MicroNano 2023 International Conference

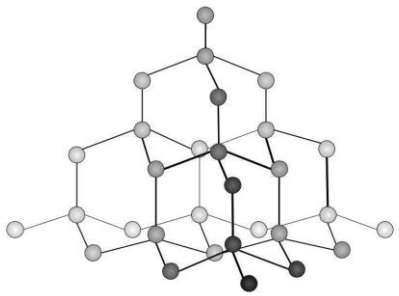
Toward selective detection of H_2S gas by AuNP-functionalized carbyne-enriched based sensors

L. A. Panes-Ruiz, L. Riemenschneider, B. Ibarlucea, G. Cuniberti

Chair of Materials Science and Nanotechnology

Carbon Allotropes

sp^3 Hybridization

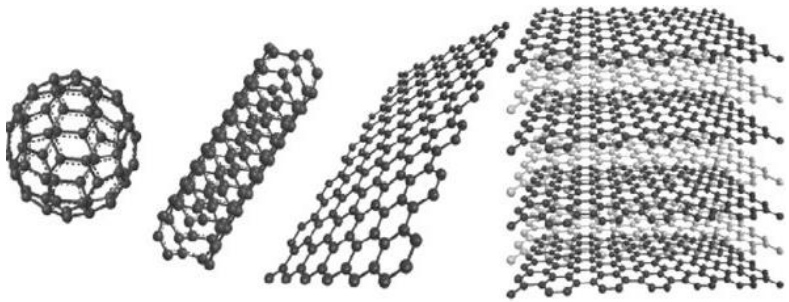


Diamond
Diamond like carbon (DLC)

- High thermal conductivity (2000 W/mK)
- High electrical resistivity (100 GΩ·m)
- High hardness (100 GPa)
- Elastic Modulus (1000 Gpa)
- Broad optical transparency

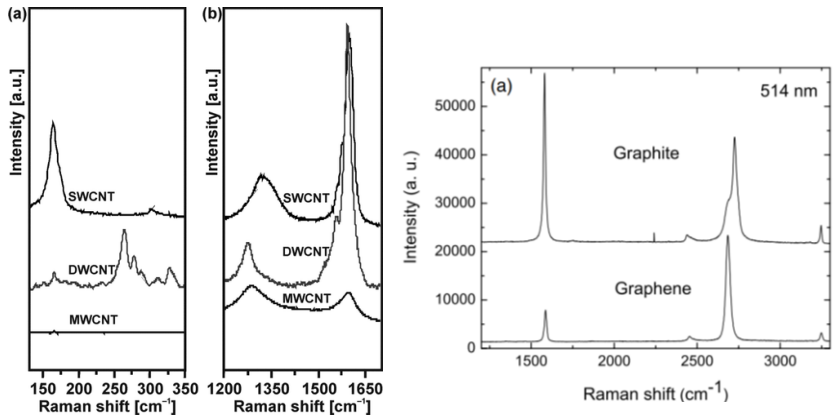
Rajak, D.K. et al. *Appl. Sci.*, **11**, 4445,(2021)

sp^2 Hybridization



0D Fullerene **1D CNTs** **2D Graphene** **3D Graphite**

Extensively studied and characterized

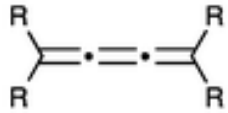


Zhou et al. *Nanoscale Research Letters*, **9:26** (2014)

sp Hybridization

Polyyene

Cumulene



Carbyne
Linear Carbon Chains (LCC)

Predicted in the 1960s:

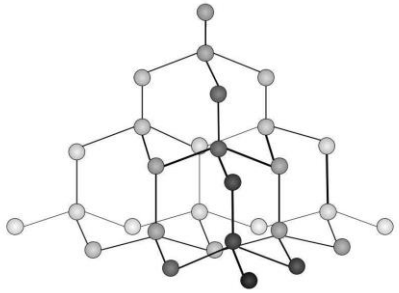
- Stronger than diamond
- Extreme tensile stiffness
- Tunable mechanical properties
- Unstable

Unexplored
Experimental synthesis
and characterization

De Boer et al *J. Phys. Chem. C* , **125,** 15, 8268−8273 (2021)
Januszewski. A., et al. *Chem. Soc. Rev.* **43**, 3184-3203 (2014)

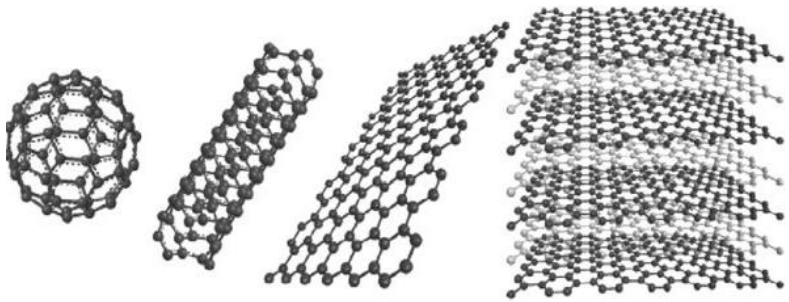
Carbon Allotropes

sp^3 Hybridization



Diamond
Diamond like carbon (DLC)

sp^2 Hybridization

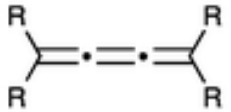


0D Fullerene | **1D CNTs** | **2D Graphene** | **3D Graphite**

sp Hybridization

Polyyene

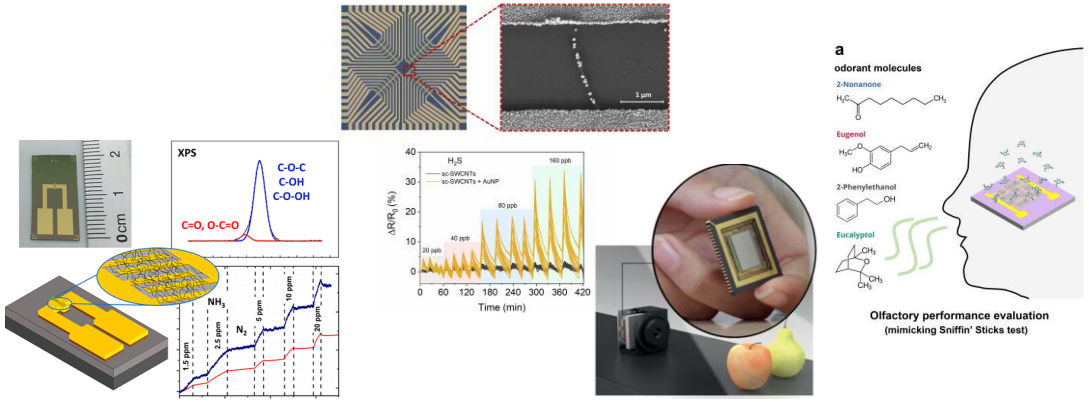
Cumulene



Carbyne
Linear Carbon Chains (LCC)

Electrical-based Gas Sensing Applications

Insulating properties



Panes-Ruiz, et al. *ACS Sens.* 3, 79−86 (2018)

Panes-Ruiz, et al. *Nano Res.* **15**, 2512-2521 (2022)

Huang. et al. *Applied Physics Reviews* **10**, 021406 (2023)

Akinwande, D. et al, *Nature* **573,** 507−518 (2019).

?

Unexplored material for sensing applications

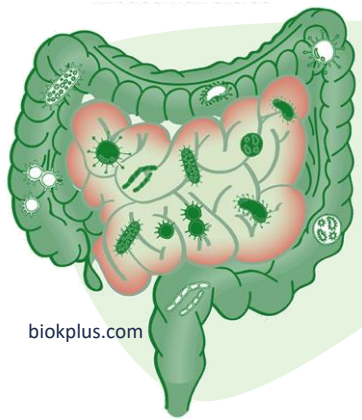
Non-invasive Diagnostics

Small Intestinal Bacterial Overgrowth (SIBO)

Symptoms

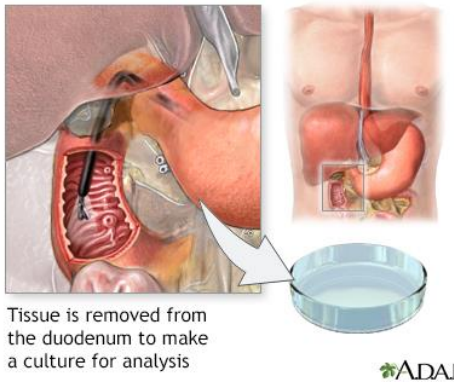
- Abdominal discomfort
- Distention and bloating
- Diarrhea
- Constipation
- Brain fog
- Joint pain

Increase of Sulfate reducing bacteria (SRB)



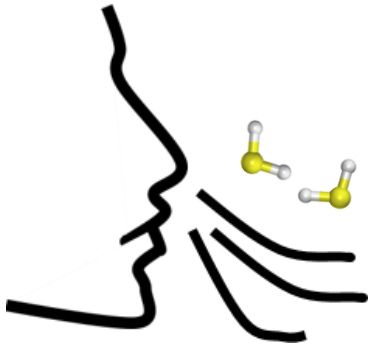
Diagnostics Gold Standards

Small intestinal fluid aspiration (Biopsy)



- Invasive
- High costs
- Inability to culture up to 70% of gut bacteria

Breath Test



- Non-Invasive
- Low costs
- Patient friendly

H_2 < 20 ppm

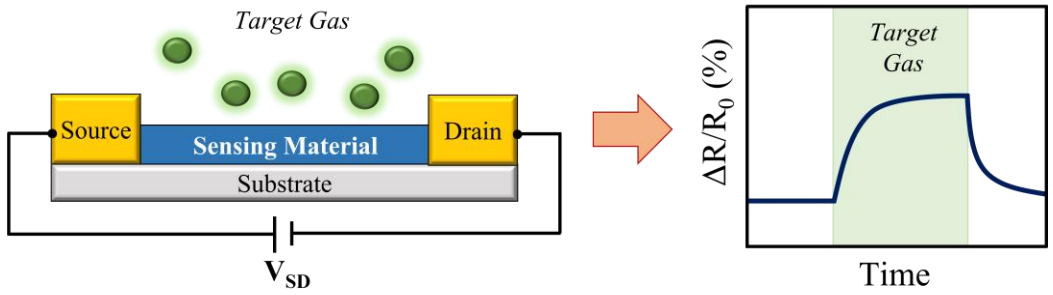
CH_4 < 10 ppm

H_2S < 1 ppm

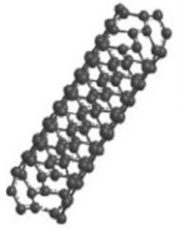
Gourab Dutta Banik et. al. *J. Breath Res.* **10** 026010, (2016)

Selective Detection of H_2S gas

Chemiresistors

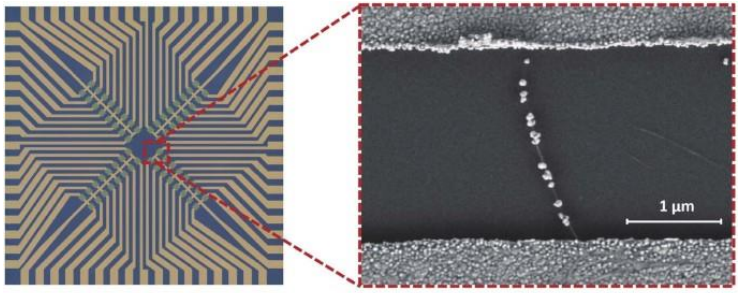


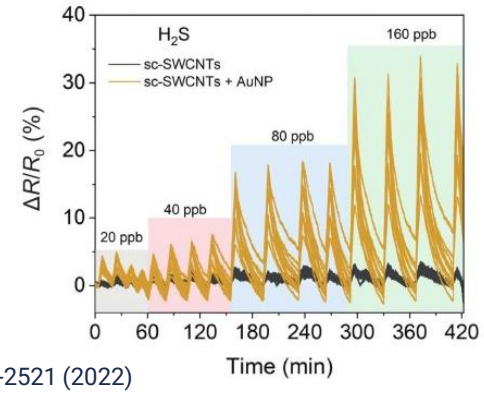
Semiconducting Single-walled Carbon Nanotubes (sc-SWCNTs)



- High surface-to-volume ratio.
- Mechanical stability.
- Low limits of detection (ppb) at room temperature
- Low power consumption.

Multichannel Device AuNP-SWCNTs





Panes-Ruiz, et al. *Nano Res*. **15**, 2512-2521 (2022)

Objectives

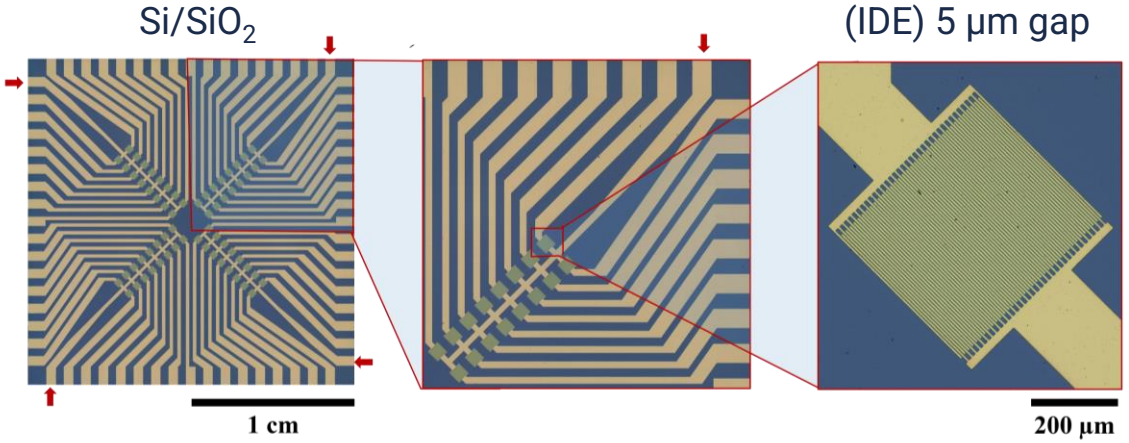
Can **Carbyne** be used as a sensor transducer for improved **H_2S gas** detection?

Tasks

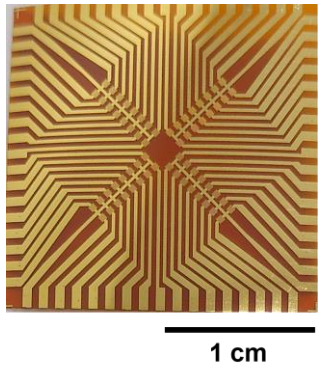
1. Deposition and characterization of carbyne-enriched films.
2. AuNP functionalization.
3. Sensing performance towards low H_2S gas concentrations.

Multichannel Device Fabrication

Standard UV-Lithography and Metal Deposition



Polyimide (Kapton)

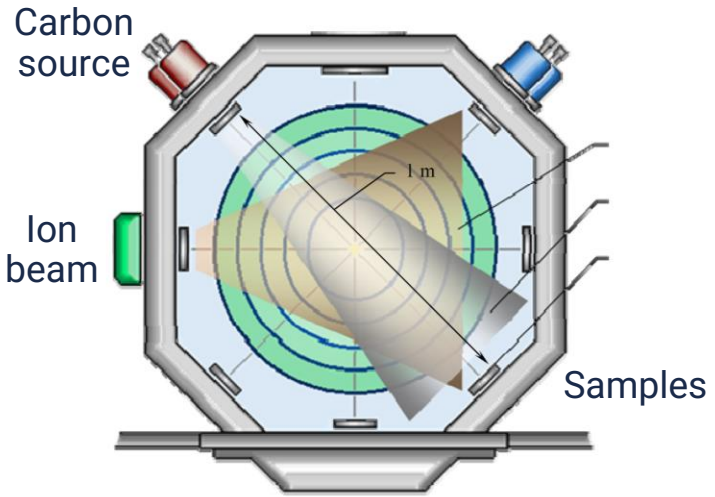


Localized film deposition by metallic stencil

Carbyne-enriched Film Deposition

Ion-Assisted Pulse Plasma Deposition Method

Company: Swissimpianti Sagl

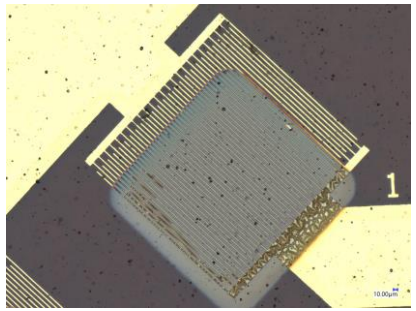


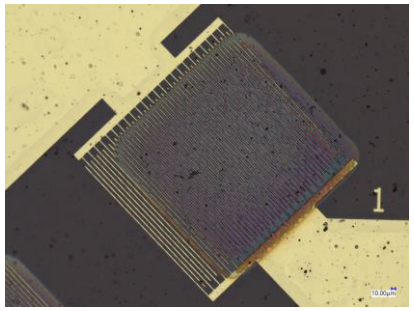
Frequency: 5 Hz
Ar ion plasma: 2 kV & 100 mA
Pressure: 1.7x10^{-3} mbar

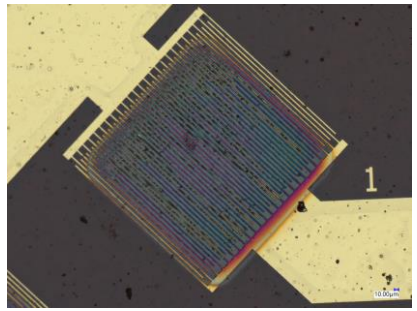
Effect of carbon plasma pulses 5000, 6000, 7000

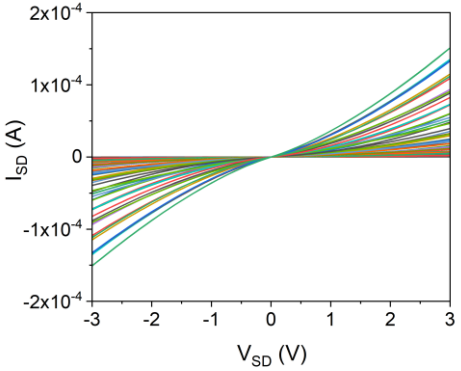
Gas Sensor Characterization

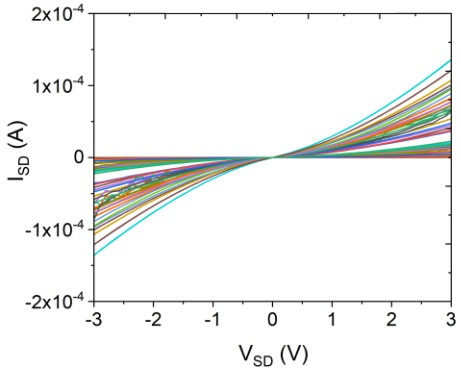
5000 C pulses | **6000 C pulses** | **7000 C pulses**

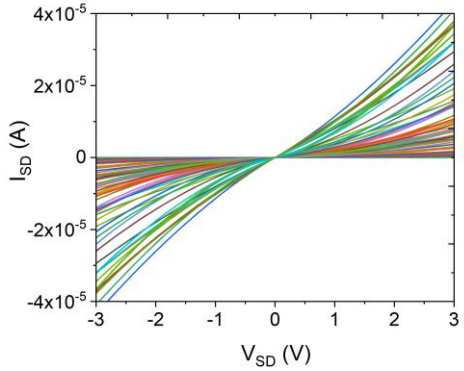




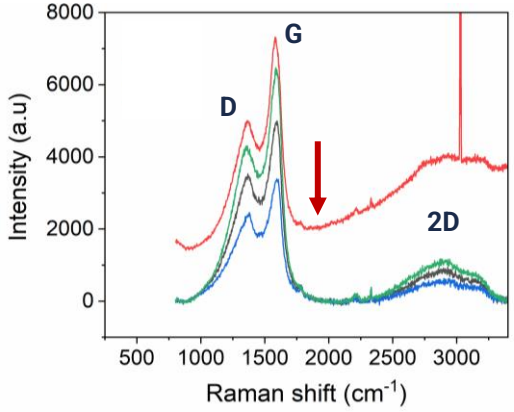


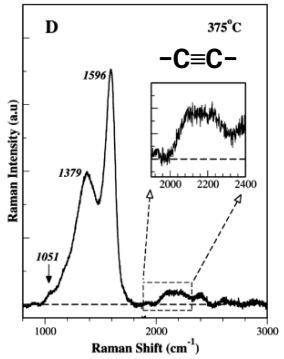


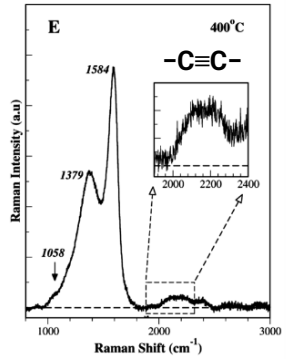




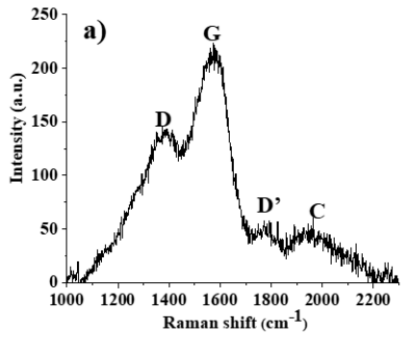
- No film delamination at high carbon pulses.
- Increased film thickness (100 nm) and conductivity by increasing the number of carbon plasma pulses.
- High electrical conductivity, suitable for gas sensing experiments.
- Presence of **carbyne fraction** along with sp^2 carbon

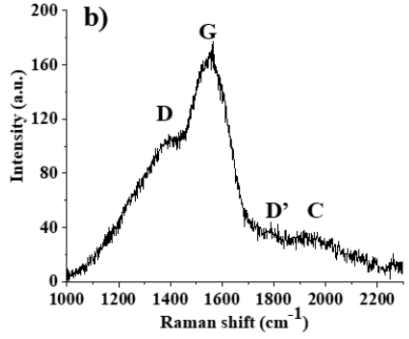






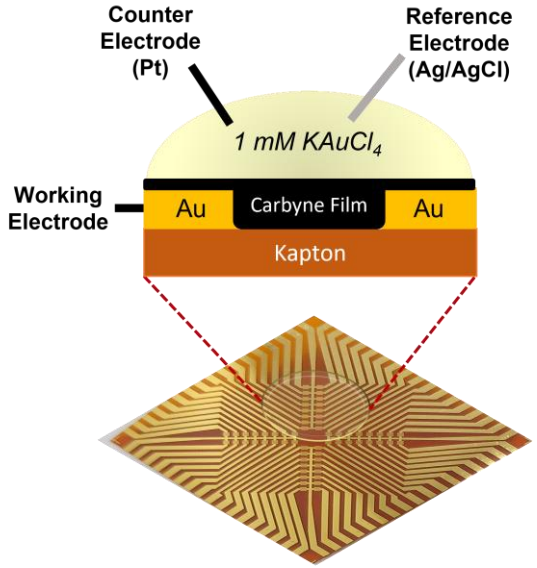
R. Khanna. et al. *Scientific Reports*, **7,1**, 1-8, (2017)

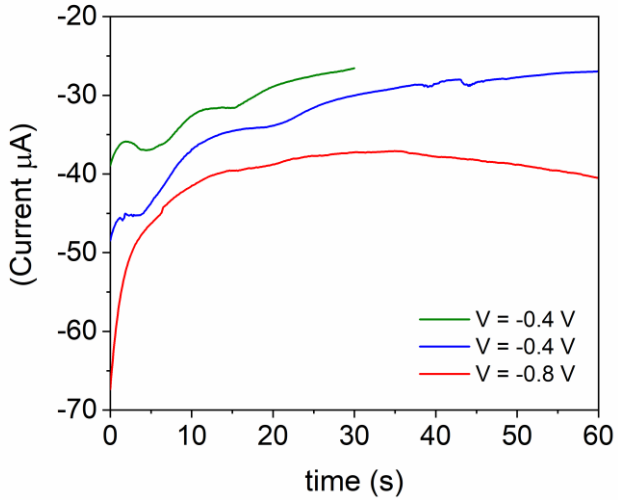




A. Piedade. et al. *Nanomaterials*, **10**, 3-19 (2020)

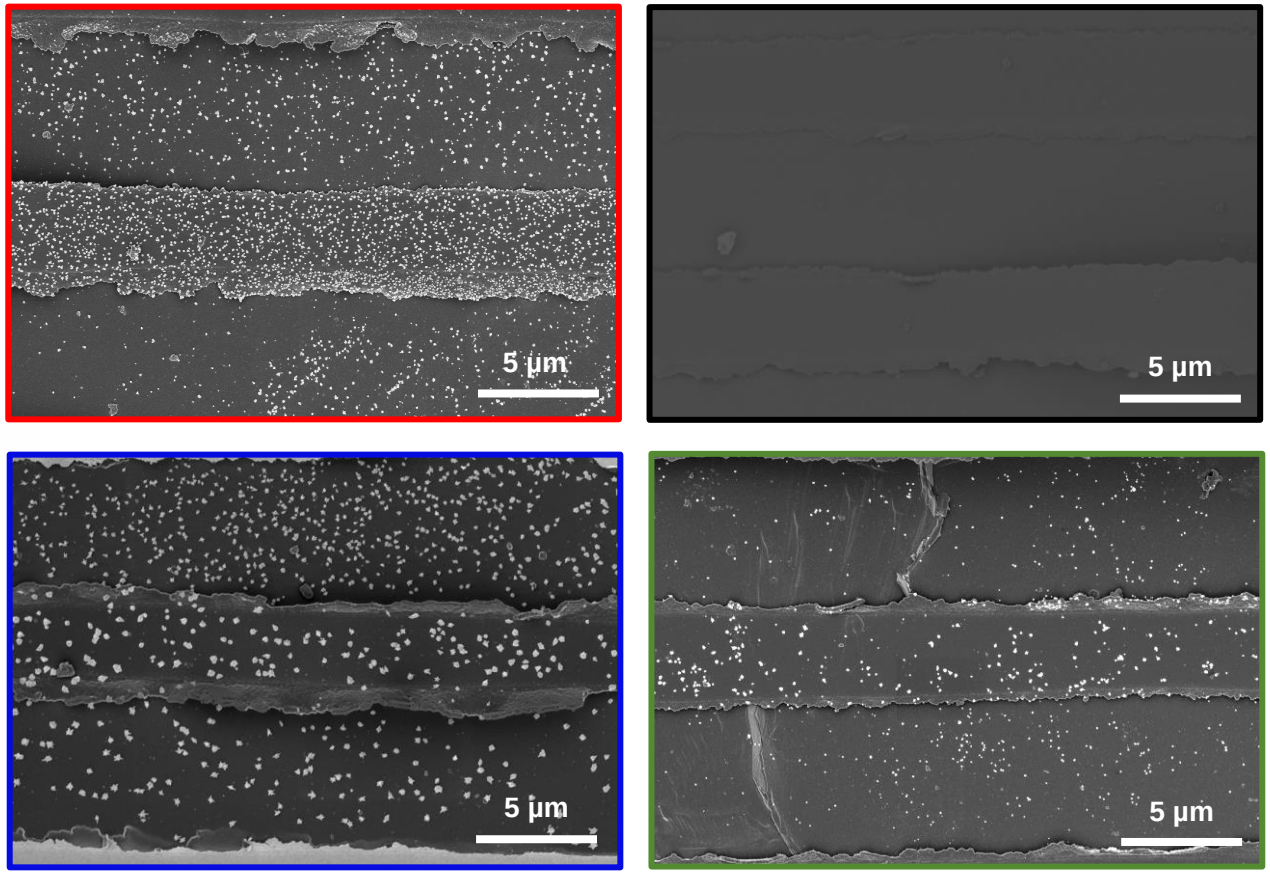
Potentiostatic Electrodeposition of AuNP



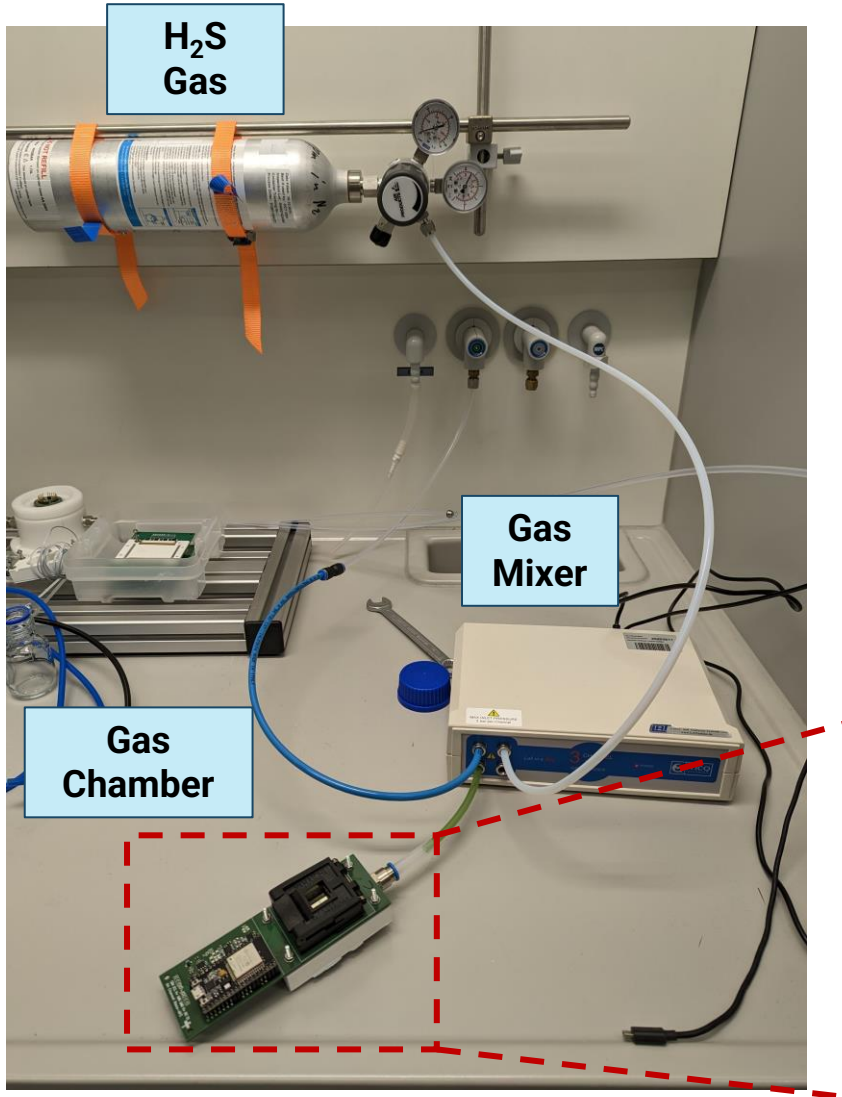


V = - 0.8 V t = 60 s	No funct
V = - 0.4 V t = 60 s	V = -0.4 V t = 30 s

SEM Characterization

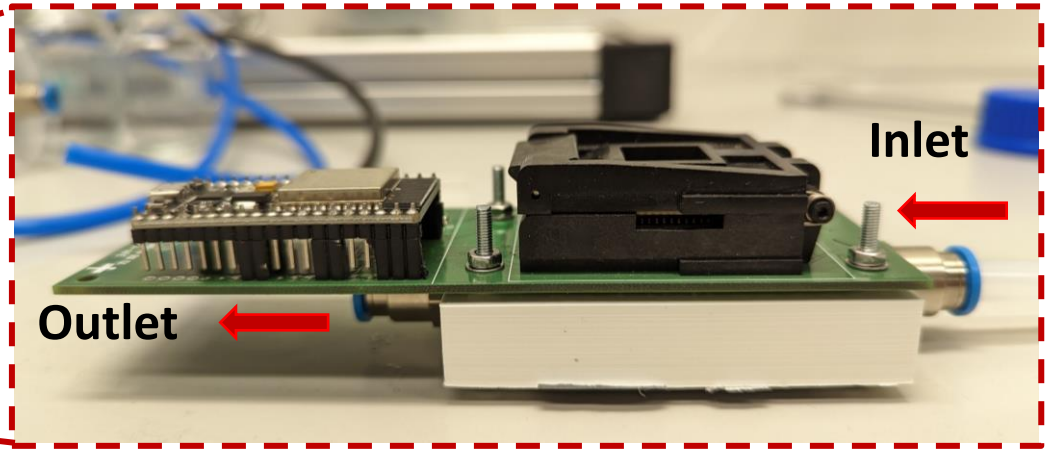


- Increased density of AuNP for higher voltages and longer deposition times.



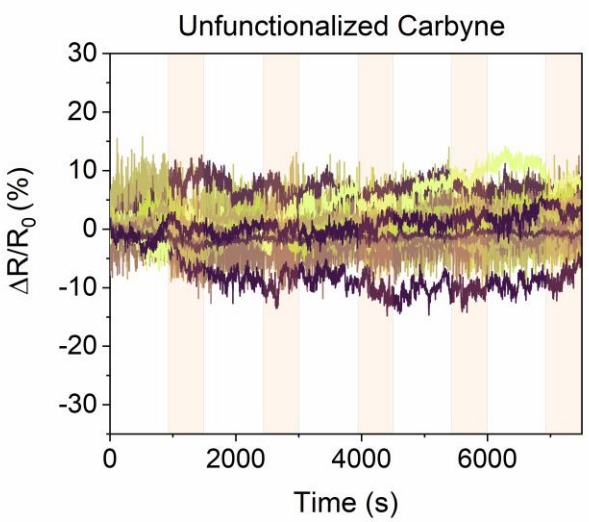
Gas Chamber Setup

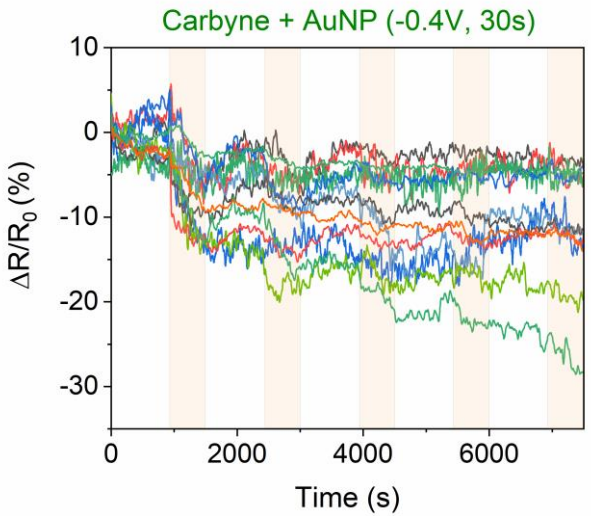
- 10 ppm H_2S gas bottle.
- Dry N_2 as carrier gas (Total flow rate = 500 sccm)
- Multiplexed electrical resistance measurement (64 channels).

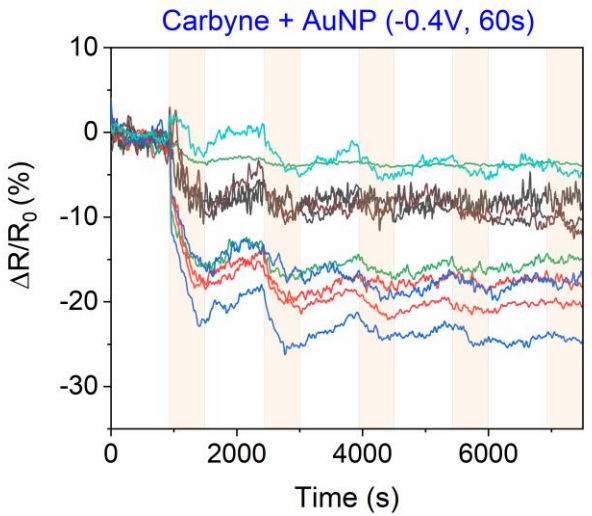


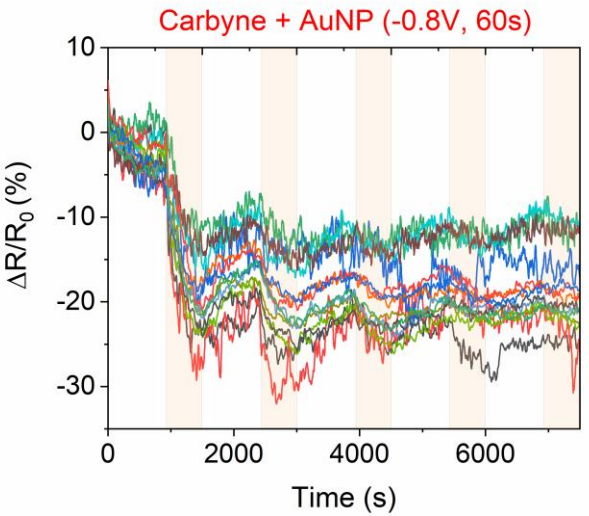
H_2S Gas Exposure Experiments (500 ppb)

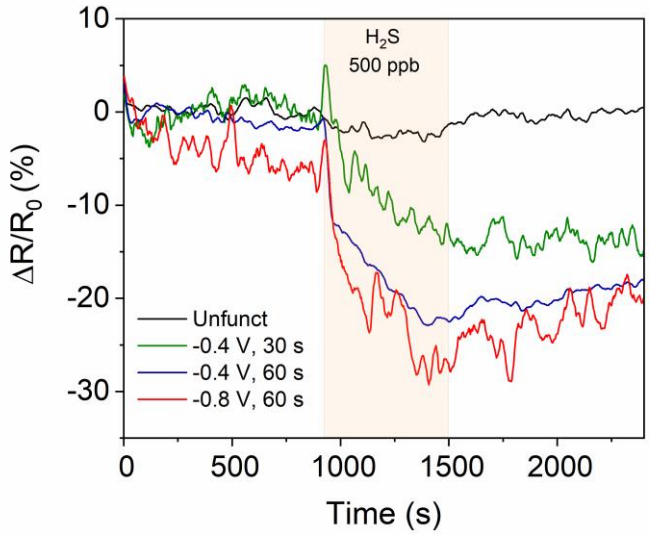
10 min **H_2S** & 15 min N_2











- Increased sensing response to **500 ppb** H_2S gas by increasing AuNP density.
- First gas exposure exhibited the highest sensitivity in all AuNP devices.
- No complete recovery after 15 min N_2 gas flushing suggests **chemisorption** of H_2S on AuNP.

Conclusions & Outlook

- Successful fabrication of H_2S gas sensors based on carbyne-enriched films.
- **Localized** deposition using **5 Hz** and **5000** to **7000** carbon pulses.
- Deposited film is a **mixture** of sp and sp^2 carbon.
- **Higher** AuNP density by **increasing** voltage and deposition time.
- Increased sensing response to **500 ppb** H_2S gas by increasing AuNP density.
- **Chemisorption** of H_2S on AuNP.
- High number of sensors (64) allows:

  - Self-validation.

  - Resilience upon malfunction.
- Sensor recovery requires **improvement** (heating or UV light).
- Analysis in humid air and exhaled breath.

Acknowledgments

GEFÖRDERT VOM

Bundesministerium für Bildung und Forschung

CarbyneSense

ERA NET: 01DJ21006

Dr. Evangelos Gogolides
National Center for Scientific Research "Demokritos"
Greece

Prof. Dr. Levent Trabzon
Istanbul Technical University
Turkey

Prof. Dr. Mariya Aleksandrova
Technical University of Sofia
Bulgaria

Dr. Andrey Brigadin
Swissimpianti Sagl
Switzerland

Thank you for your attention !

Contact: luis_antonio.panes_ruiz@tu-dresden.de