# European Network on New Sensing Technologies for Air Pollution Control and Environmental Sustainability - *EuNetAir*

## COST Action TD1105

## WGs and MC Meeting at LINKOPING, 3 - 5 June 2015

Action Start date: 01/07/2012 - Action End date: 30/06/2016

Year 3: 1 July 2014 - 30 June 2015 (*Ongoing Action*)

# Graphene Metal-oxide hybrids for gas sensor tuning

**Jens Eriksson**

Applied Sensor Science, Linköping
University / Sweden

cost
EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

EuNetAir
European Network on New Sensing Technologies
for Air-Pollution Control and Environmental Sustainability

COST is supported
by the EU Framework Programme

European Science Foundation
ESF provides the COST Office
through a European Commission contract

# Why Graphene sensors?

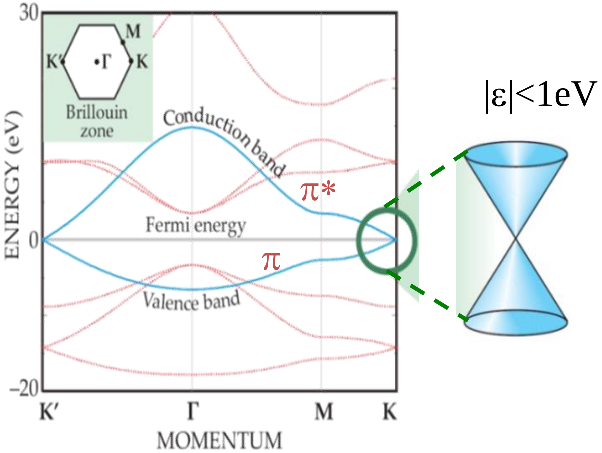
- Ultra-high sensitivity necessary for Air Quality Monitoring
- Low density of states near the Dirac point ($E_D$) – small changes in the number of charge carriers result in large changes in the electronic state
- Every atom at the surface – ultimate surface to volume ratio
- Low mass, low noise
- Has potential as a low noise, ultra-sensitive transducer.

❑ WHO: **99.000** premature annual deaths in Europe due to household pollution

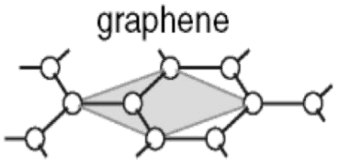
❑ **Potential applications where ultra-high sensitivity is required**

❑ **Air quality control: Monitoring of highly toxic gases in normal living environments**

  - VOCs (formaldehyde, benzene, naphthalene…)
  - NOx



Graphene sensors are normally highly sensitive, but suffer from poor reproducibility, selectivity, and speed of response...



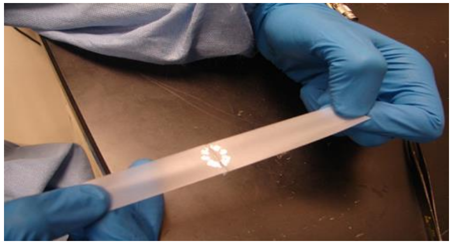
Reproducibility is an issue that partly arises from the graphene synthesis

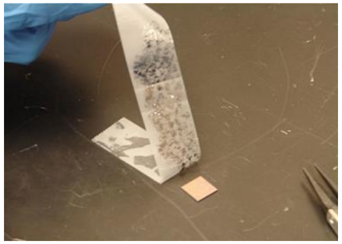
# 2007: First graphene sensor

## Detection of individual gas molecules adsorbed on graphene

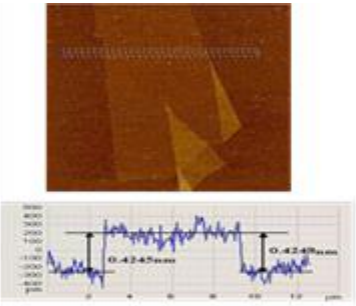
Nat Mater. 6 652-655 (2007)

F. SCHEDIN[1], A. K. GEIM[1], S. V. MOROZOV[2], E. W. HILL[1], P. BLAKE[1], M. I. KATSNELSON[3] AND K. S. NOVOSELOV[1]*

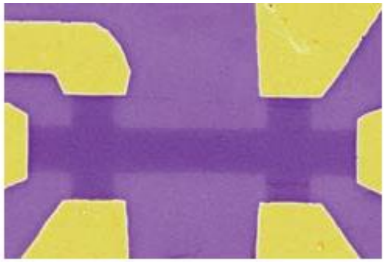




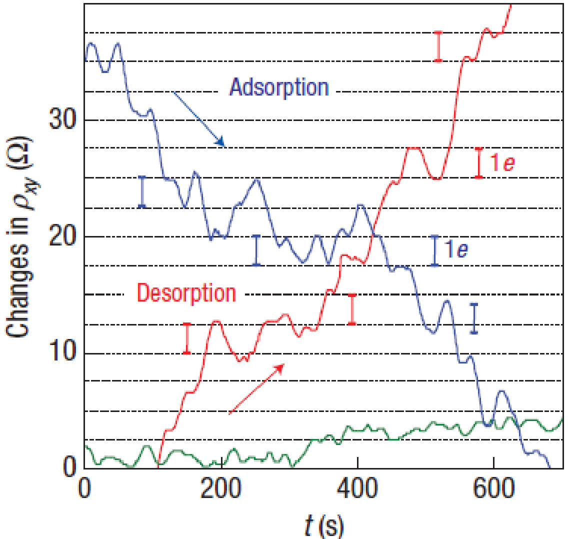
Flakes < 10 μm



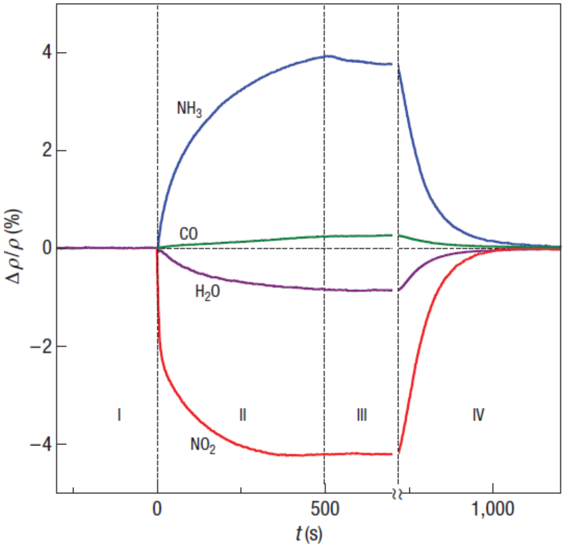
Hall bars



Detection of individual $NO_2$ and $NH_3$ molecules! (… under optimized conditions)



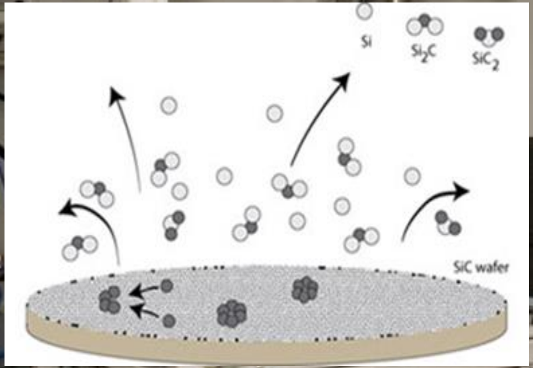
But... There is a (another) problem

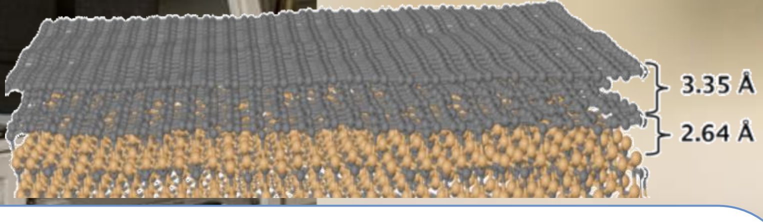


# Graphensic

manufactures and supplies

# Graphene on SiC





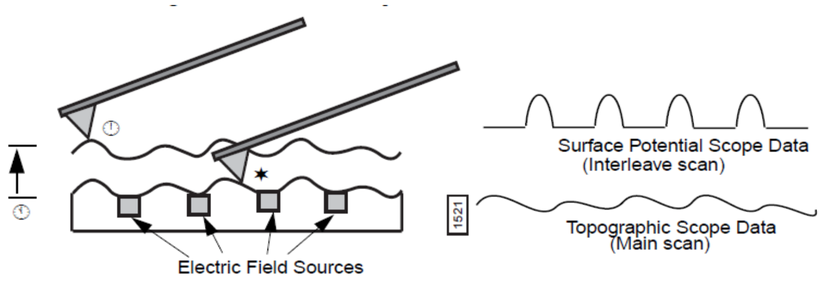
- Sublimation of Si from SiC in Ar at 2000°C
- Scalable, wafer-scale films compatible with standard semiconductor processing
- High thickness uniformity (> 90% ML, rest 2 ML)
- Thickness controlled by temperature
- Can be cost-effective!

**Spin off from Linköping University, Sweden**

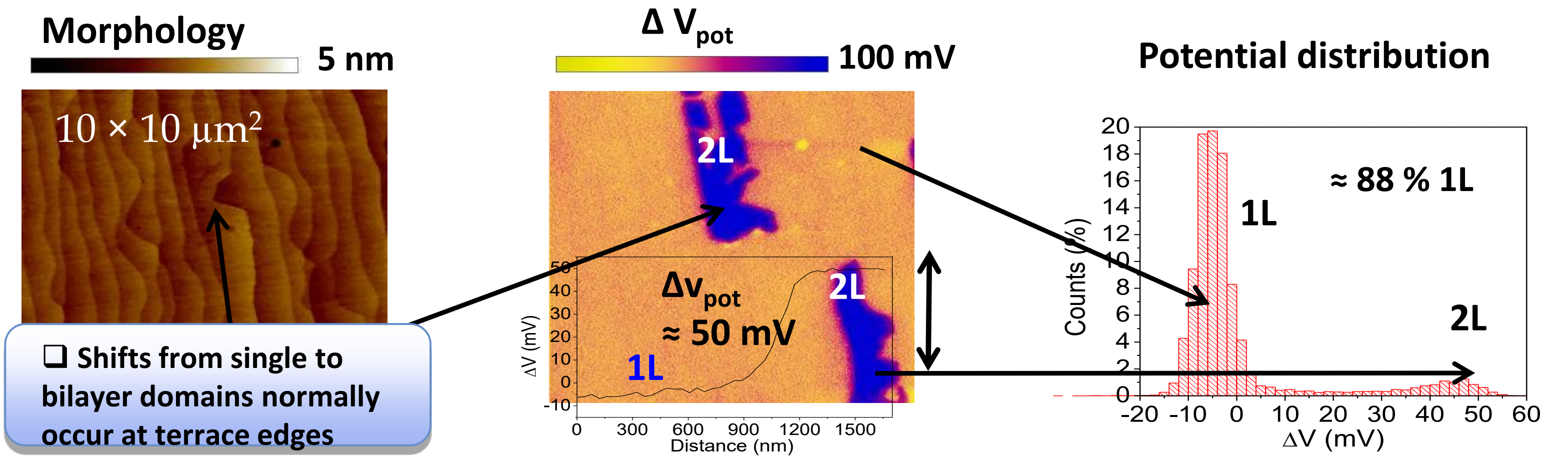
**22.11.2011**

# Scanning Kelvin probe microscopy – work function mapping

**Nanoscale mapping of graphene thickness uniformity and doping**



- Topography is mapped in 1st pass
- Surface Potential is mapped in 2nd pass
- Maps change in work function



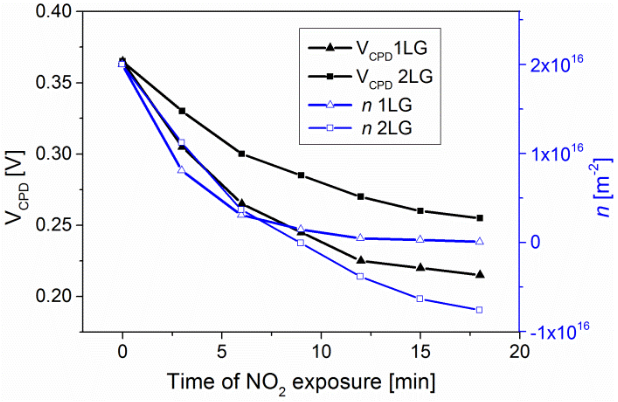
☐ Shifts from single to bilayer domains normally occur at terrace edges

- **ΔΦ between 1LG and 2LG allows nanoscale mapping of graphene thickness**
- **Controllable environment allows observing changes in 1LG and 2LG upon gas interaction**

*Eriksson et. al.,Applied Physics Letters 100 (2012) 24160*

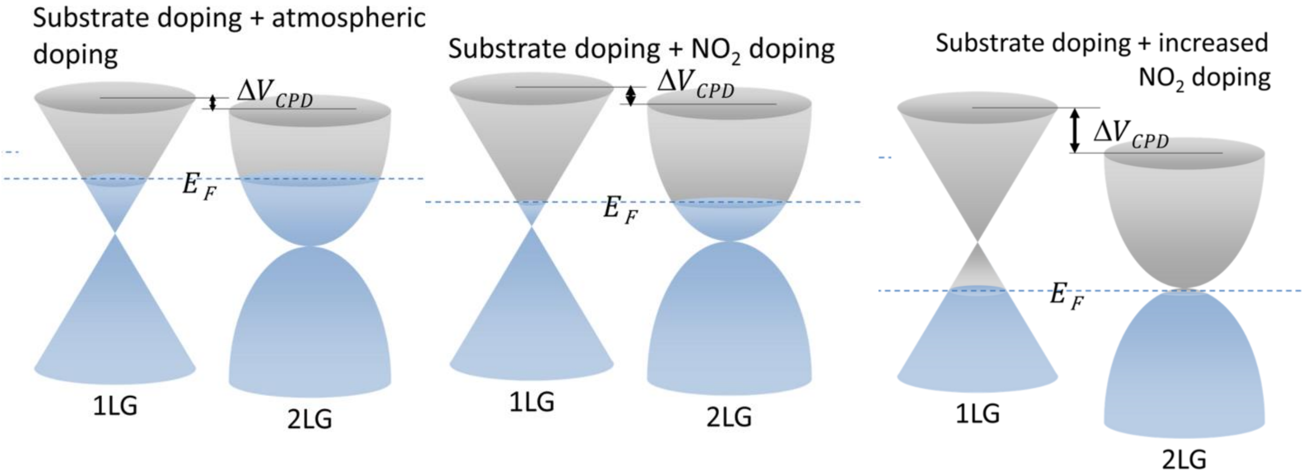
# Different sensitivity for 1LG and 2LG?

Response to < 1 ppm $NO_2$ vs. time



Different energy dispersions

- Linear for 1LG
- Parabolic for 2LG



Substrate doping + atmospheric doping

Substrate doping + $NO_2$ doping

Substrate doping + increased $NO_2$ doping

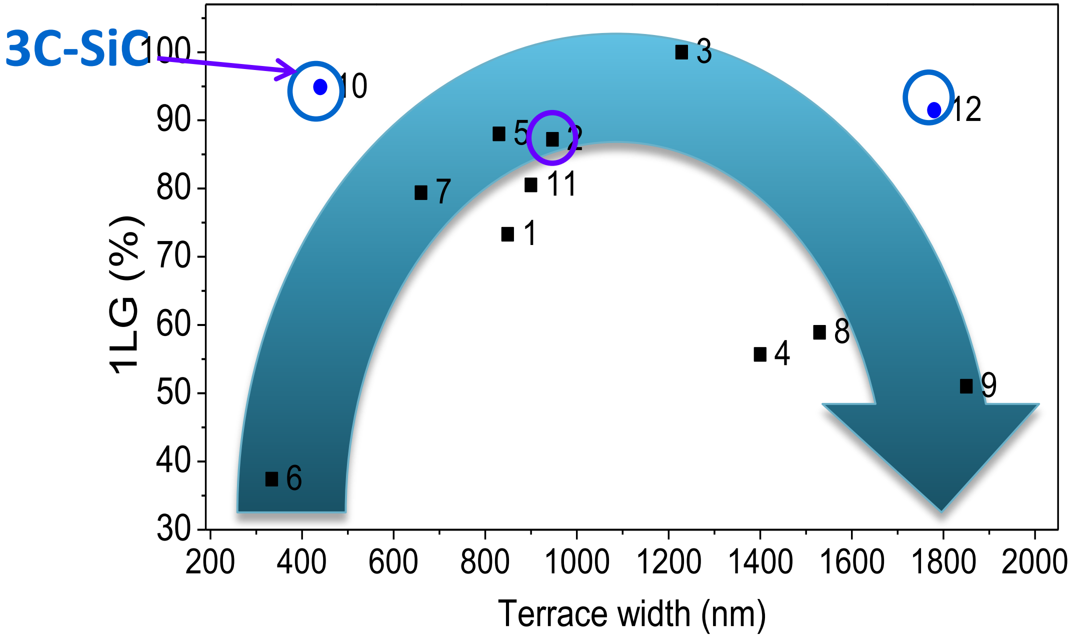
$$(1) \qquad \Delta n \text{ 1LG} = \frac{2e\, \partial V_{CPD} \sqrt{n}}{\hbar\, \upsilon_F \sqrt{\pi}} - \frac{(e\, \partial V_{CPD})^2}{\hbar^2\, \upsilon_F{}^2 \pi}$$

$$(2) \qquad \Delta n \text{ 2LG} = \frac{\delta V_{CPD}\, e\, 2m^*}{\hbar^2 \pi}$$

*R. Pearce, J. Eriksson, T. Iakimov, L. Hultman, A. Lloyd Spetz and R. Yakimova, ACS Nano 7 (5), pp 4647–4656 (2013)*

- Calculated change in carrier concentration not the same for 1 and 2LG
- Different responsivity for 1 and 2LG doesn't account for all difference in sensitivity
- Different sticking coefficients also important

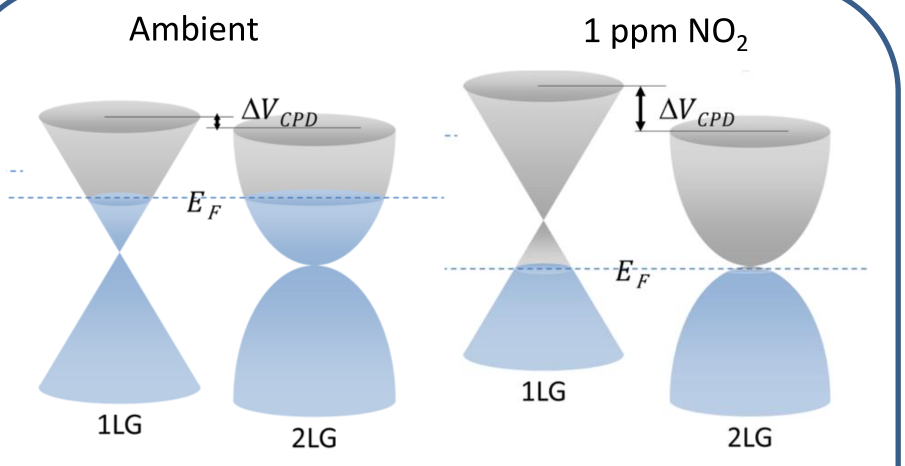
# Controlling layer uniformity and doping



- As the terrace width increases, the area covered by 1LG increases
- Bilayer graphene growth starts at step edges; many step edges → many nucleation sites
- Terrace width > 1200 nm – gradual decrease of 1LG - Island growth in the absence of steps
- Substrate polytype and doping for hexagonal SiC (n-type 6H-SiC or SI 4H-SiC) do not significantly influence uniformity
- 3C-SiC – higher 1LG % for lower terrace width , 1LG % independent on terrace width

# Uniform 1LG leads to very reproducible sensor characteristics

## ΔS depends on thickness due to differing band structures for 1LG, 2LG... MLG

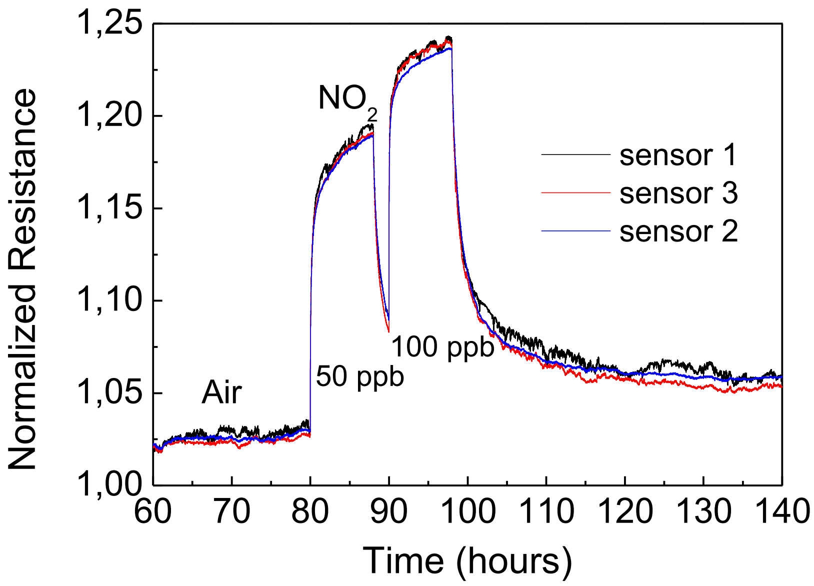


- $NO_2$ withdraws electrons

**Same change in charge carriers causes larger shift of the Fermi level for 1LG**

R. Pearce, J. Eriksson, T. Iakimov, L. Hultman, A. Lloyd Spetz and R. Yakimova, ACS Nano 7 (5), pp 4647–4656 (2013)

## Uniform 1LG leads to very reproducible sensor characteristics



**$NO_2$ sensing** interesting for:
- Emission control (few ppm)
- Air quality control (few ppb)

1LG is more sensitive to NOx than 2LG or MLG

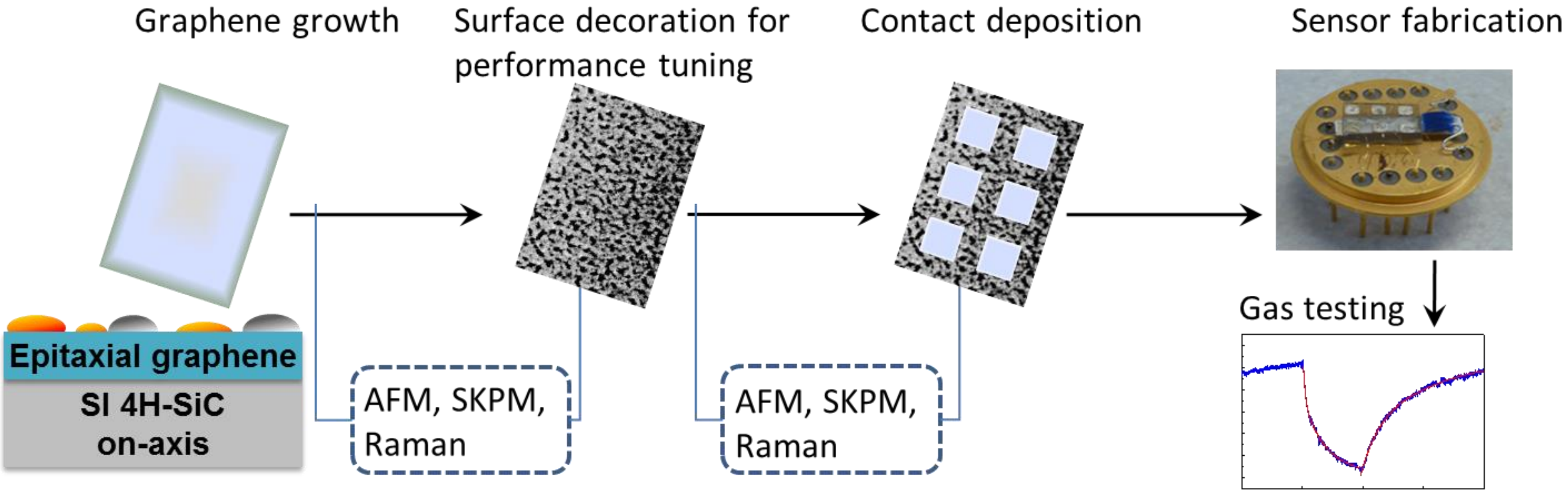
Uniform 1LG required for maximum sensitivity and reproducibility

Different sensors fabricated on 100% 1LG show identical response

Epitaxial graphene on SiC enables **highly reproducible** sensor fabrication

# Functionalization with metal and metal oxide nanostructures for selectivity tuning

- **Obstacles: sensitivity, selectivity, response/recovery time, reproducibility**



Graphene growth

Surface decoration for performance tuning

Contact deposition

Sensor fabrication

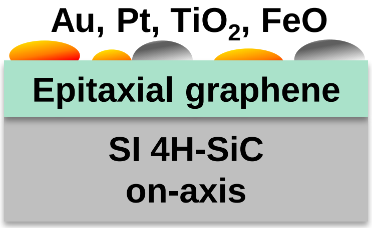
Gas testing

AFM, SKPM, Raman

AFM, SKPM, Raman

**Aim:** To develop a reproducible method for functionalization with nano structures

- Thin layers of nano-porous Au and Pt DC sputtered onto EG/SiC at elevated pressure
- Nanoparticles of $TiO_2$ or FeO core-shell structures deposited by hollow cathode sputtering
- Ideally we want islands or nanoparticles to maximize metal-graphene-gas boundaries

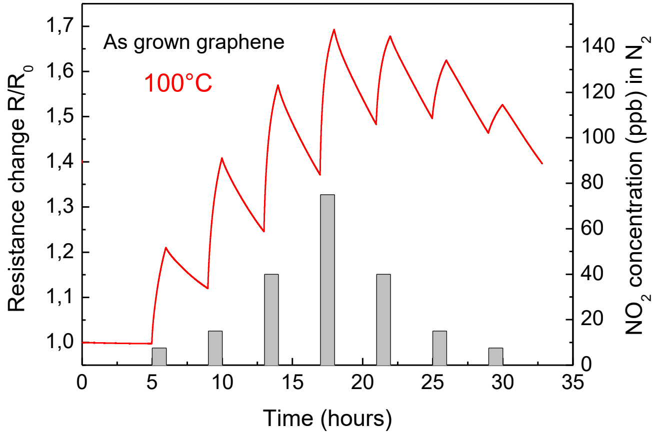


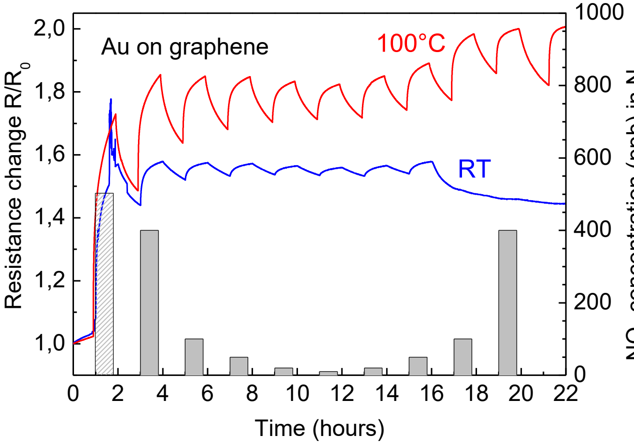
# Effect of decoration on sensor response

## As-grown graphene

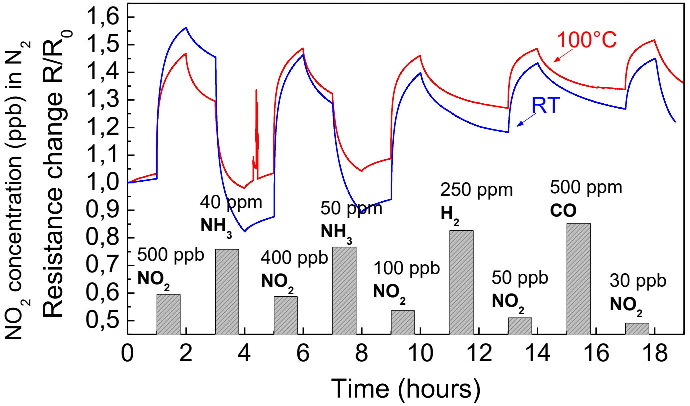
## Au decorated graphene

### Response to ppb concentrations of $NO_2$





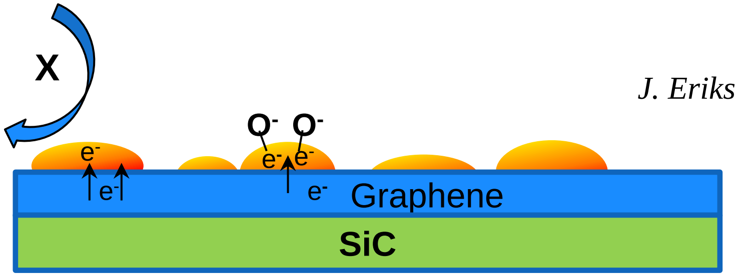
### Selectivity



❑ **Effects of metallization:**

- **Improved speed of response**
- **Improved detection limit (< 1 ppb)**
- **More stable base line**
- **Suppressed response to $H_2$/CO while maintaining $NO_2$ response (Au < 5 nm)**

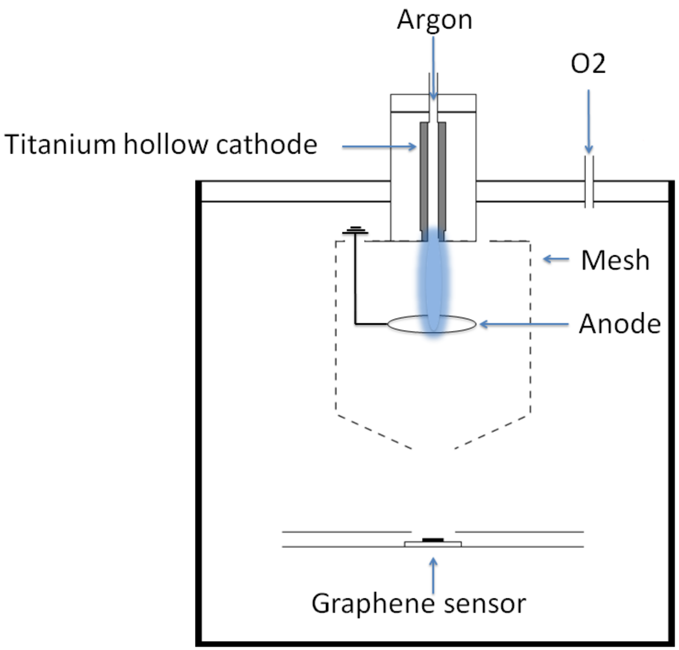
| Response % | Response Time (min), 50 ppb $NO_2$ | | | Recovery Time (min) | | |
|---|---|---|---|---|---|---|
| | As-grown | Au, 5 nm | Pt, 5 nm | As-grown | Au, 5 nm | Pt, 2 nm |
| 30% | 6 | 1.5 | 2.3 | 316 | 14 | 14,8 |
| 60% | 23 | 9 | 10.9 | 834 | 47 | 49 |
| 90% | 99 | 74 | 41.7 | 2136 | 135 | 175,5 |

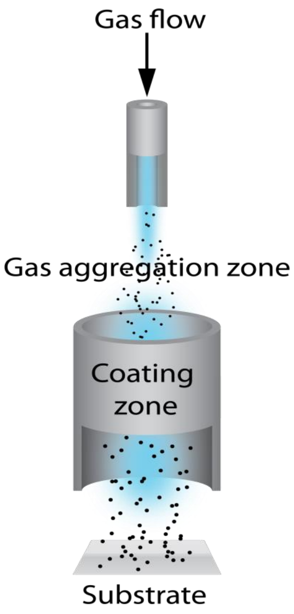


*J. Eriksson, D. Puglisi, Y. H. Kang, R. Yakimova, A. Lloyd Spetz , Physica B 439, 105–108 (2014)*

# Designed Nanoparticles by Pulsed Plasma Hollow Cathode Sputtering

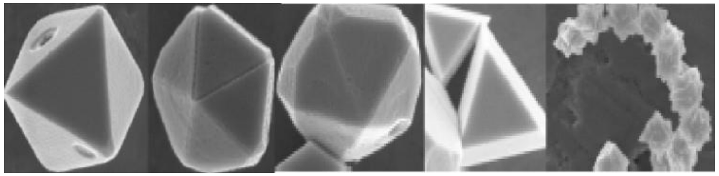
It is expected that decoration with different metals or metal-oxide nanostructures will allow careful targeting of selectivity to specific molecules

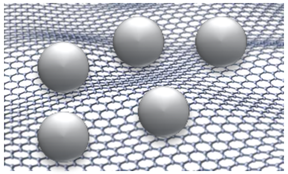




R. Gunnarsson, P&CP, IFM, LiU

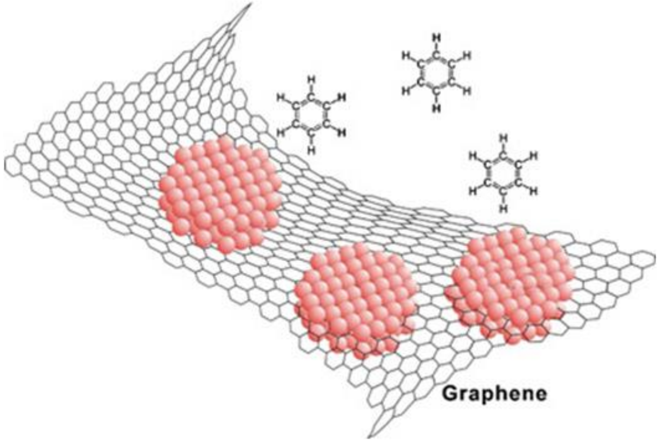
- Hollow-cathode based nanoparticle sputter process
- Highly reproducible thin film deposition technique
- Scalable

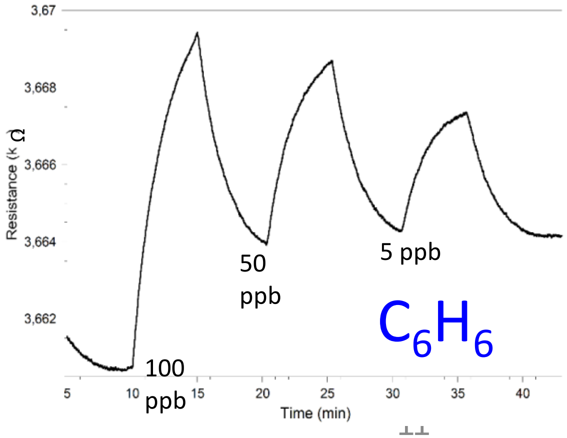




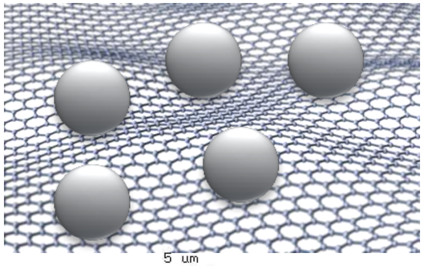
Ø > 50 nm

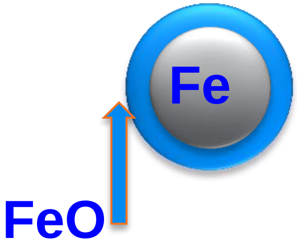
- Utilize MOx sensitivity and selectivity, with EG as ultra-sensitive transducer
- $TiO_2$ and FeO NPs allow enhanced sensitivity towards formaldehyde and benzene

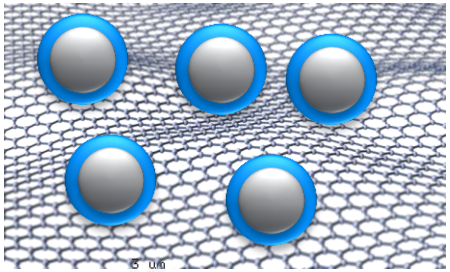


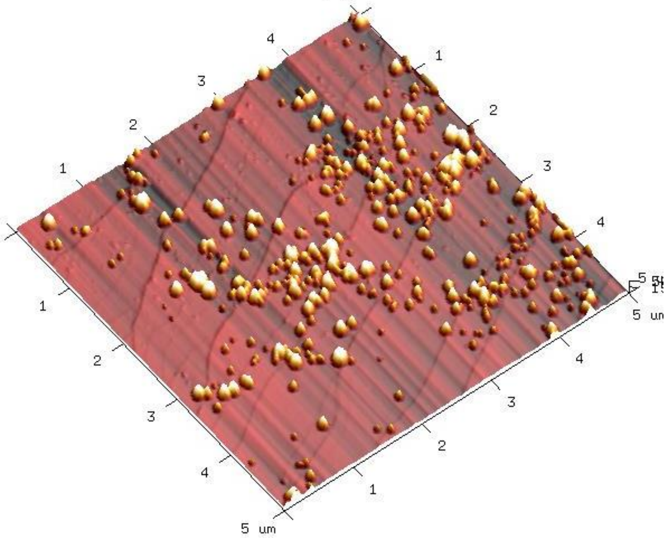


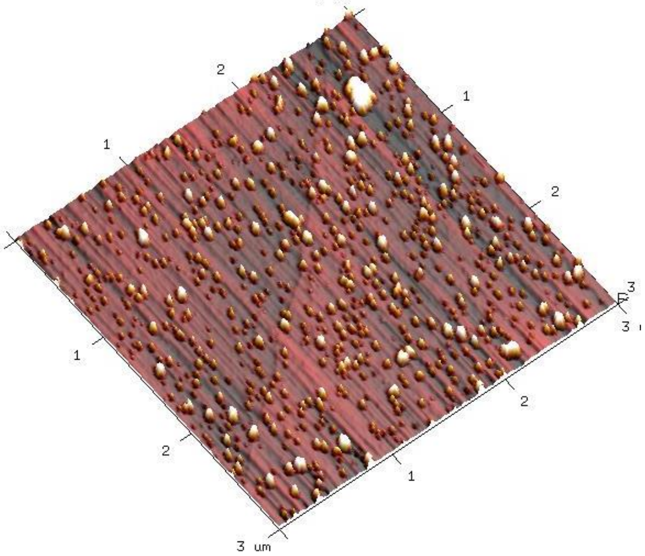
# Designed Nanoparticles by Pulsed Plasma Hollow Cathode Sputtering

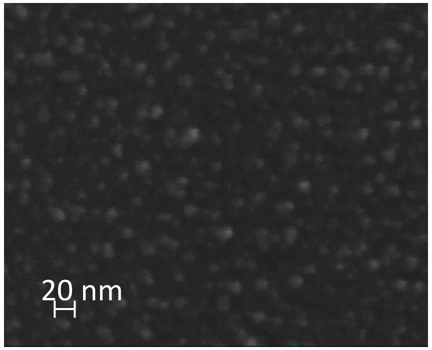


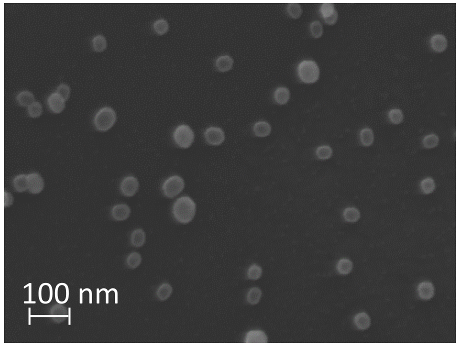






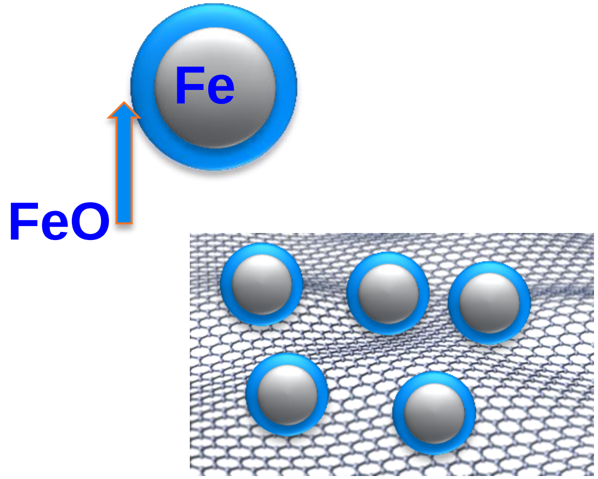






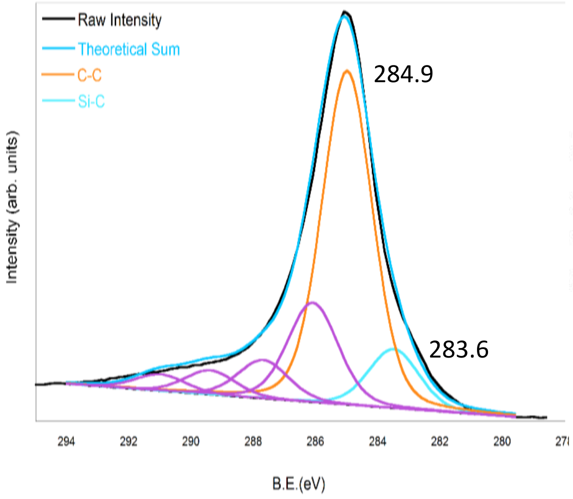
- Deposition is inhomogeneous
- Deposition does not follow steps or other morphological features
- Size and dispersion can be controlled during growth

# XPS: FeO core-shell decorated graphene

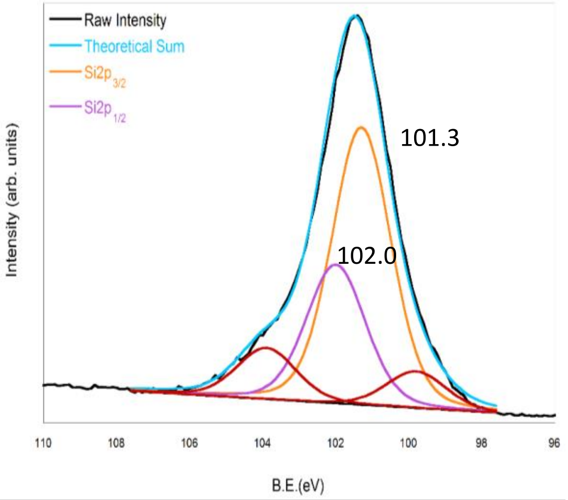


## As-grown EG

C1s

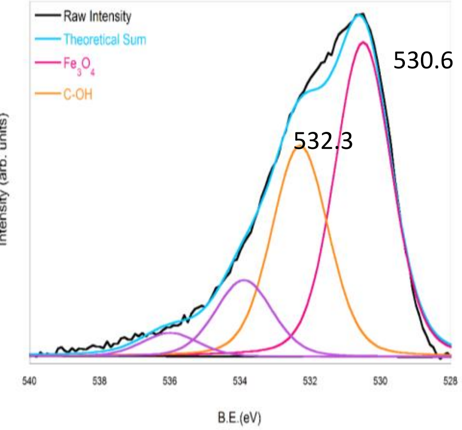


Si2p

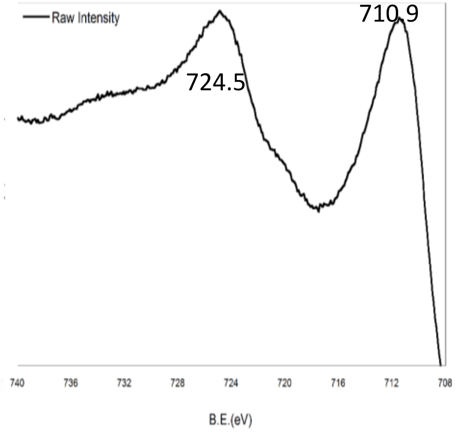


## EG + FeO

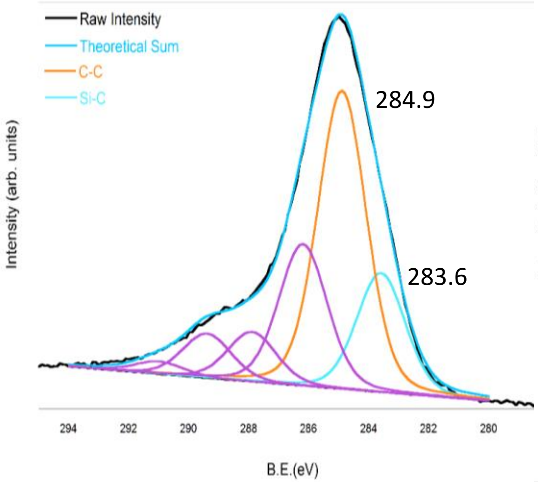
O1s



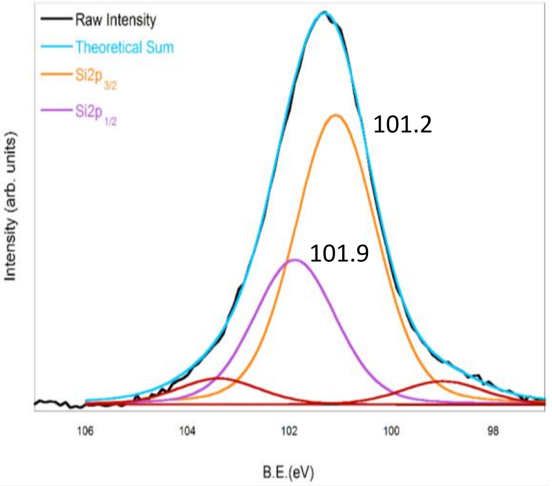
Fe2p



C1s

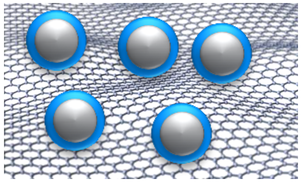


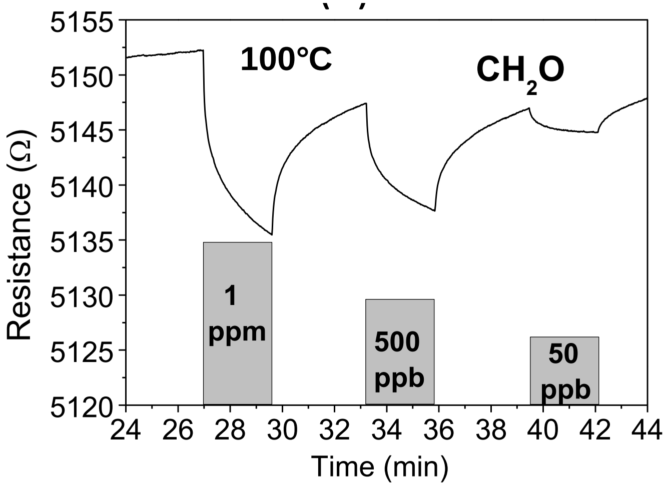
Si2p

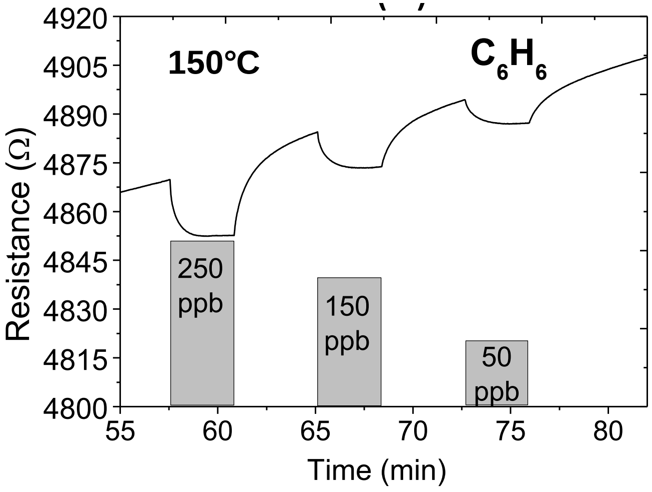


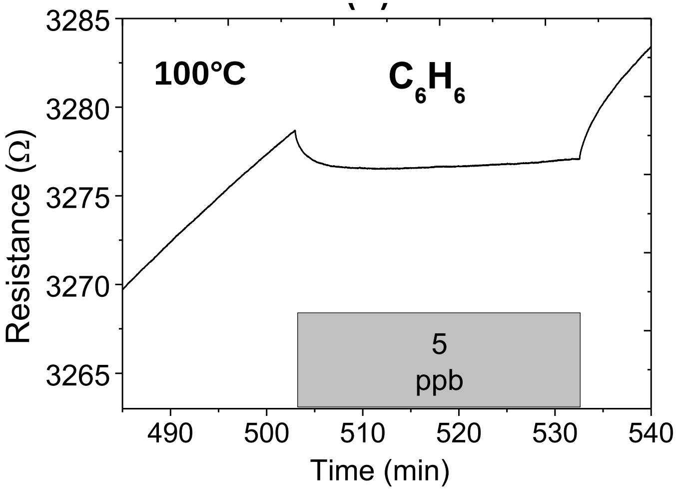
# Sensor response to formaldehyde and benzene

FeO core-shell, low surface coverage

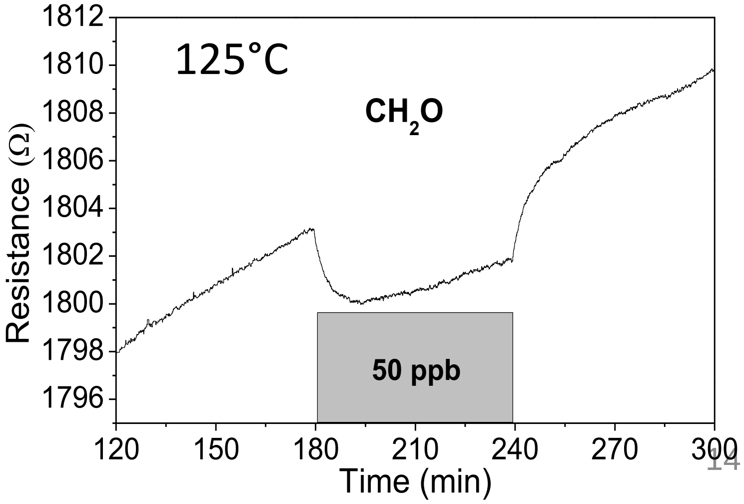


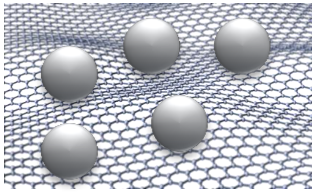




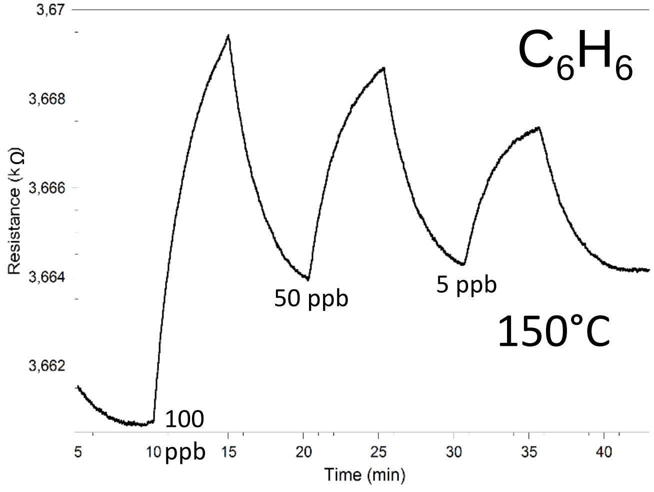


TiO$_2$, Φ < 5 nm, low coverage



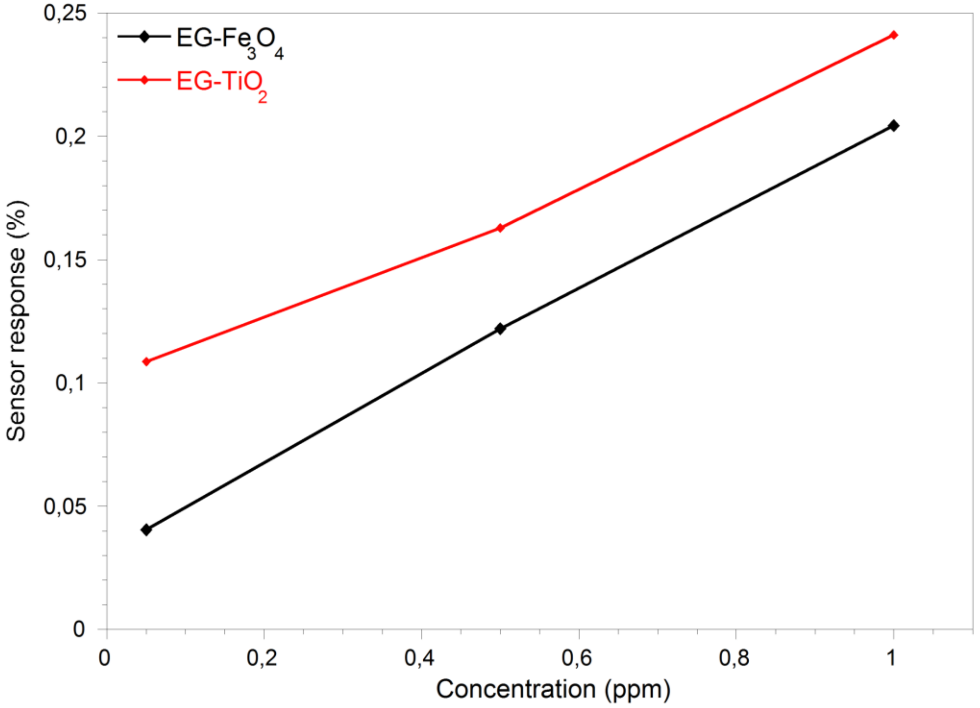


TiO$_2$, Φ > 50 nm, high(er) surface coverage

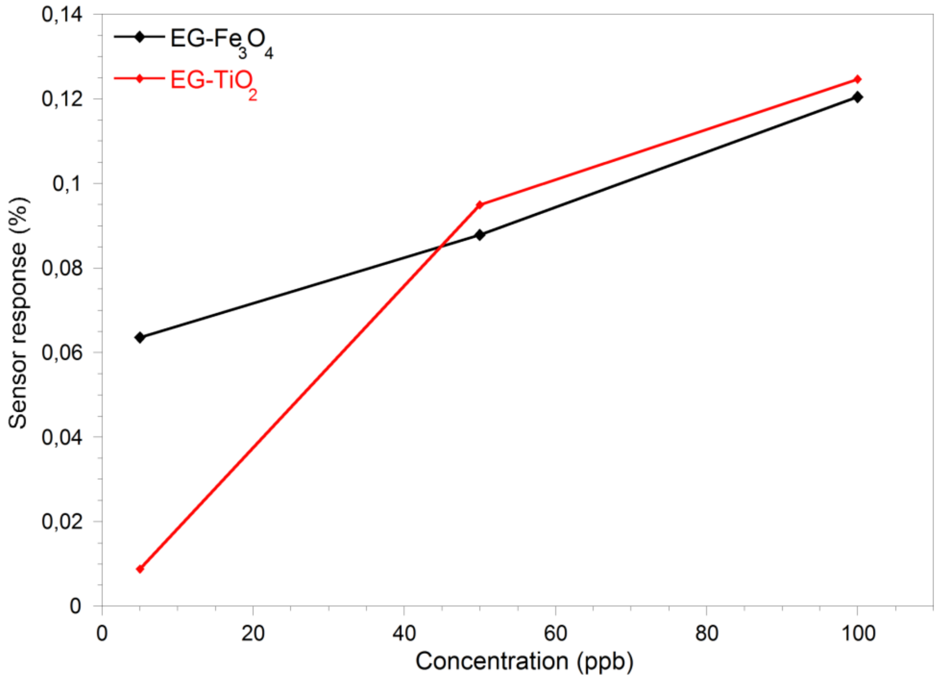


# EG-$TiO_2$ and EG-FeO core-shell sensitivity

$CH_2O$



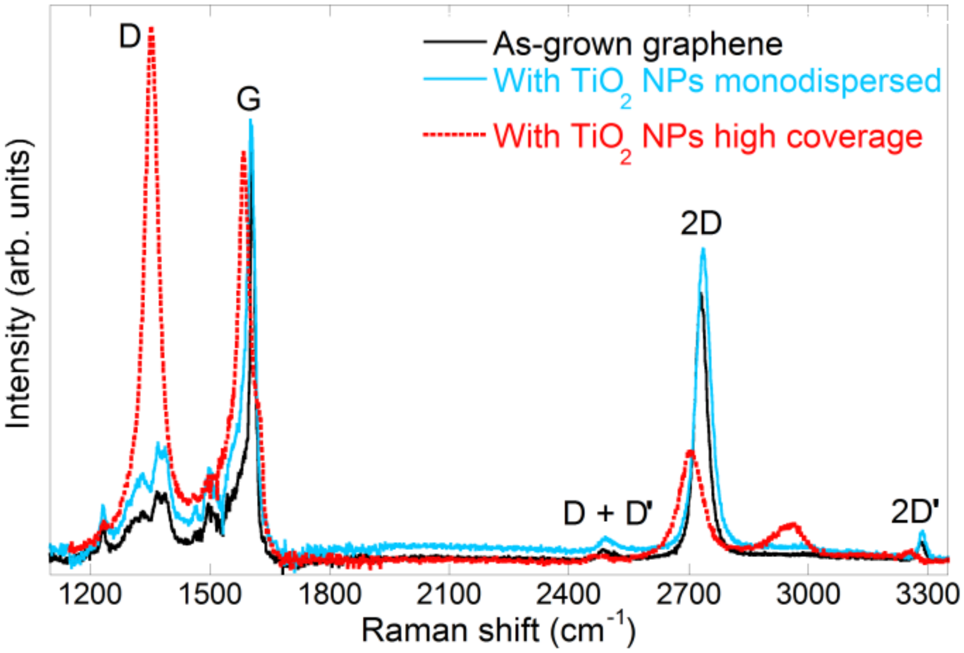
$C_6H_6$

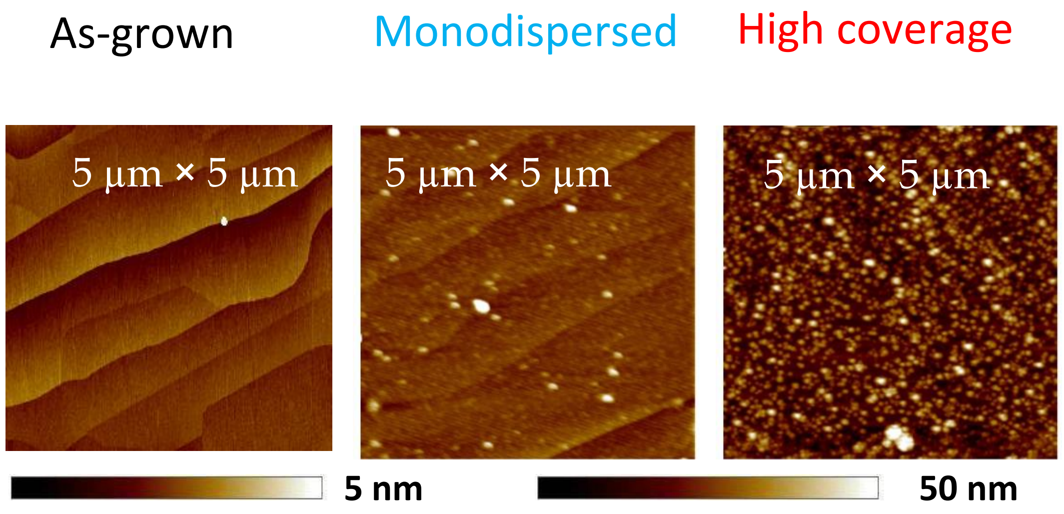


☐ Detection of 50 ppb $CH_2O$ and 5 ppb $C_6H_6$

☐ Lower concentrations not available…

# Micro-Raman and AFM analysis





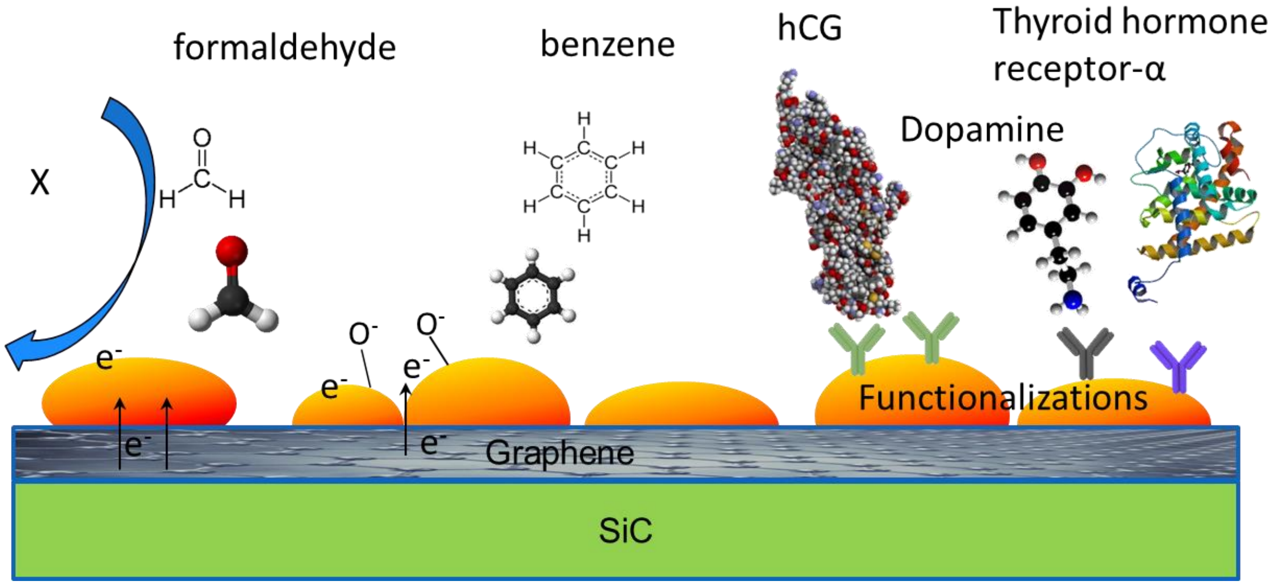
| | |
|---|---|
| Effects of decoration | Monodispersed: Shape of characteristic peaks unaffected. G peak blue-shifted -> p-type doping |
| | High surface coverage: Structural damage |

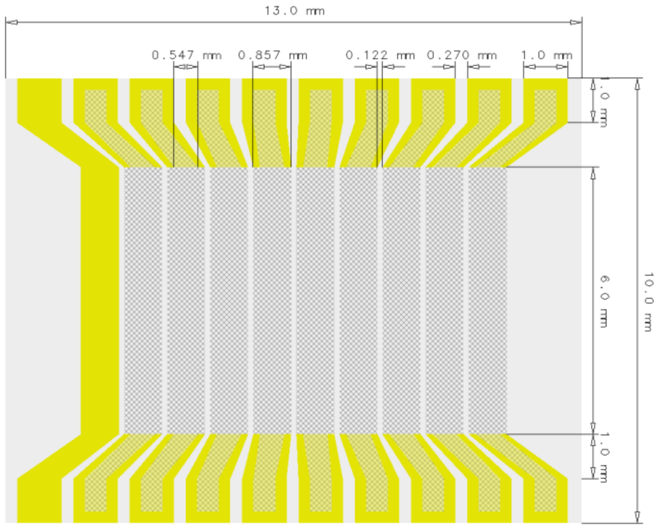
# Areas of strength in Sweden

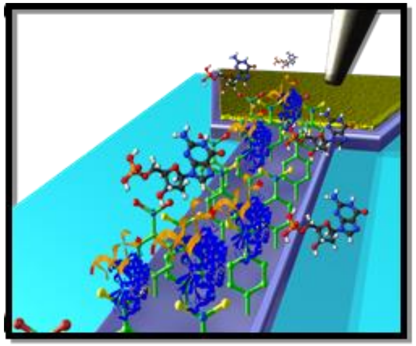
SIO GRAFEN

| | 2016 | 2020 |
|---|---|---|
| **Manufacturing** | Graphene and graphene based composites available for R&D needs in Sweden. | Graphene and graphene based composites available on market for product manufacturing. |
| **HF Communication** | Proof of concept in prototype, for high mobility in mixer or power amplifier application. | High frequency transistor demonstrated. |
| **Energy** | Electrodes based on graphene demonstrated. | Energy storage product on market.<br>Power cables on market. |
| **Barrier** | Functionality of properties demonstrated. | Used in commercial application. |
| **Sensors** | Gas sensor demonstrated. | Gas sensor on market. Prototype of selective sensors, mass sensors, chemical sensors. |
| **Printed Electronics** | Printed antenna demonstrated. | Commercial supplier of graphene ink for flexible electronics. |
| **Life Science** | Biosensors demonstrated. | Prototype for biosensors for niche medical applications. |

# Epitaxial Graphene sensor platform

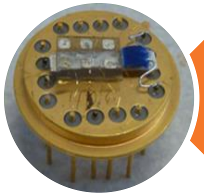




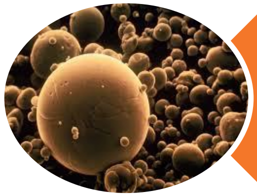


graphensic

# CONCLUSIONS

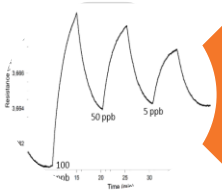


Sensing with epitaxial graphene – promising, ppb level $NO_2$, $CH_2O$, and $C_6H_6$ detection



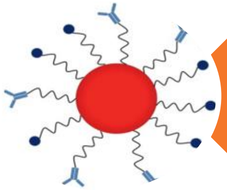
Decoration with Au, Pt, $TiO_2$, FeO core-shell NPs can result in improved selectivity, sensitivity, stability, and response/recovery times

- The effect depends on the choice, thickness, and nanostructure of the decoration



Preliminary tests show that $TiO_2$ and FeO NPs allow sensitive detection of formaldehyde and benzene. Potential candidate for VOC detection in living environments

Precaution is necessary in order not to damage the graphene through the modification



Biofunctionalization of NPs on EG will allow extremely sensitive detection of target disease biomarkers