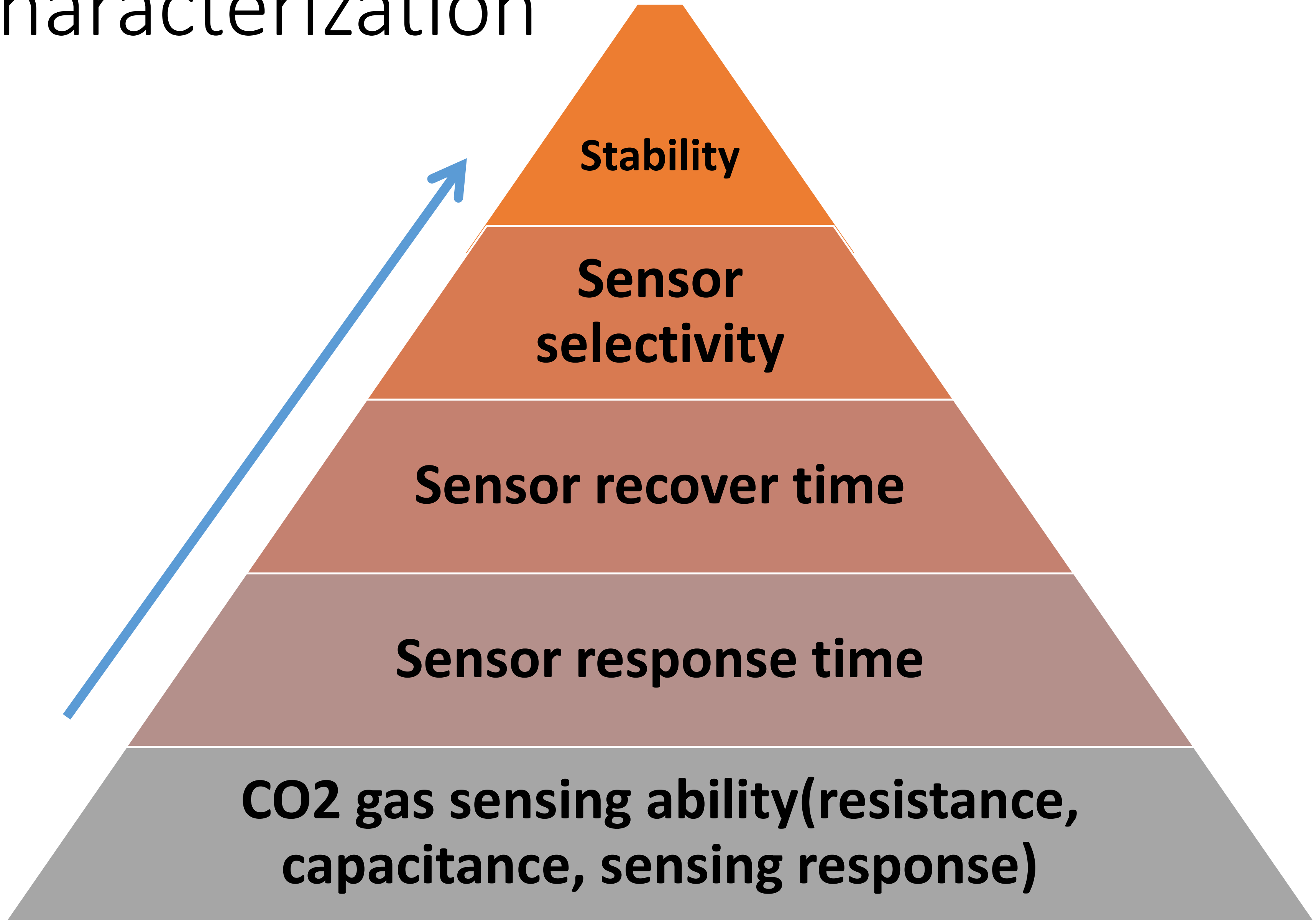
- **40 mg TiO_2**
- **20ml electrolyte (ethanol & acetylacetone 1:1)**

- **100V / cm**
- **Pt for anode and sensor for cathode**

- **Use water wash sensor surface to remove the stick TiO_2**

SEM after coating (coming soon)

Sensor characterization



Sensor measuring

Two methods to measure CO2 gas sensing ability:

multimeter

electrochemical workstation

+

Resistance method:

Use multimeter measure the resistance change under different CO2 concentration

Capacitance method:

Use electrochemical workstation measure the capacitance change

+

Sensor measuring

Sensing response

Typically, sensor response data will be represented as a relative response:

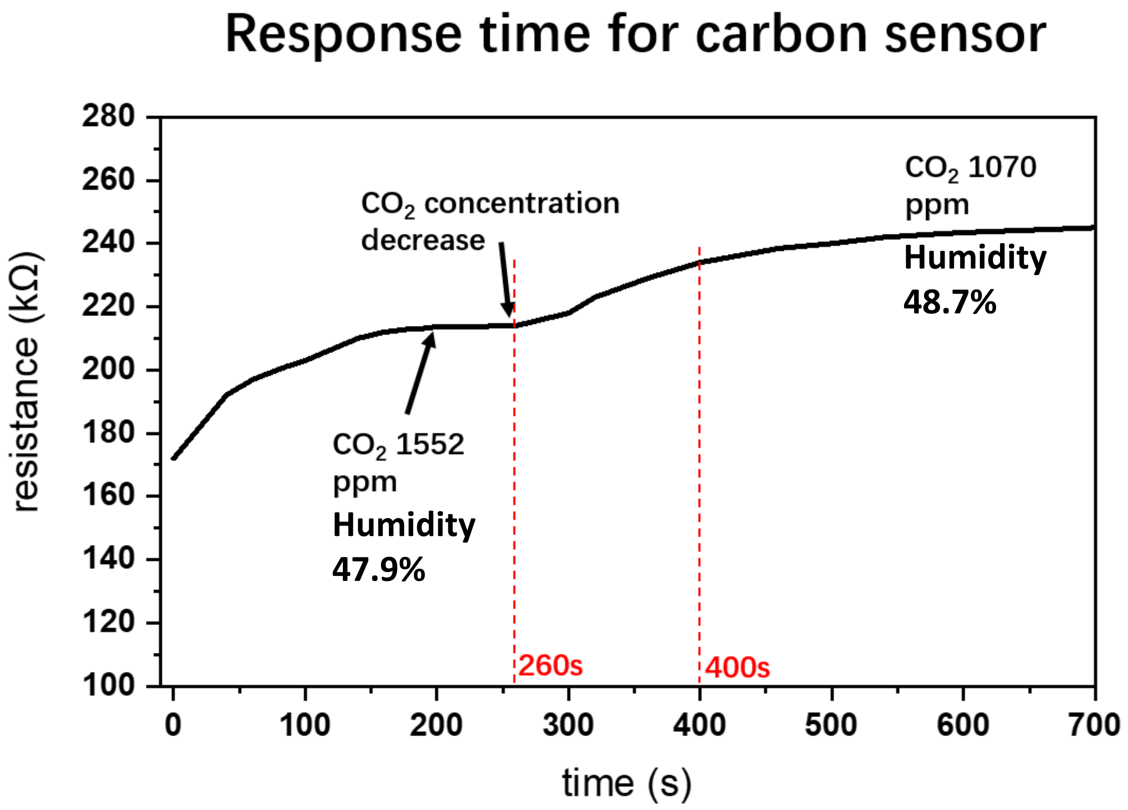
- Relative Sensor Response = (X - Y) / Y, where:
- X = the maximum value of your sensor's measured response parameter in the presence of the analyze.
- Y = the initial value of your sensor's measured response parameter in the absence of the analyze.

In this experiment, the sensing response value ***S*** is defined as the ***change in resistance*** in the presence of gas (R_g) to the resistance in the presence of air (R_a):

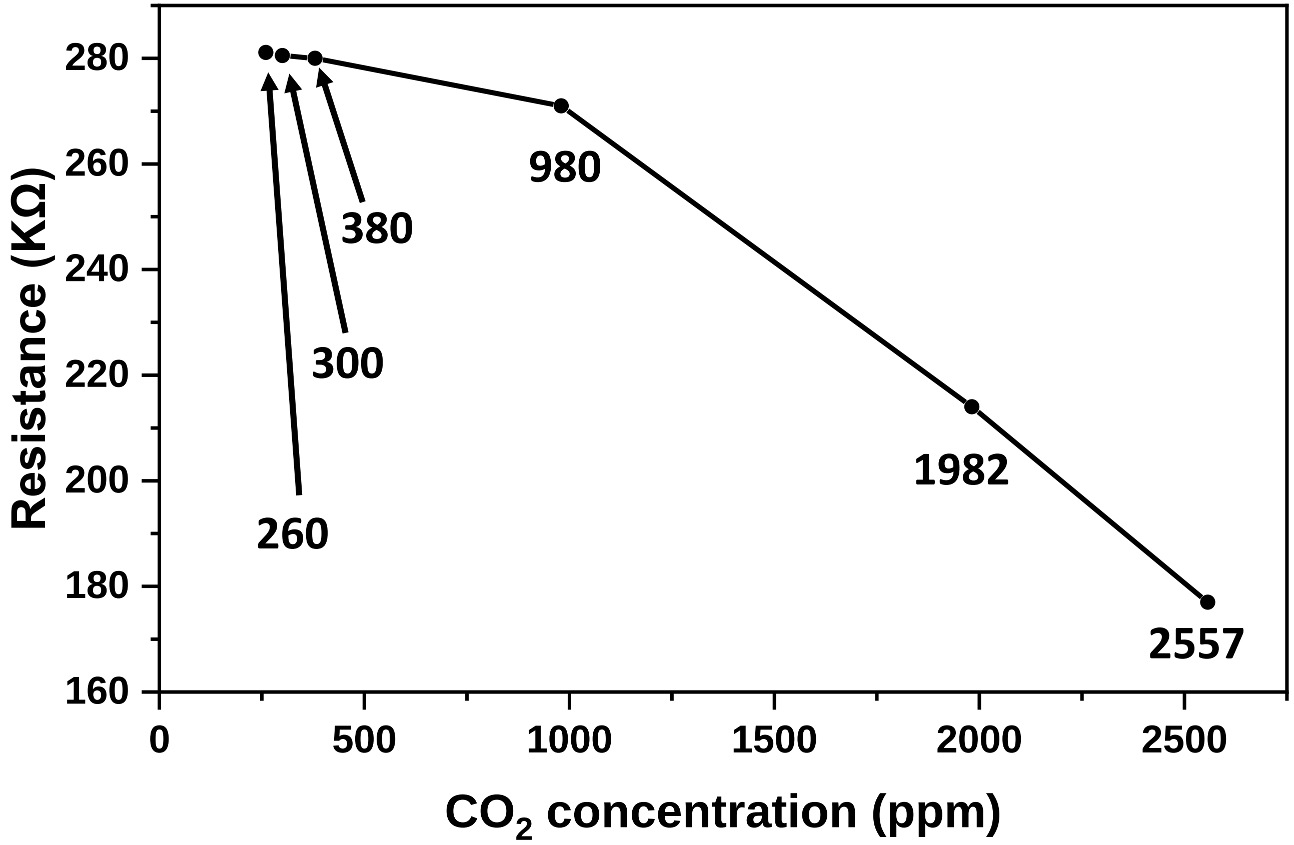
$$S = \frac{R_g}{R_a}$$

Sonker, R. K. , Sabhajeet, S. R. , & Yadav, B. C. . (2016). *Journal of Materials Science: Materials in Electronics*.

Results: Carbon electrode sensor



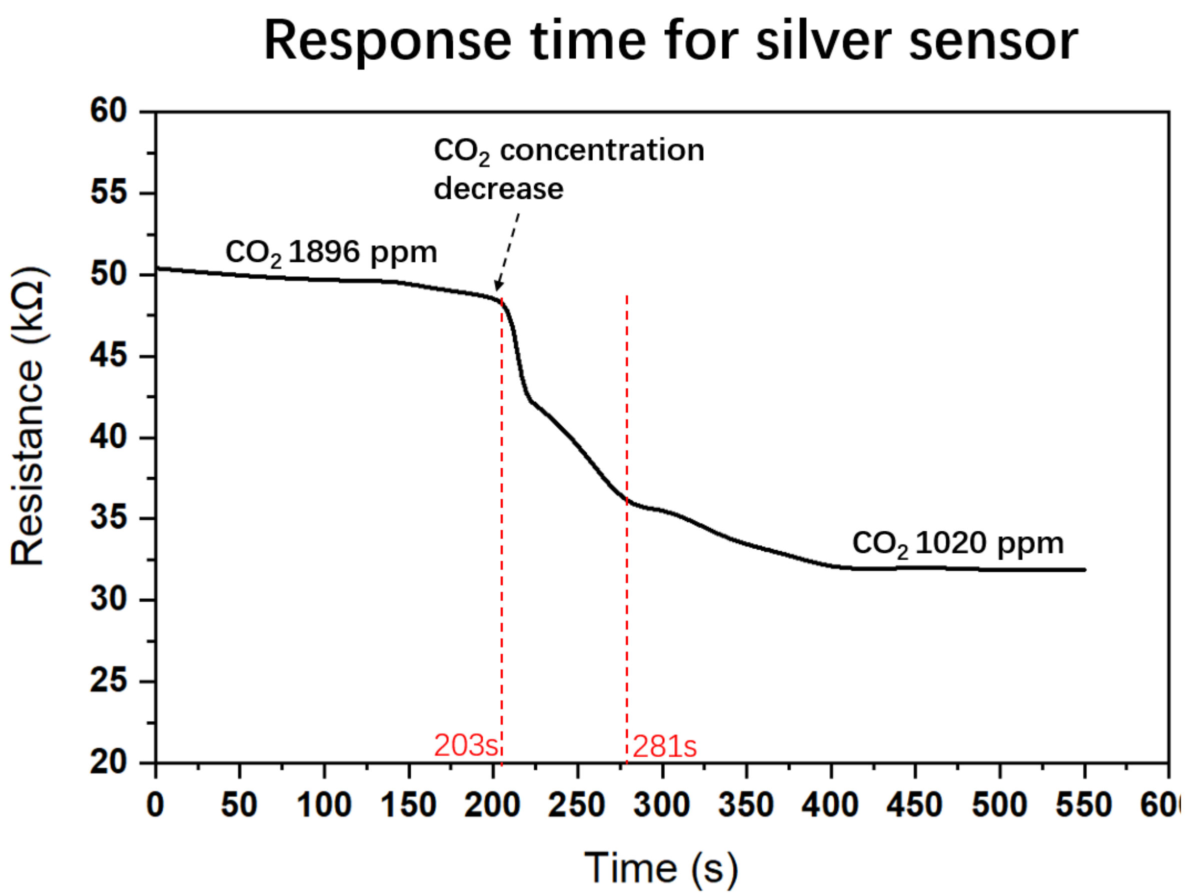
Typical resistance change for CO2 at 1552 ppm

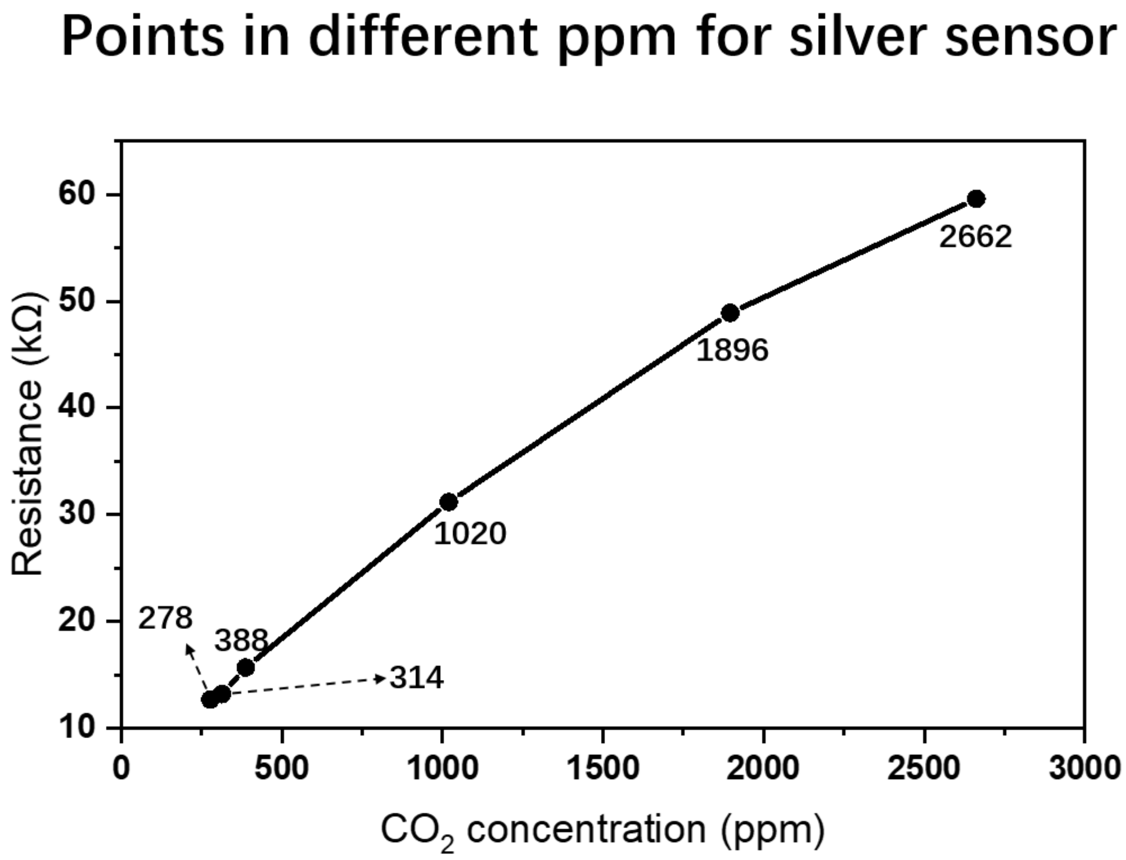


TiO2/C/polyaniline resistance as a function of CO2 concentration

For carbon sensor with TiO_2 and polyaniline, as the CO_2 concentration raises up the resistance will decrease, the resistance change is nearly linear function of the CO_2 ppm.

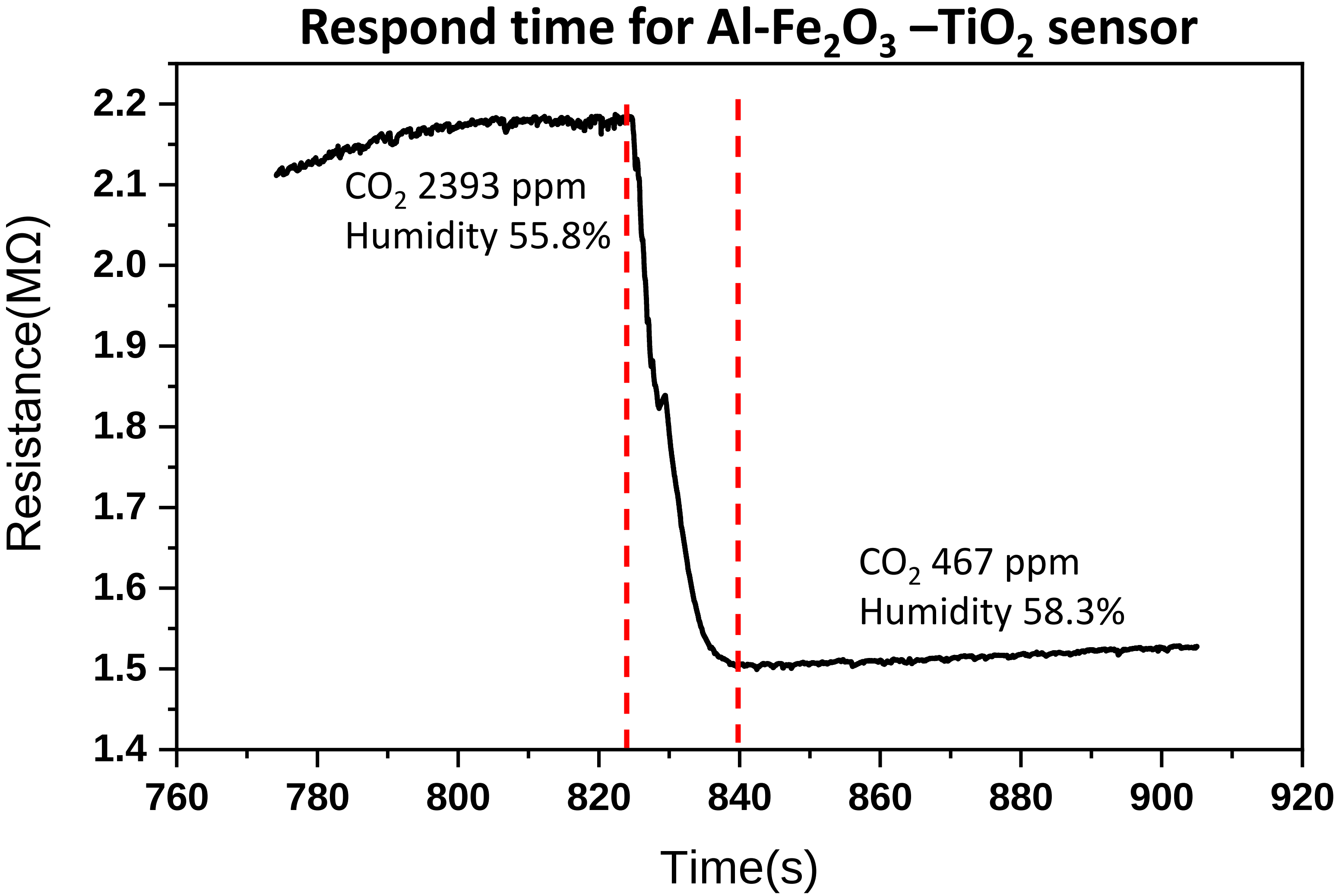
Results: Silver electrode sensor



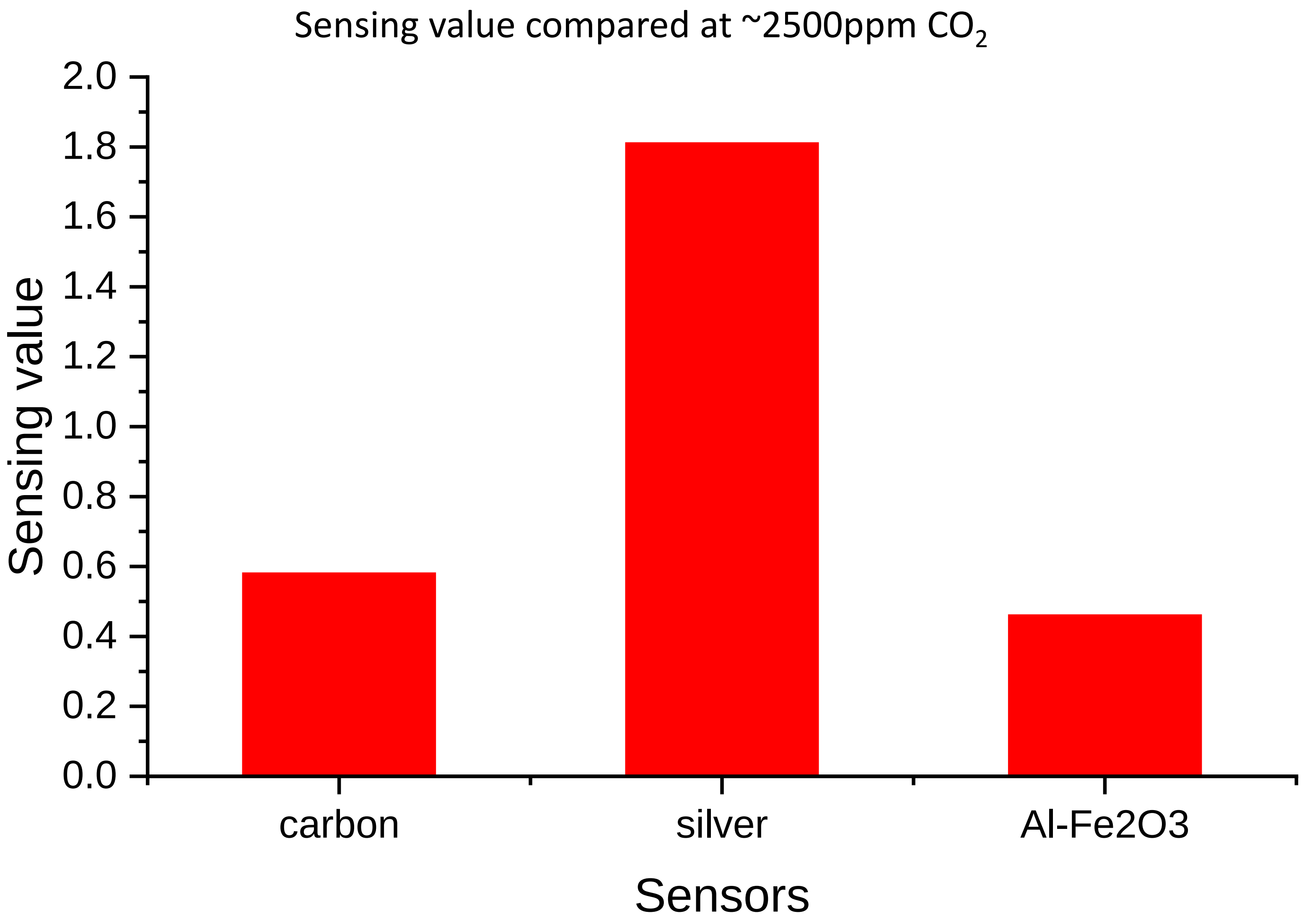


For silver sensor with TiO_2 and polyaniline, as the CO_2 concentration raises up the resistance also increases. The resistance change is a nearly linear function of the CO_2 ppm. The response speed of a silver sensor is faster than a carbon sensor. The recovery time is 32 s.

Results: Al-Fe_2O_3 – TiO_2 sensor

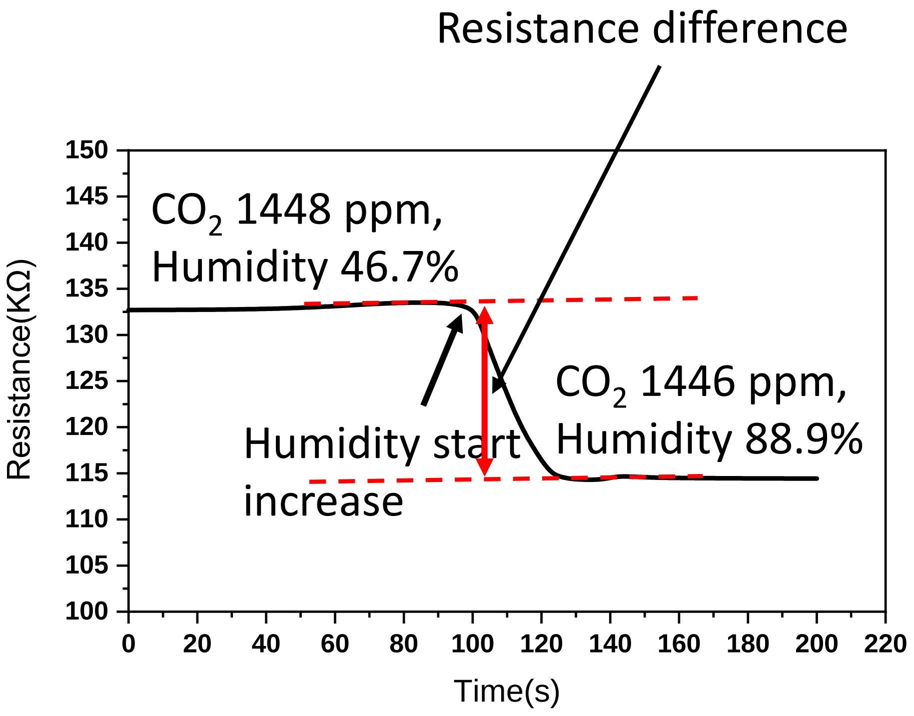


Results: Relative sensing response values



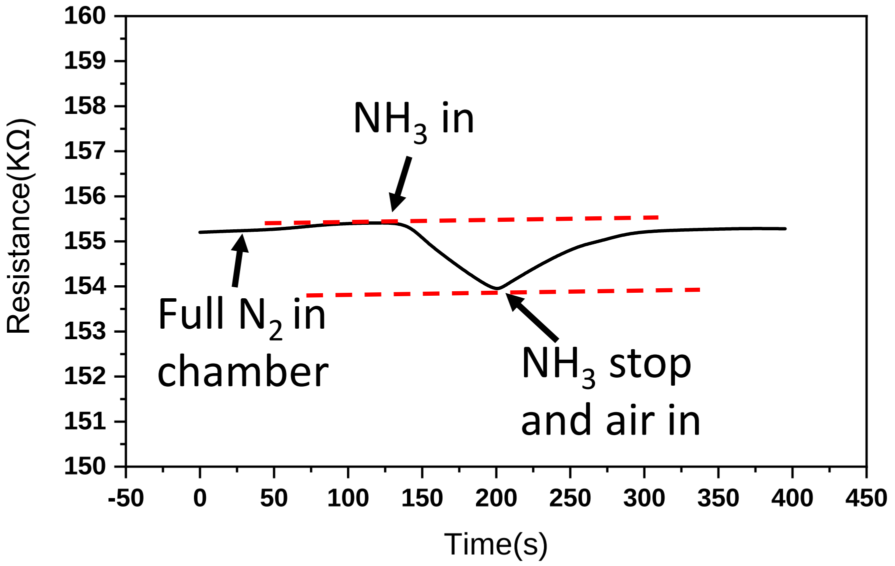
Sensor humidity interference

- Carbon electrode sensor:



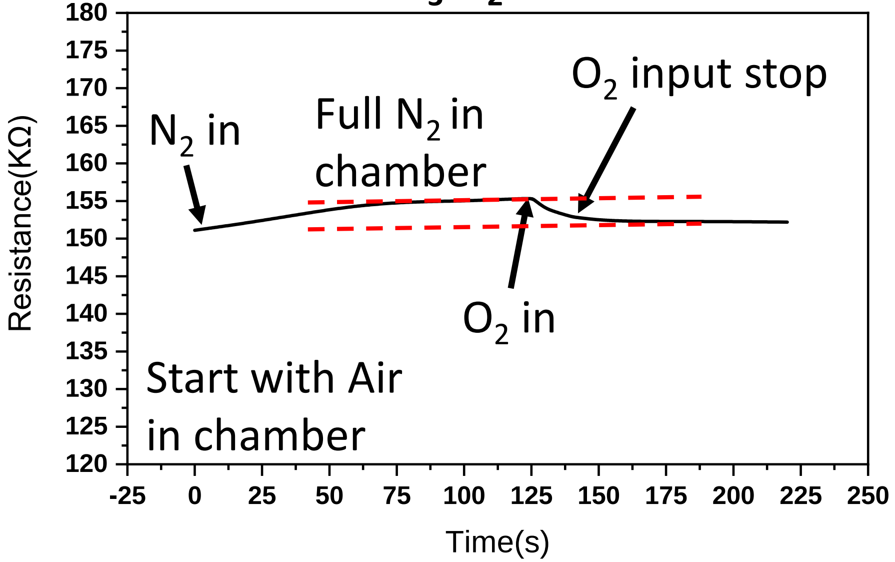
Humidity test

Resistance difference =
132.7-114.3 = 18.4KΩ



$NH_3 \cdot H_2O$ test

Resistance difference =
154.5-153.9 = 0.6KΩ

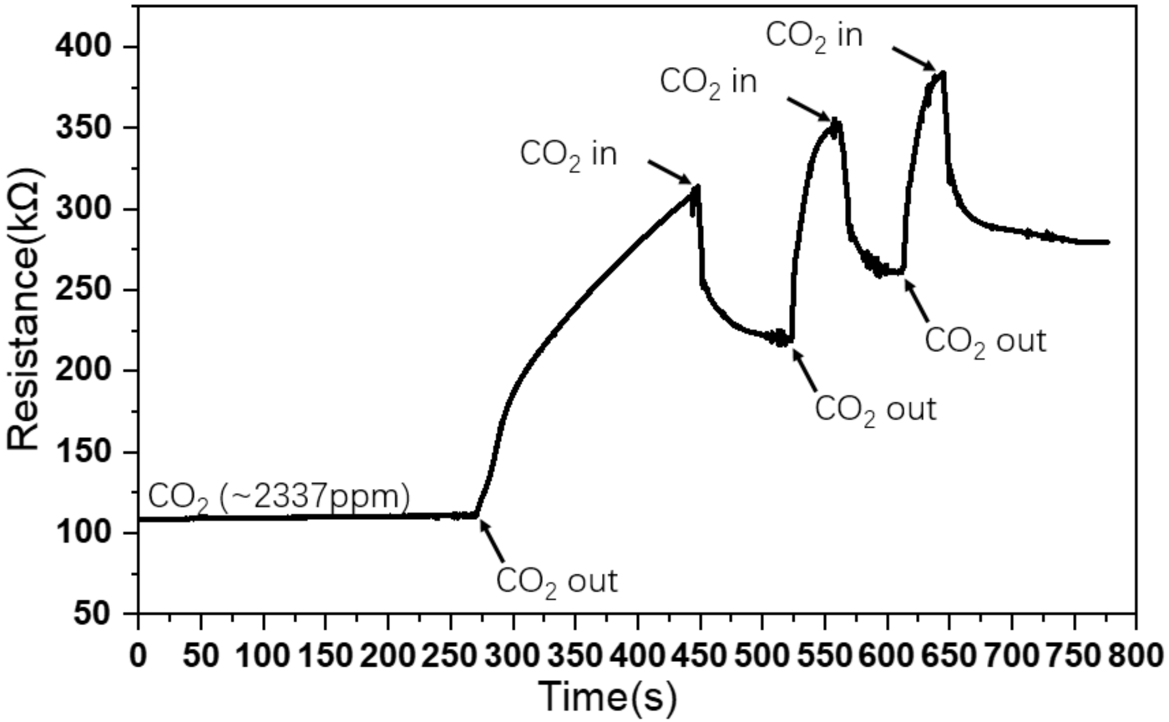


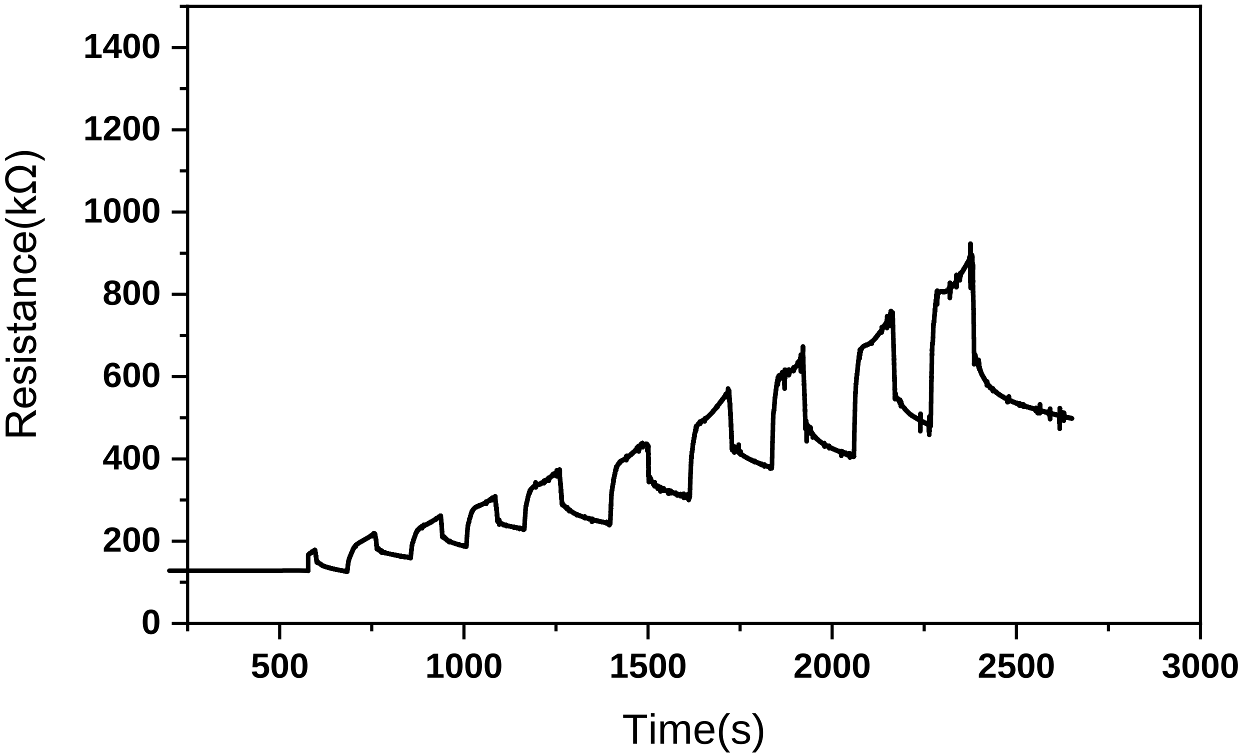
Oxygen test

Resistance difference =
154-152.2 = 2.8KΩ

Sensor stability

Carbon sensor recover time





Conclusions

- We have successfully developed a CO_2 sensor on polyimide substrates by integrating 3D printing, laser writing and laser curing. Three electrodes are tested with carbon, silver and Al/Fe_2O_3.
- Nano-TiO_2 functionalized sensors display a detection of limit down to 280 ppm CO_2 with a detection limitation down to 300 ppm, a response time of around 1 min, and a recovery time of 2-4 min at room temperature. These data are better than a bulky commercial sensor.
- The sensor displays high selectivity at a wide relative humidity and temperature range.
- The relevant fabrication techniques can be applied to other gas sensing by changing different nanoscale sensing media.

Acknowledgement

- Funding: NASA-MSFC-UTK CAN Project (80MSFC19M003)

- Collaborators: Dr. Josh Pooran (ORNL)
  Dr. Jayne Wu (UTK-EECS)