



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

COST Action TD1105

**1<sup>ST</sup> International Workshop as Open Satellite to *Transducers 2013* on  
*New Sensing Technologies and Transducers for Air Quality Monitoring***

**Barcelona International Convention Centre, Barcelona, Spain, 20 June 2013**

# CARBON BASED NANOMATERIALS FOR GAS SENSING





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CSIRO Australia

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# Carbon-Based Nanomaterials for Gas Sensing

Workshop Barcelona 20 June 2013

## COST Action TD1105 - EuNetAir

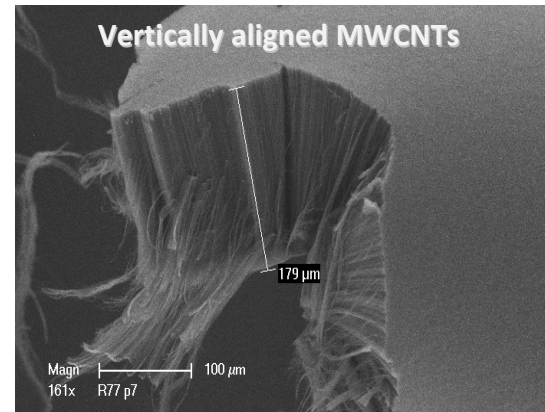
European Network on New Sensing Technologies for  
Air-Pollution Control and Environmental Sustainability - EuNetAir

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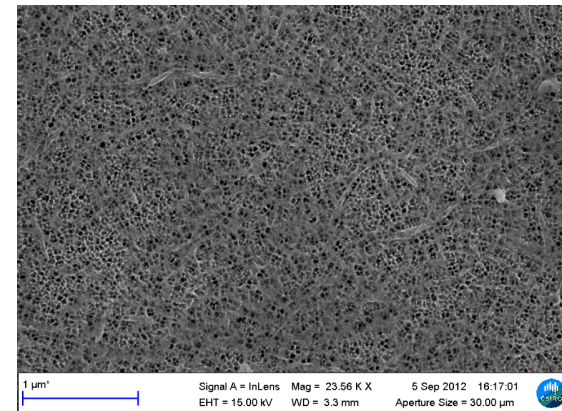
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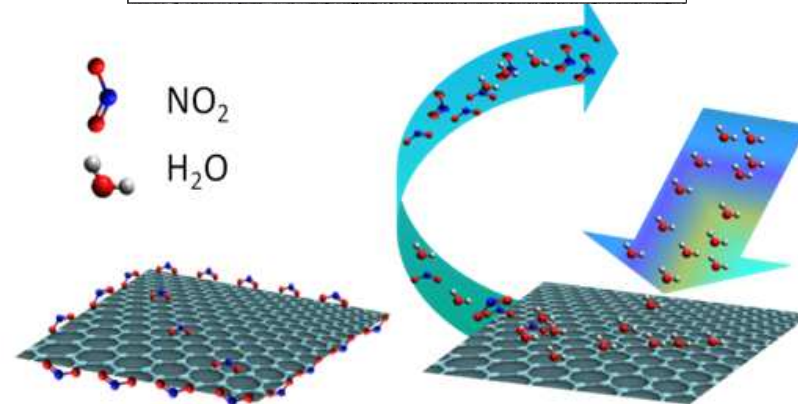
# 1. MWCNT yarn sensors

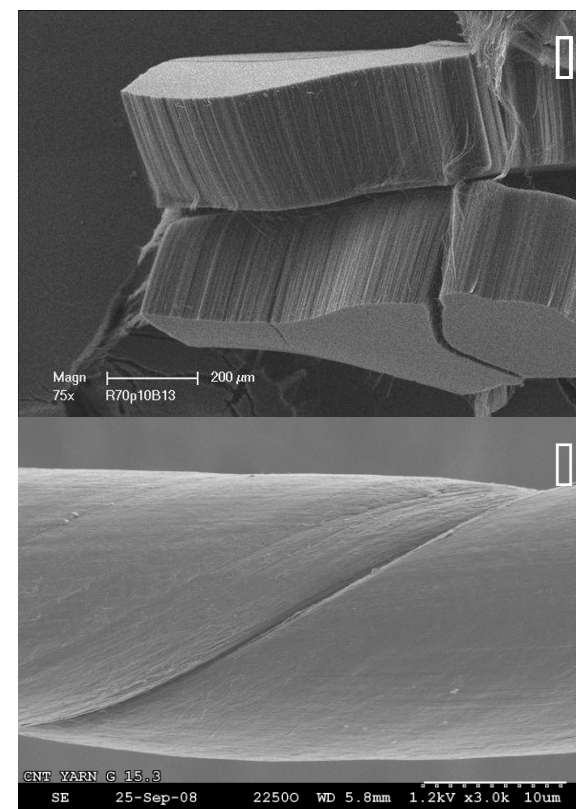
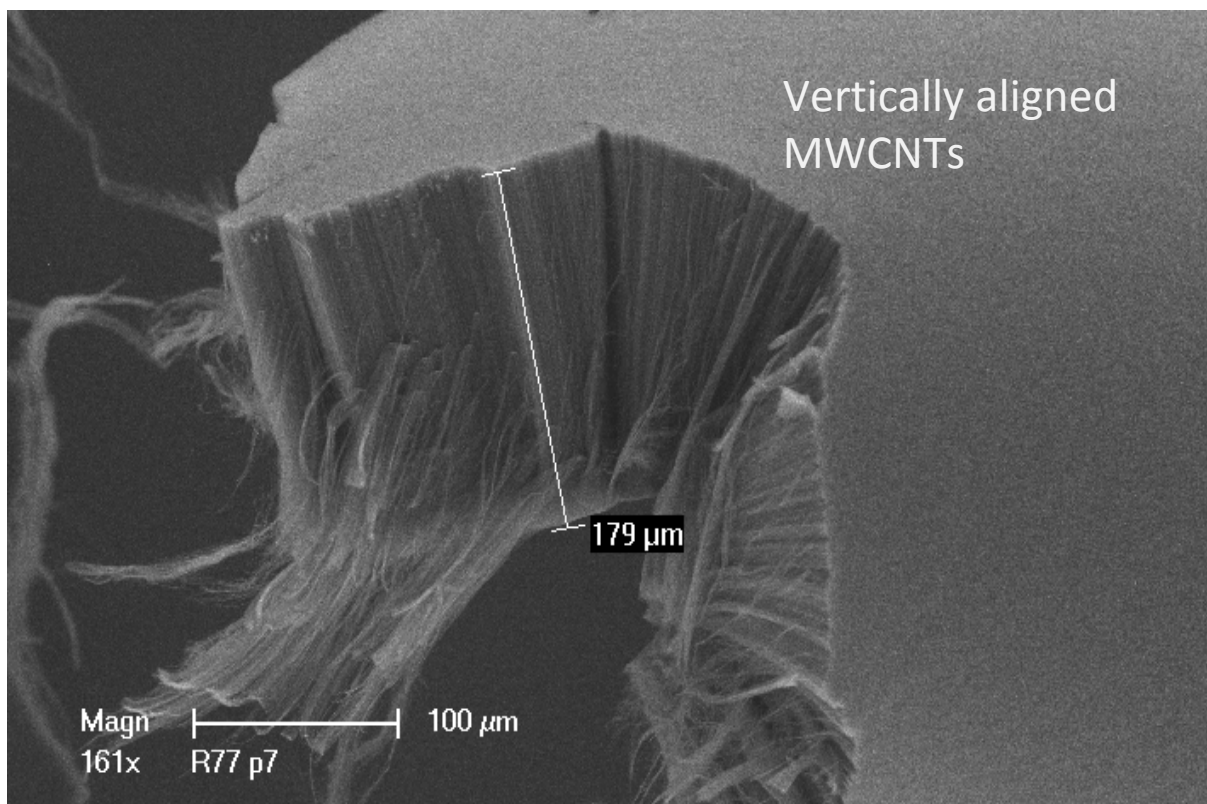


# 2. SWCNT sensors



# 3. Graphene





## *Carbon nanotube yarns for environmental gas sensing applications*

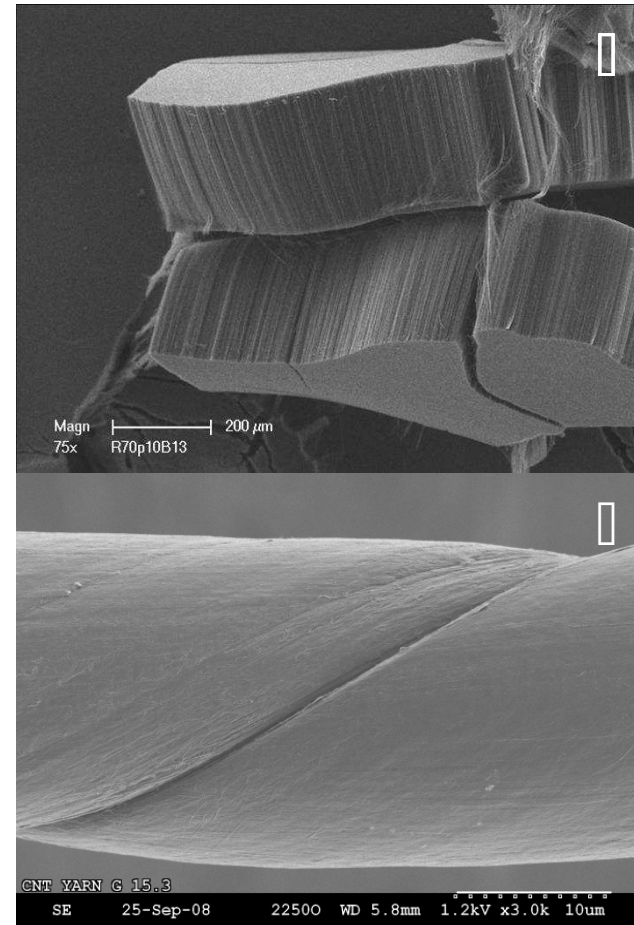
# Carbon nanotube yarns

## Advantages of carbon nano tubes

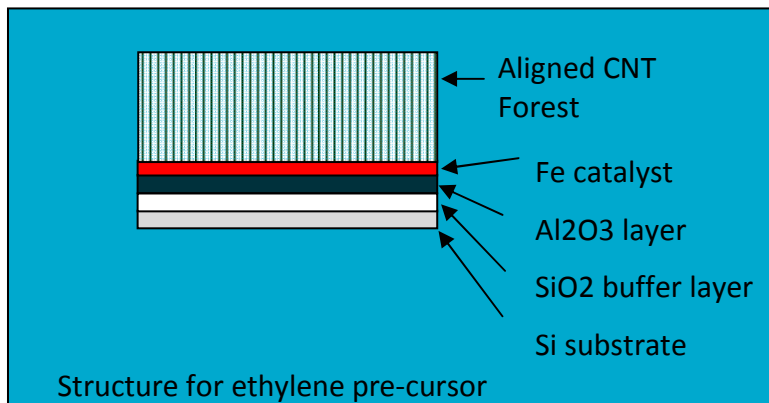
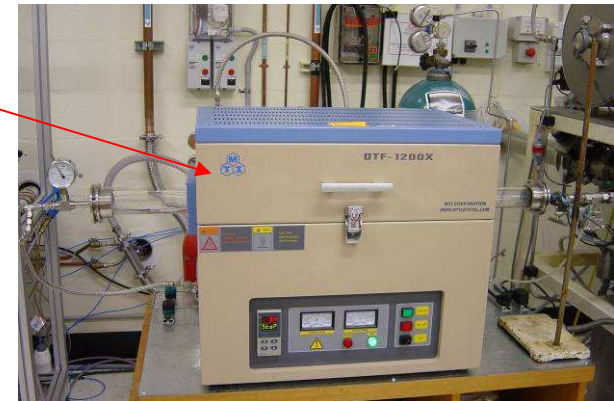
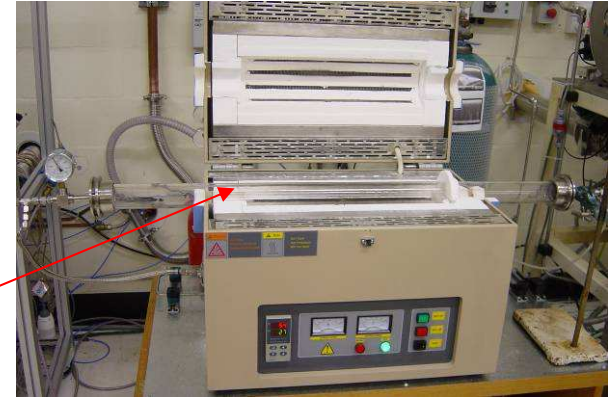
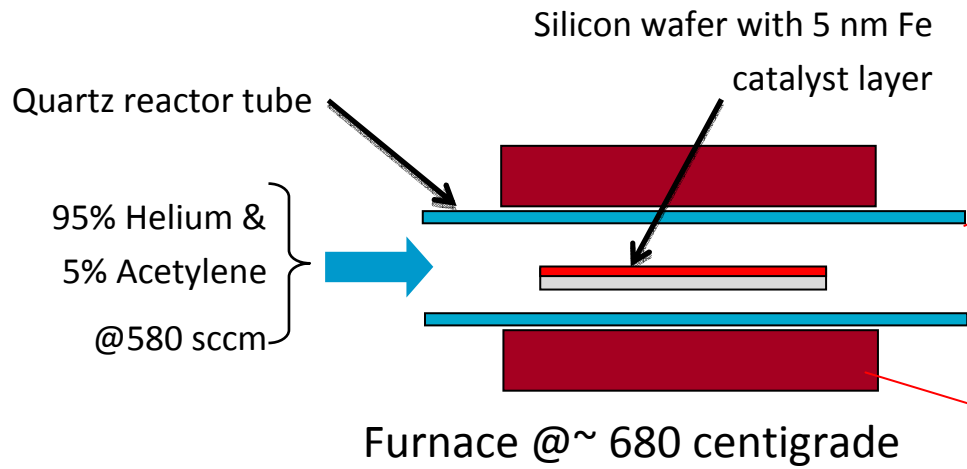
Gas adsorption capability,  
Large specific surface area,  
High sensitivity,  
Low operating temperature

## Advantages of carbon nanotube yarns

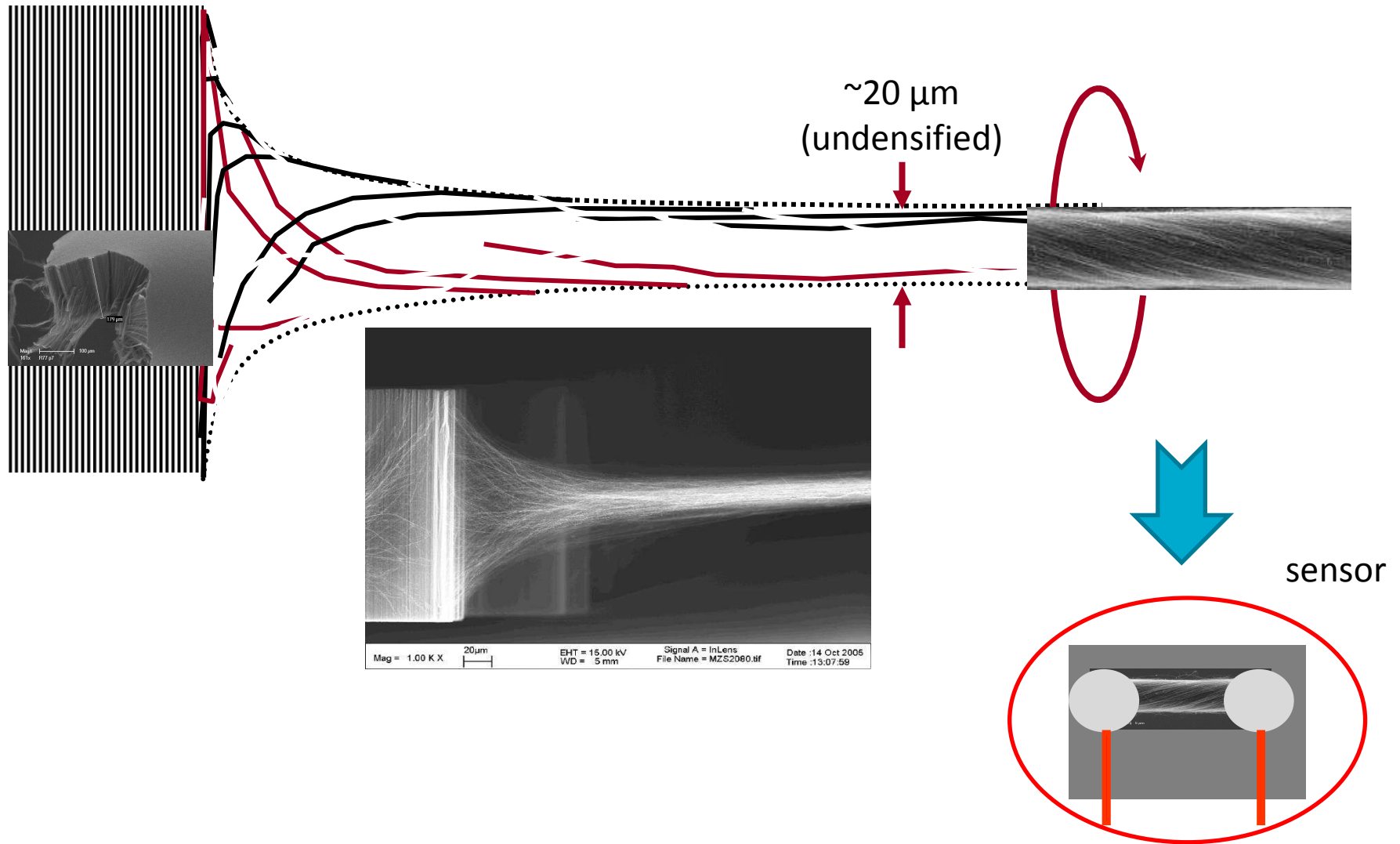
Functional surface available  
Mechanically robust structures  
Easy to functionalise and handle  
Can be used as a simple chemiresistor



# Growth of Vertically Aligned MWCNTs



# Schematic of web formation



# CNT Yarn Properties

## •Data for CNT Yarns

### •Electrical Conductivity (S/cm):

- Singles yarn ~300

### •Density/(g/cm<sup>3</sup>):

- Singles yarn ~0.8

### •Modulus/GPa: (Singles 24° twist)

- ~100

### •Strength/GPa: (Singles 24° twist)

- ~0.92

### •Toughness/(J/g):

- Singles Yarn ~14
- Twofold Yarn ~20

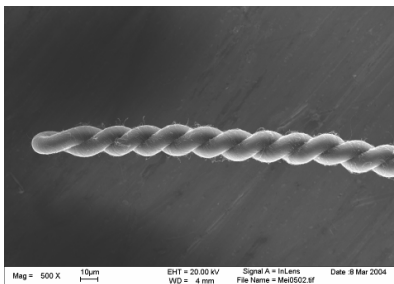
### •No creep:

- >20 h at 6% strain (~50% breaking strain)

### •Knots do not degrade tensile strength:

### •Retain flexibility/strength :

- after heating in air at ~450°C
- when immersed in liquid N<sub>2</sub>



## •Comments and comparisons

### •Electrical Conductivity/(S/cm):

- Graphite CF: ~167 – 3333

### •Density/(g/cm<sup>3</sup>):

- Graphite CF ~1.8

### •Modulus/GPa:

- Graphite CF ~300

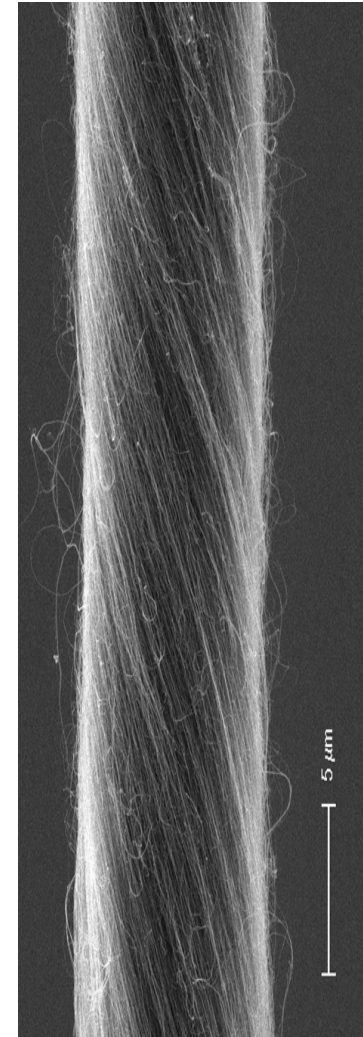
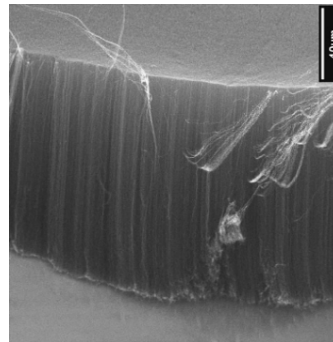
### •Strength/GPa:

- Graphite CF ~3

### •Toughness/(J/g)

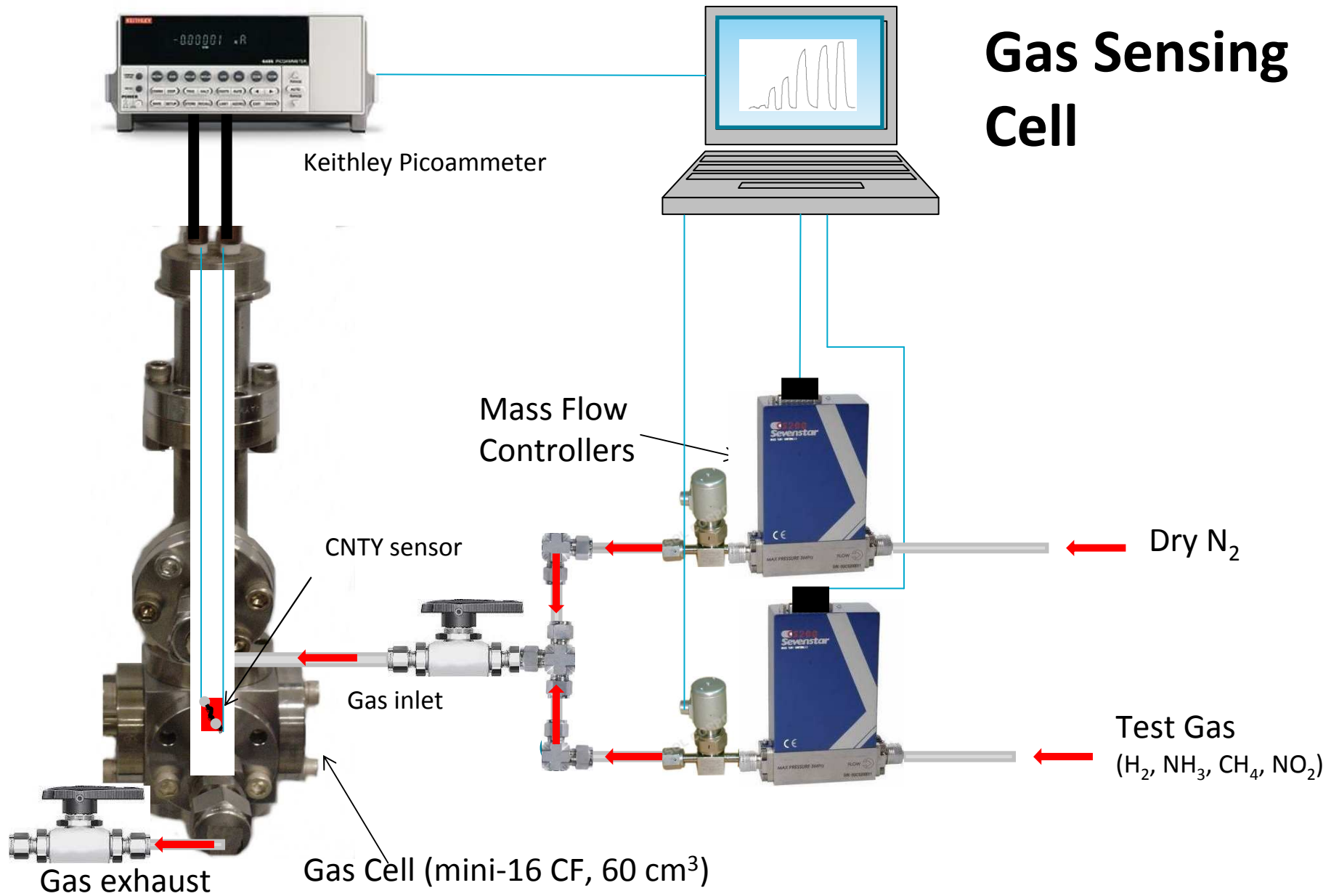
- Graphite CF ~12
- Solution-spun SWNT/PVA yarns ~600

### •Knots degrade tensile strengths of most textile fibres





# Gas Sensing Cell



# Functionalization of the Yarns

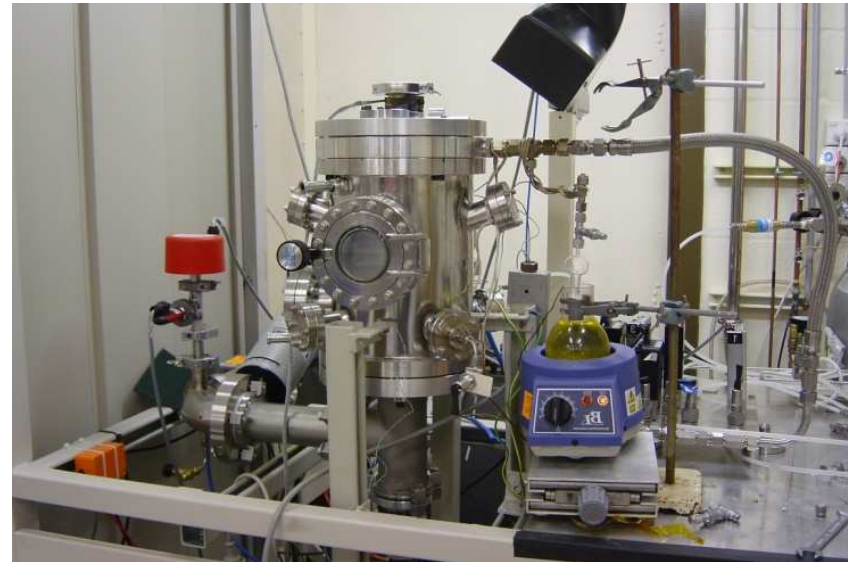
P-type semiconductor ( $500 - 600 \text{ Scm}^{-1}$ )

Surface treatments (create active sites)

Plasma and acid methods  
Introduce various functional groups  
(Carboxylic, N-, S-), and defects (oxygenated  
vacancies, pentagon-heptagon pairs etc.)

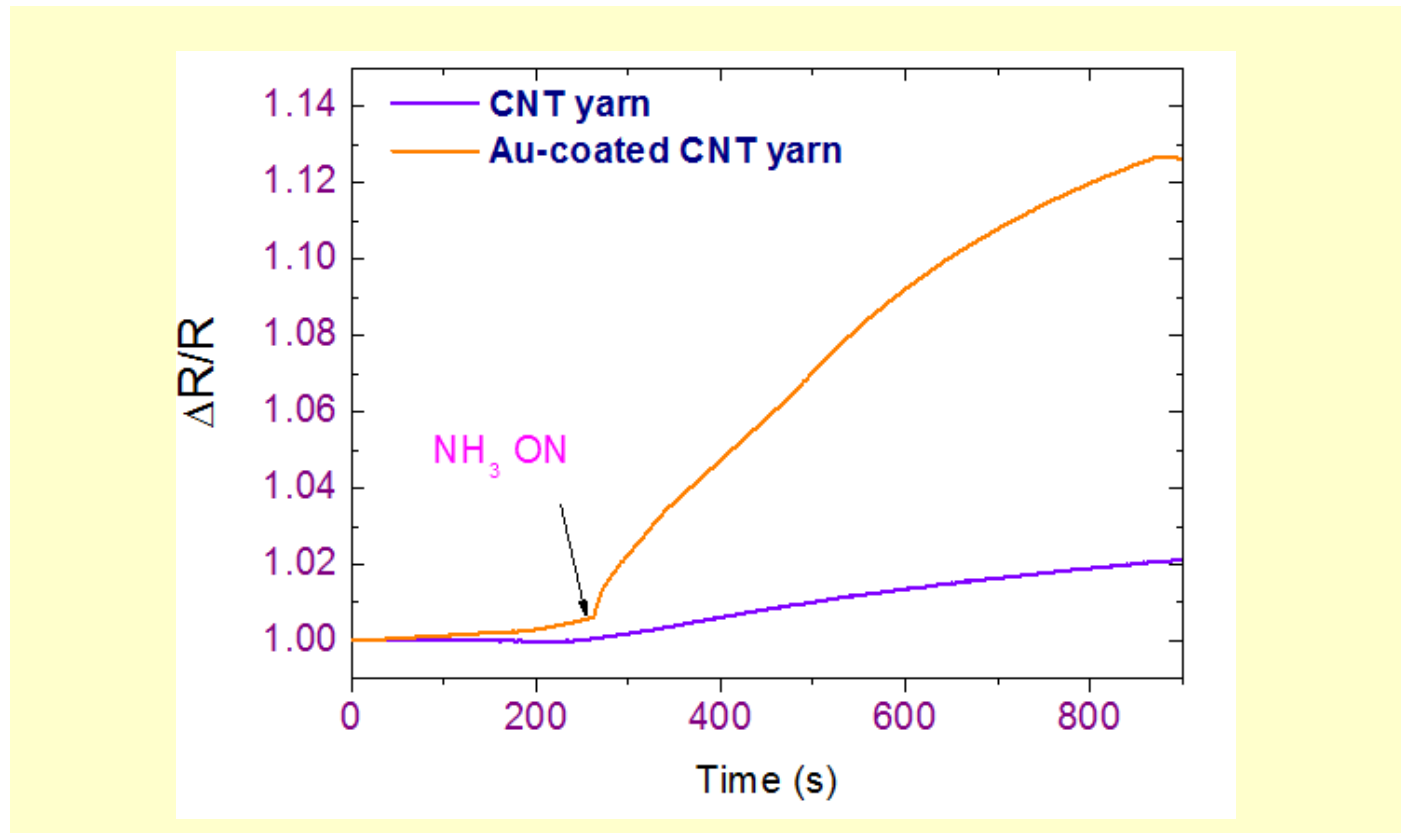
Incorporation of metal nano clusters  
(improves specificity)

Sputtering techniques  
Electrochemical techniques (self-  
fuelled electrodeposition, SFED)



Pulsed-DC PECVD system used for  
surface functionalisation

# Ammonia Sensing with Au-decorated CNT yarns



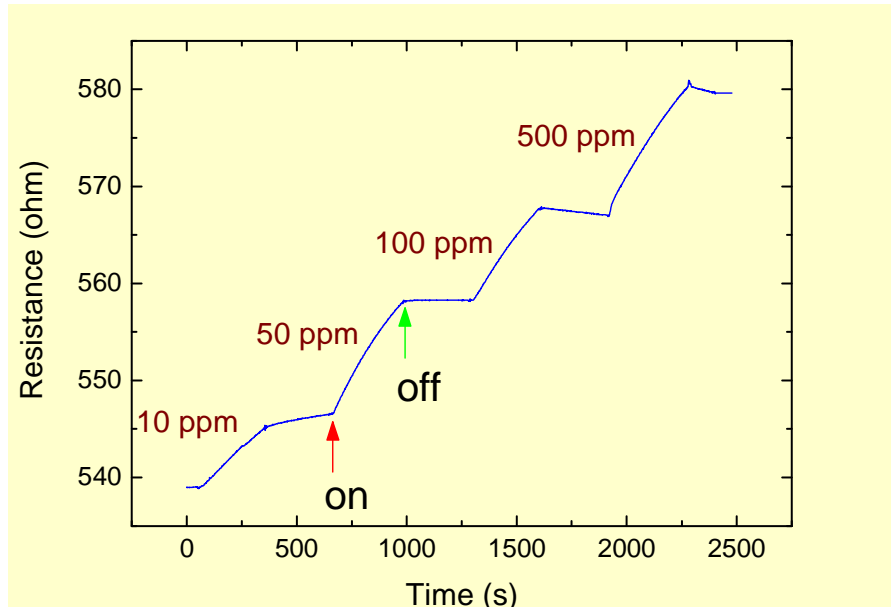
Decoration with Au enhances the sensitivity (factor of 5 – 8)

*Mechanism is unclear; could be related to the modulation of the Schottky barrier*



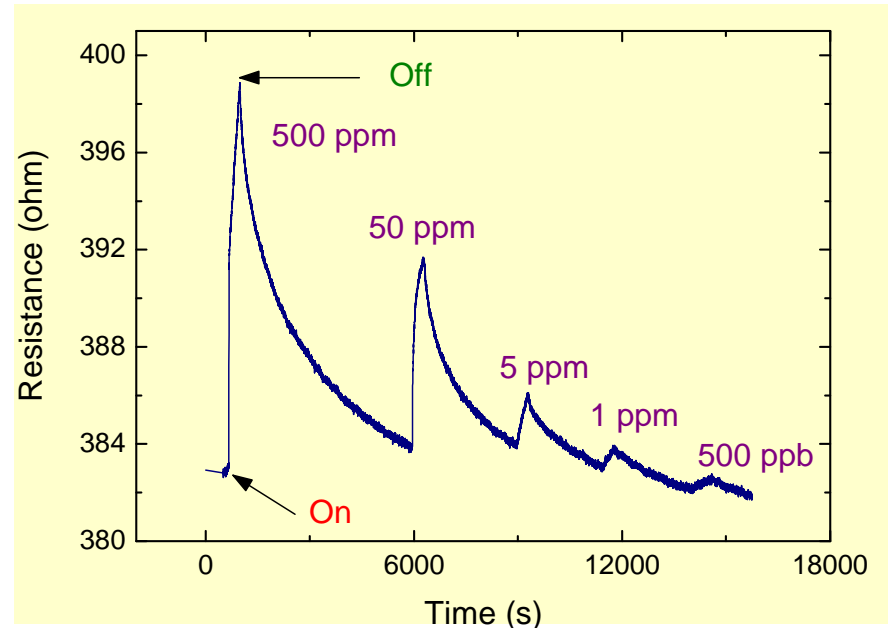
# CNTY Surface Treatment

NH<sub>3</sub>



Acid-treated sample

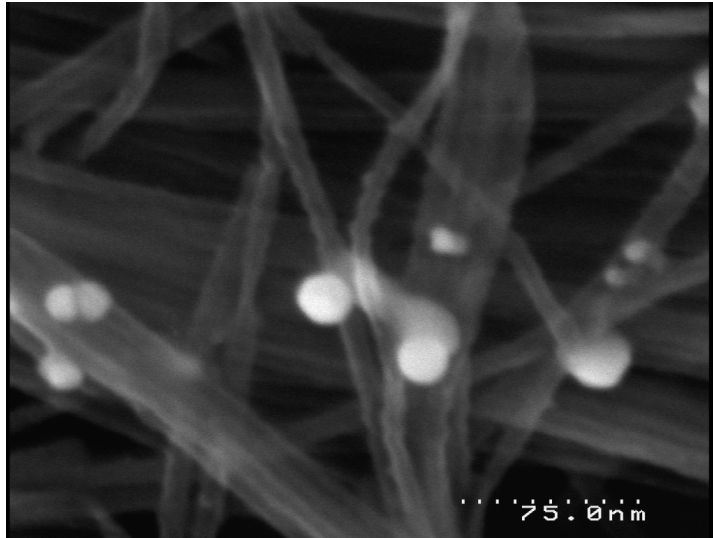
- Quick response
- Long or no recovery
- Low concentrations
- Non-reproducible



Plasma-treated sample

- Quick response
- Good recovery
- Low concentrations
- Reproducible

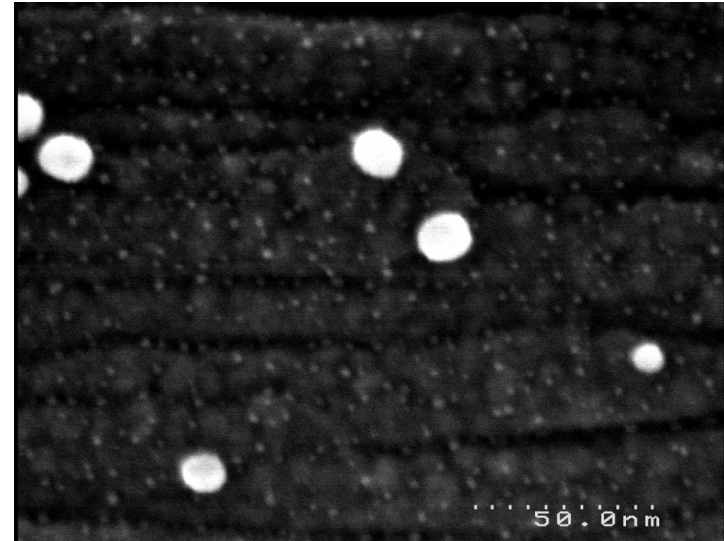
# CNTY Surface Treatment



**Acid-treated sample**

- Particle sizes 10 – 20 nm
- Sparsely distributed

Diffusion out of smaller particles easier ??



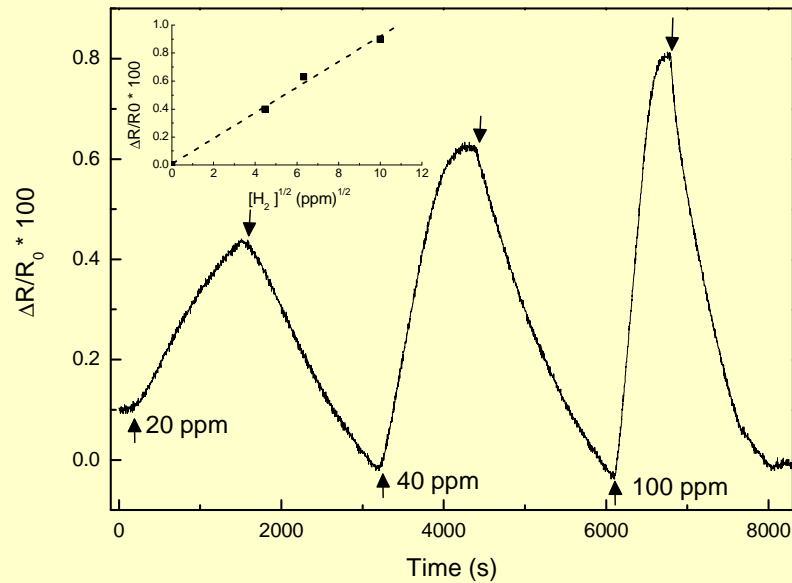
**Plasma-treated sample**

- Dual populations
  - Sparse 10-20 nm
  - Dense and uniform 2 -3 nm

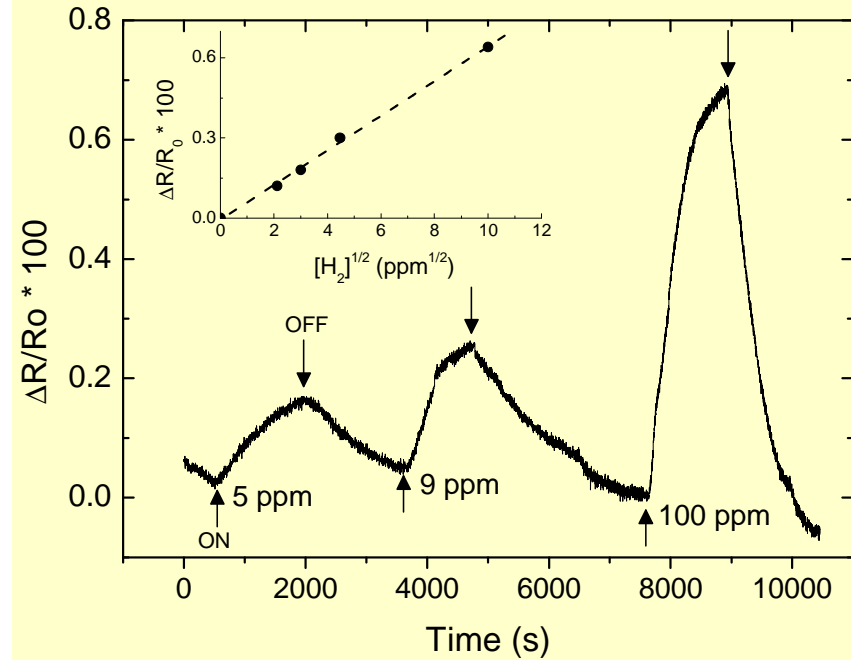
# Hydrogen detection using Pd and Pd-Pt coated yarns (low concentrations)

H<sub>2</sub>

Pd Only

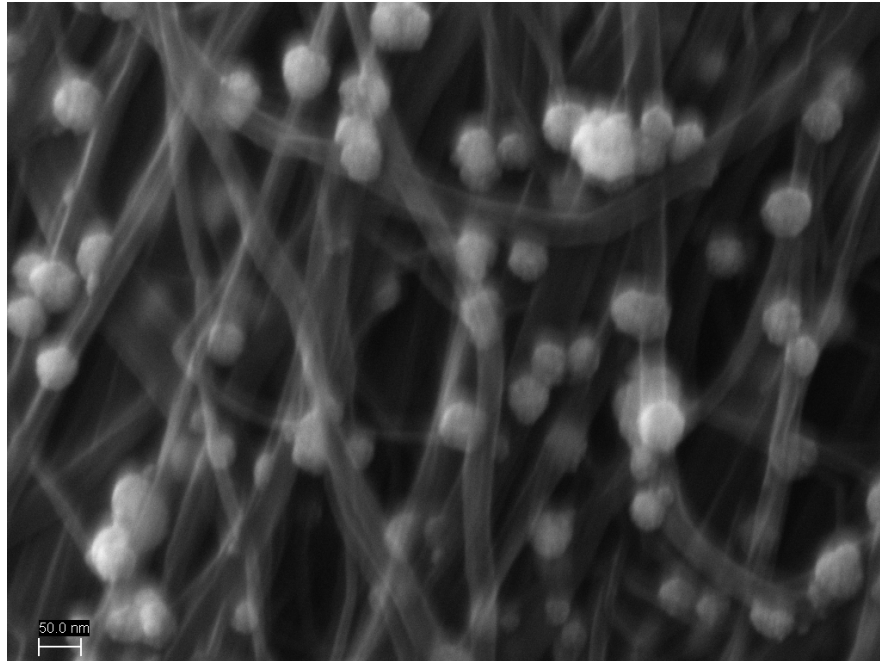


Pd-Pt layered structure

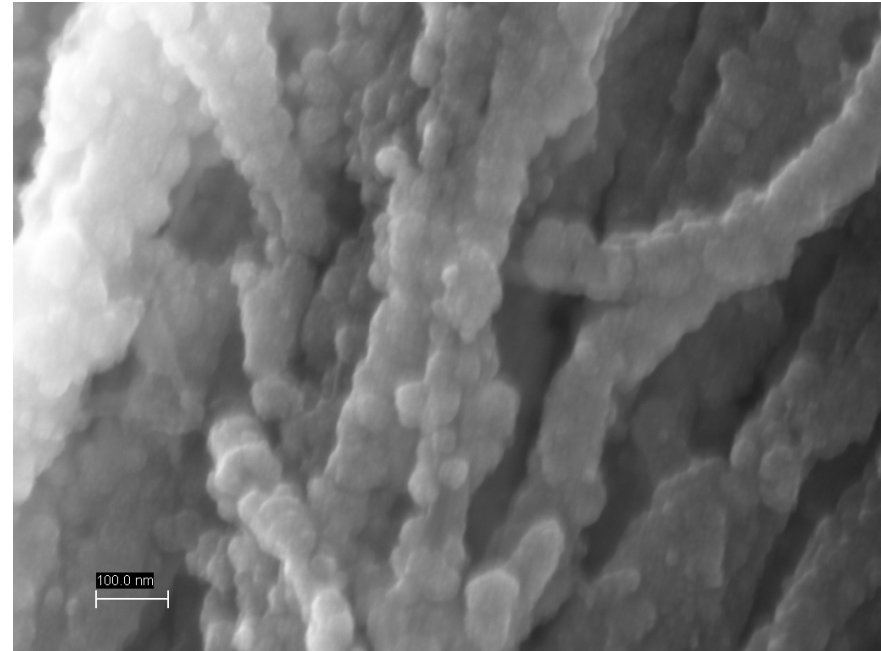


Addition of Pt layer enables the detection of lower concentrations

# CNTY: Pd and Pd-Pt nanostructures



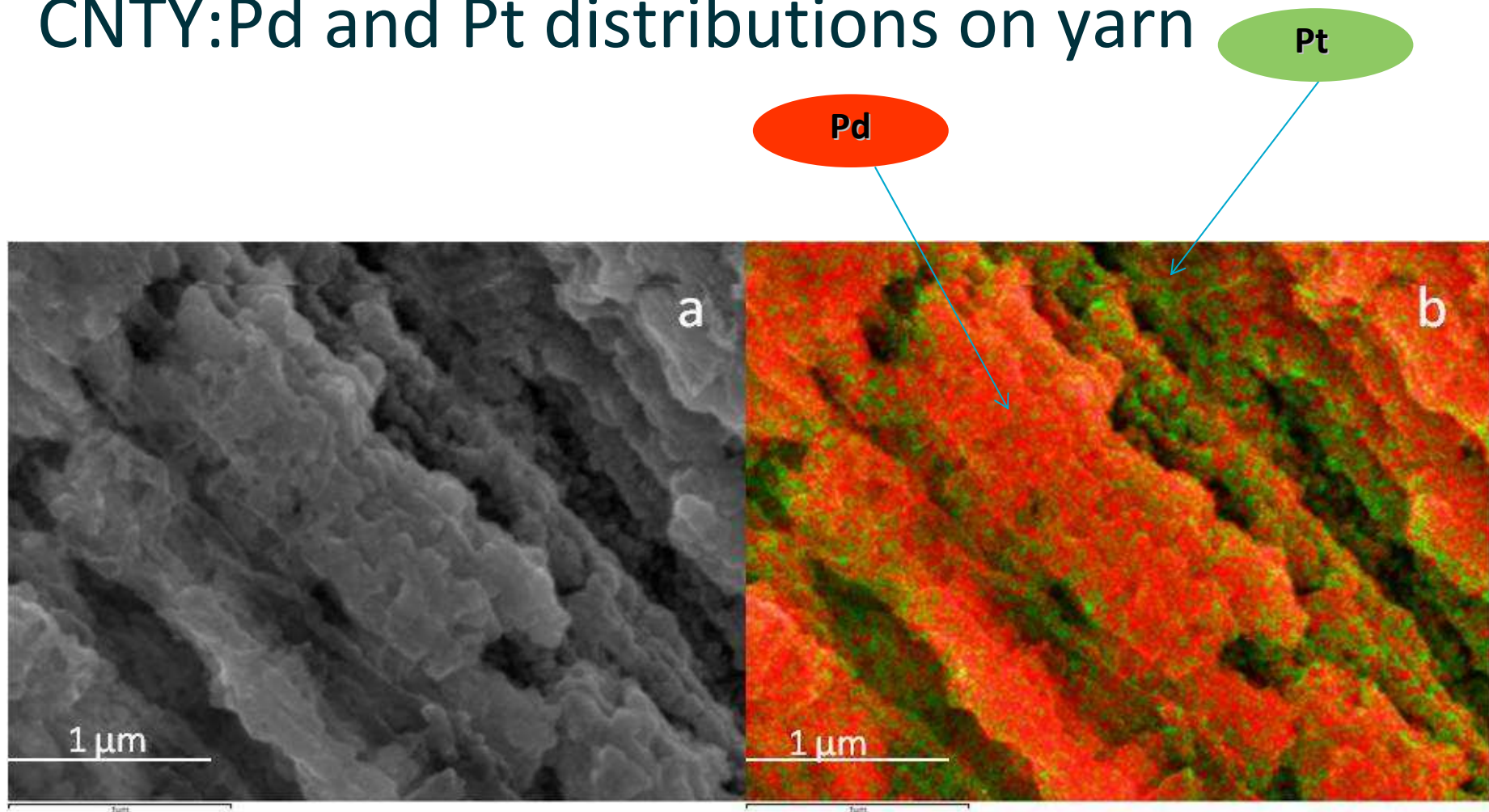
Pd: Sparse Pd populations



Pd-Pt: Dense Pd populations



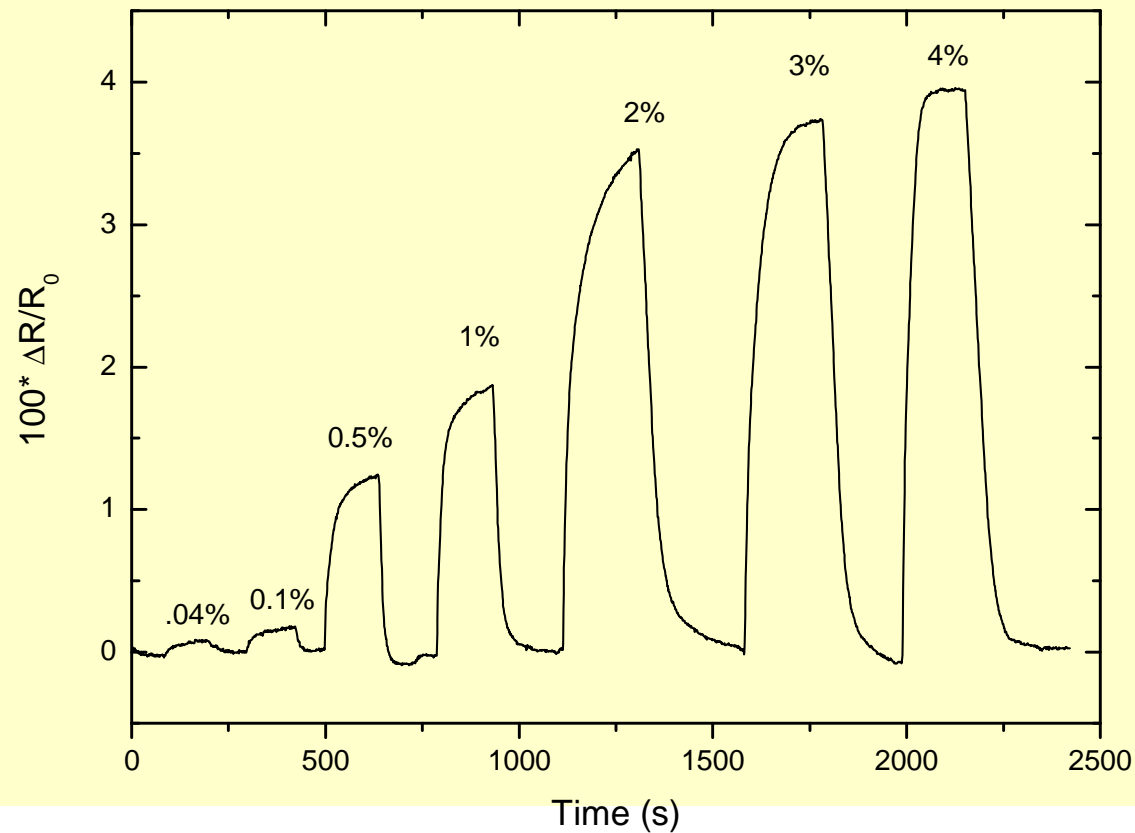
# CNTY: Pd and Pt distributions on yarn



**Pt is dispersed particulates on larger Pd grains**

# CNTY

## Hydrogen detection using Pd-Pt-coated (higher concentrations in air)



**Excellent response times and recovery times**

# Hydrogen detection using Pd and Pd-Pt-coated CNT yarns

Work function of Pd and lattice parameters are sensitive to hydrogen

Room-temperature detection

Concentrations from 20 ppm to 2 % (20,000 ppm) are detectable with Pd-MWCNT-yarn chemiresistor

Concentrations from 5 ppm to 2 % (20,000 ppm) are detectable with Pt-Pd-MWCNT-yarn chemiresistor

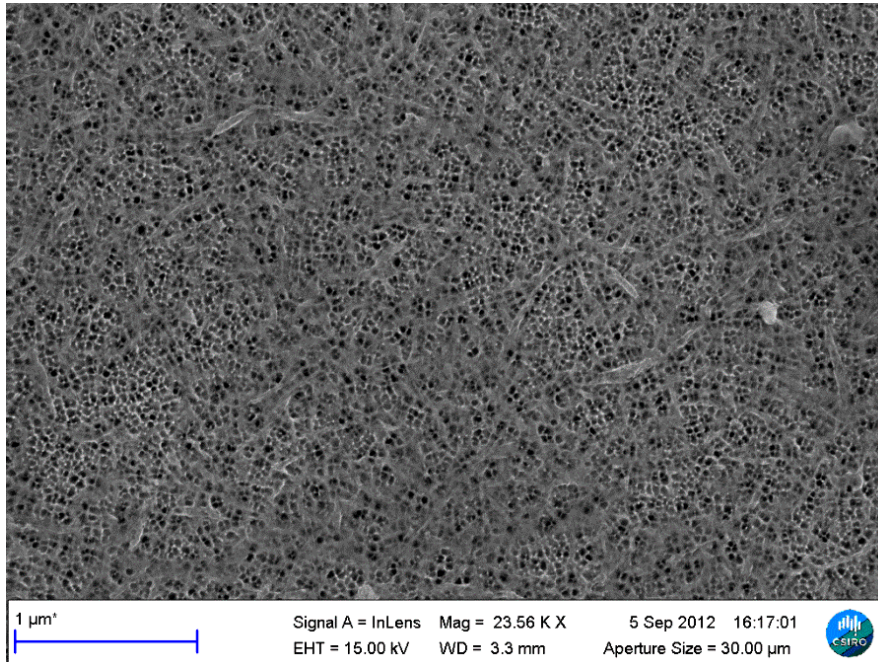
Excellent response times and recovery times are obtained

Flexible, robust and simple chemiresistor systems

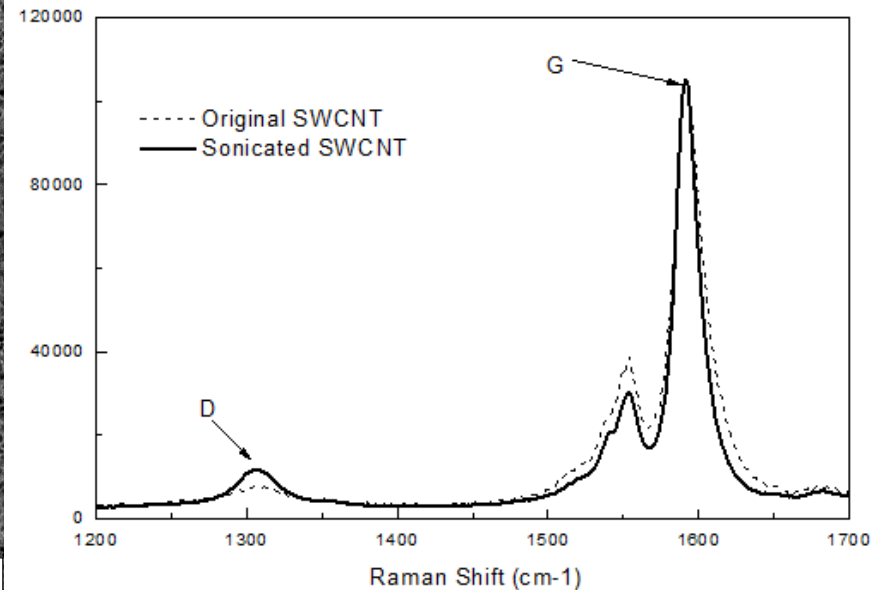
# CNTY: Summary

- CNT yarn has potential to be used as gas sensors
- Robustness
- Easy handling
- Easy to functionalise
- Room-temperature operation
- SFED method is a quick and reliable method for incorporating nanocrystalline metals (onto semi-conducting and conducting substrates)
- Particle size has a significant impact on the recovery of  $\text{NH}_3$  and hydrogen sensors
- Addition of Pt on Pd increases sensitivity at low concentrations

# SWCNT

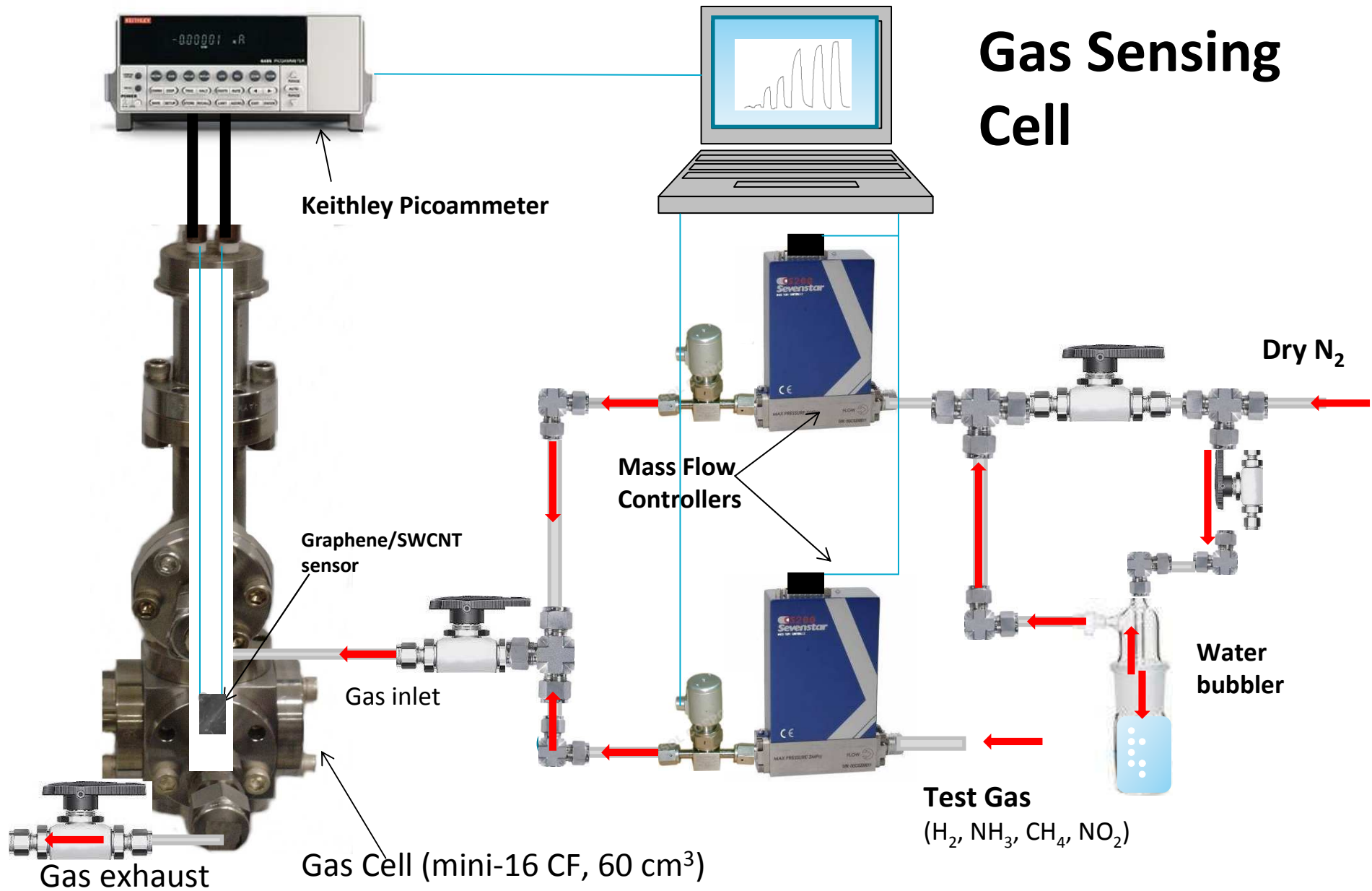


SEM diagram showing thinly-spread bundles of CNT on a mesoporous alumina membrane. The resistance ( $\sim 3 \text{ mm} \times 5 \text{ mm}$ )  $\sim 1.6 \text{ M}\Omega$  under ambient conditions.



Raman shift for original (without ultrasonic treatment) and ultrasonic-treated samples. The increase in D peak intensity with respect to that of G peak is attributed to the increase in defects caused by ultrasonic treatment.

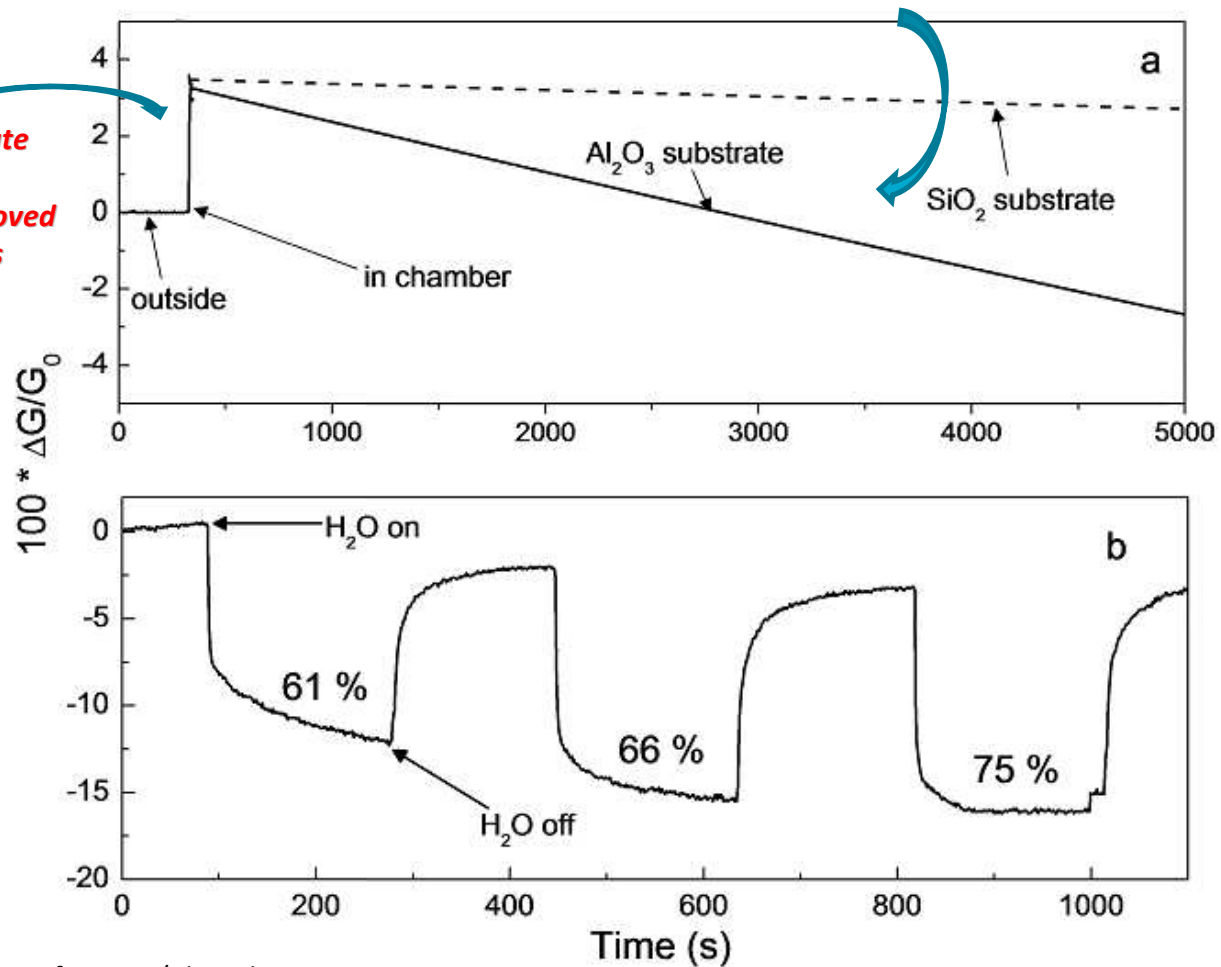
# Gas Sensing Cell



# SWCNT

**Mode -1-Slow**  
 More tightly bound water molecules donate holes  
 When slowly removed conductivity decreases

**Mode -2-Fast**  
 Water molecules donate electrons to p-type conductor. When removed conductivity increases



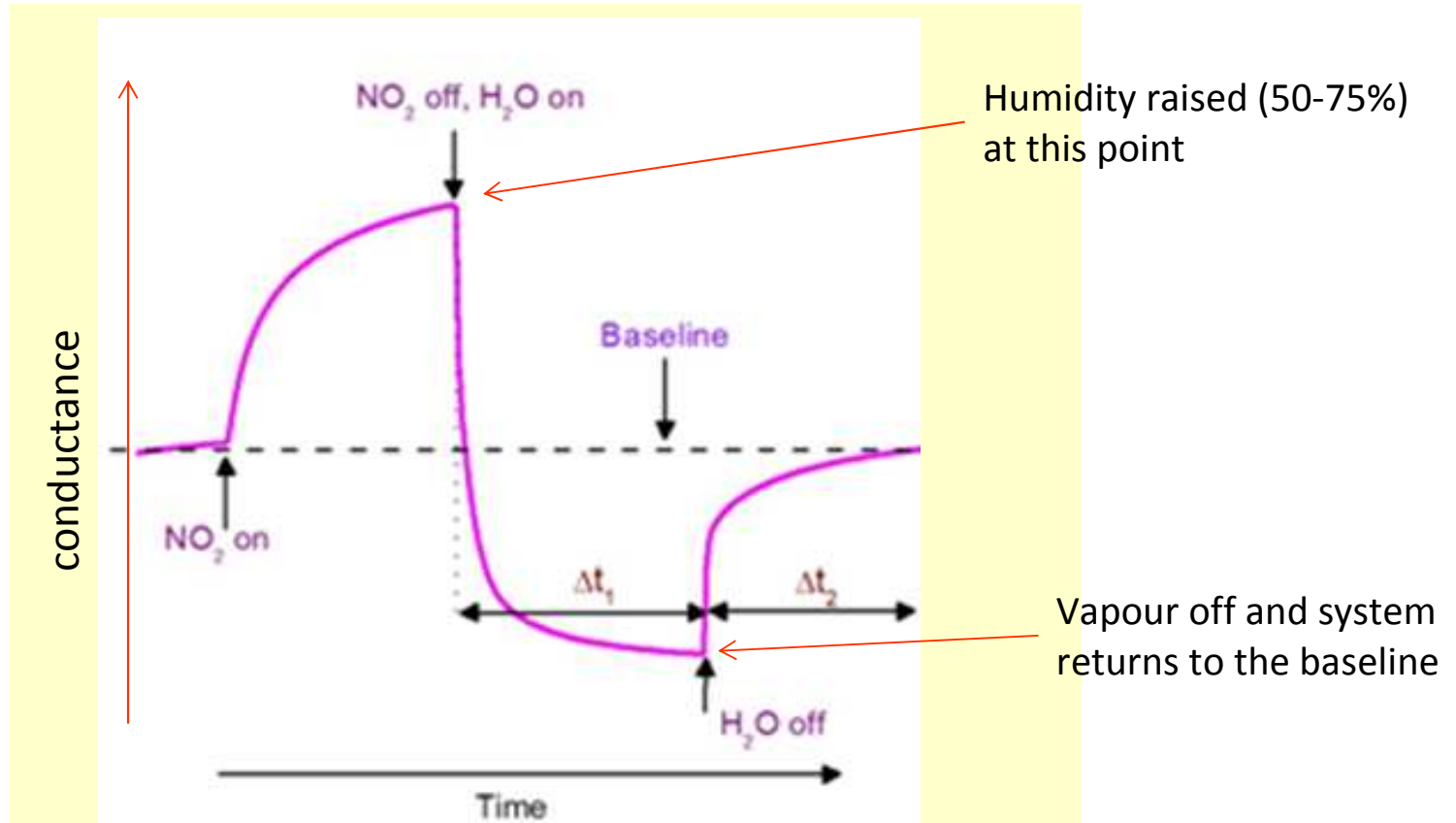
Two modes of response of SWCNT/Al<sub>2</sub>O<sub>3</sub> chemiresistors to water vapour.

(a) response change with time when a chemiresistor equilibrated under ambient conditions is introduced into the chamber under dry air flow. The resistance first drops due to drop in humidity (mode 2 response) and then rises slowly as the water molecules come off (mode 1 response).

(b) Mode 2 responses of the chemiresistor to injections of water (by diverting a fraction of buffer gas flow through an enclosed bubbler) which temporarily raise the humidity in the chamber to the levels marked.

# SWCNT

NO<sub>2</sub>

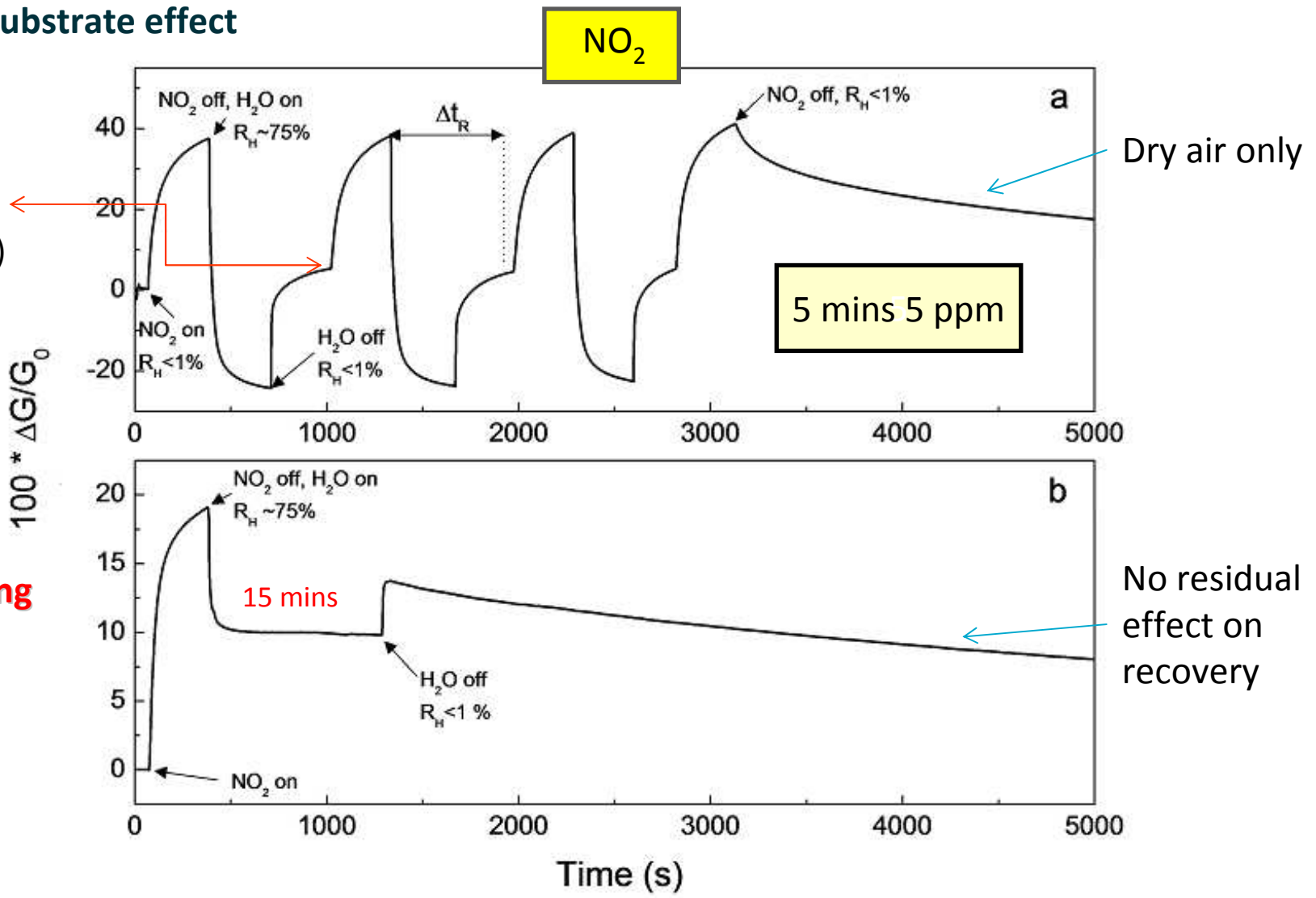


Scheme used for NO<sub>2</sub> measurements using water-assisted recovery



# SWCNT: substrate effect

**Al<sub>2</sub>O<sub>3</sub>**  
 recovery time  
 $\Delta t_R (= \Delta t_1 + \Delta t_2)$   
 $\sim 10$  min



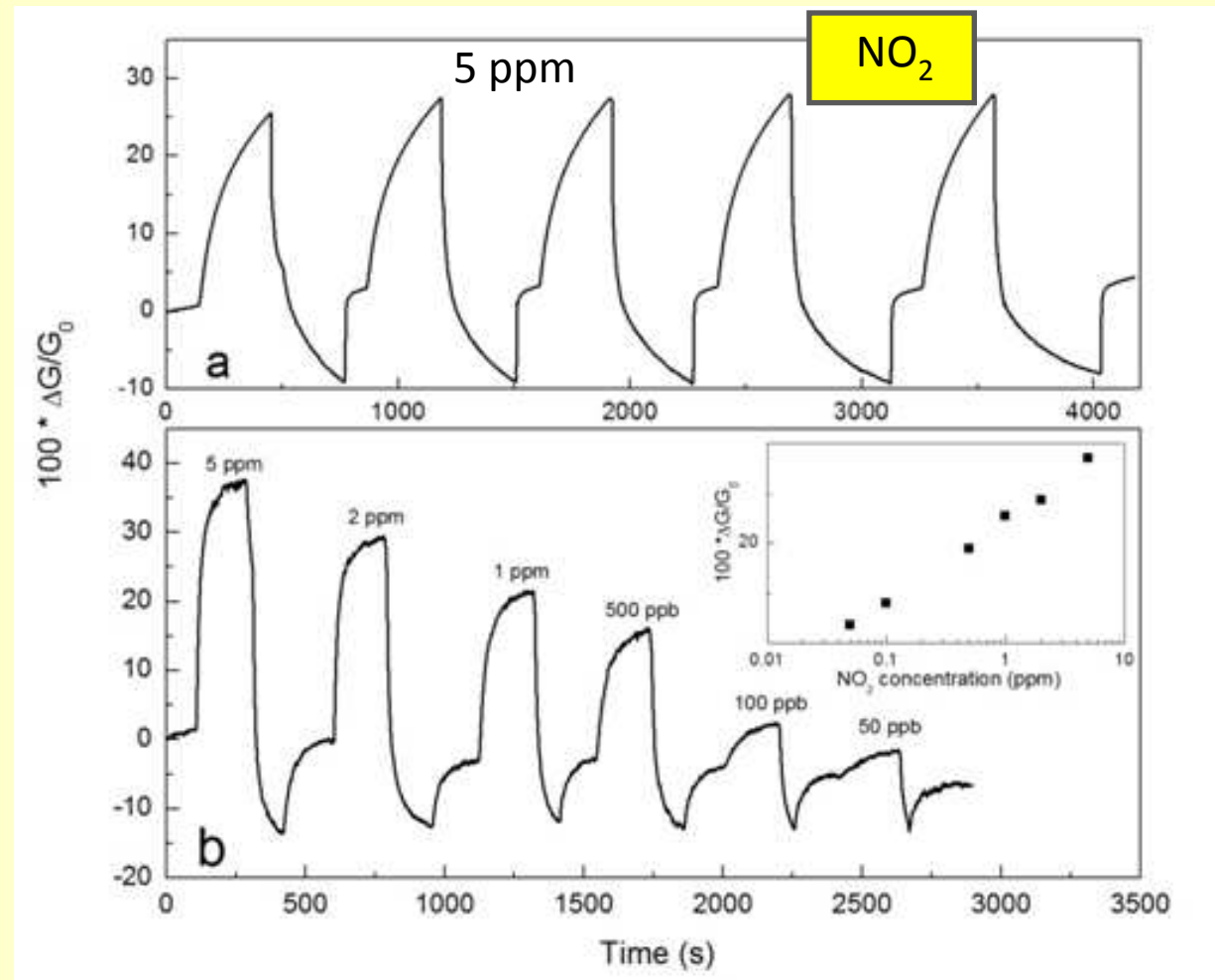
**Free standing film**

SWCNT  
on

$\text{SiO}_2$



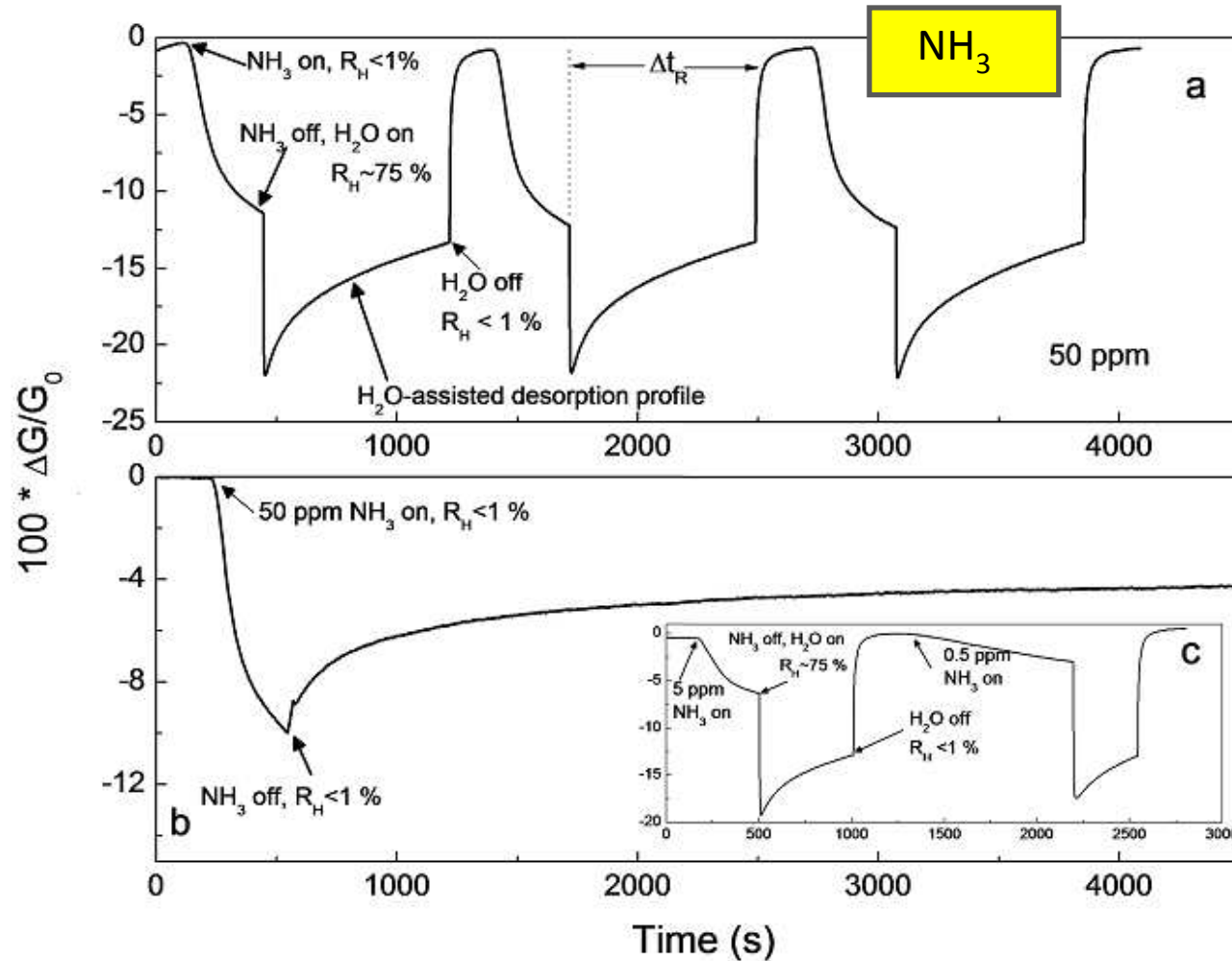
$\text{Al}_2\text{O}_3$



(a) repeated detection of 5 ppm NO<sub>2</sub> using SWCNT deposited on Si wafer with natural oxide layer (SWCNT/SiO<sub>2</sub> chemiresistor). Chemiresistor is exposed to NO<sub>2</sub> for 5 min Water-enriched airflow is maintained for 5 min in each case before reverting to dry airflow. (b) Measurement of different concentrations of NO<sub>2</sub> with 3-min exposures in each case followed by water-assisted recovery. A SWCNT/Al<sub>2</sub>O<sub>3</sub> chemiresistor was used. -Inset to (b) shows a response versus log concentration curve.

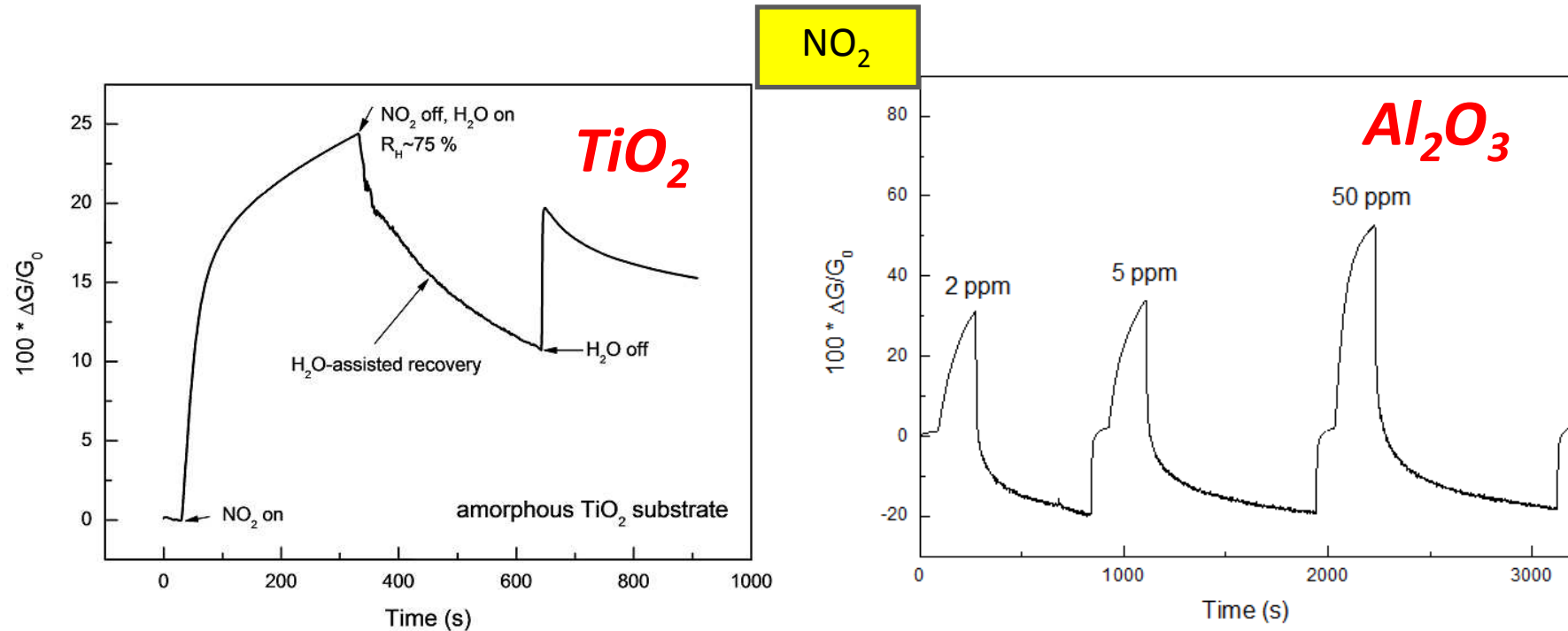
SWCNT  
on

$\text{Al}_2\text{O}_3$



Detection of ammonia using a SWCNT/ $\text{Al}_2\text{O}_3$  chemiresistor; the response is calculated as a percent increase in conductance. (a) Repeated detection of 50 ppm with water-assisted recovery time ( $\Delta t_R$ ) of about 15 minutes when humidity is raised to  $\sim 75\%$ ; (b) partial and very slow recovery in dry air; (c) detection of 5 ppm and 500 ppb using the same method. In all cases 5-minute exposure to ammonia used except for the detection of 500 ppb where a longer exposure time was used.

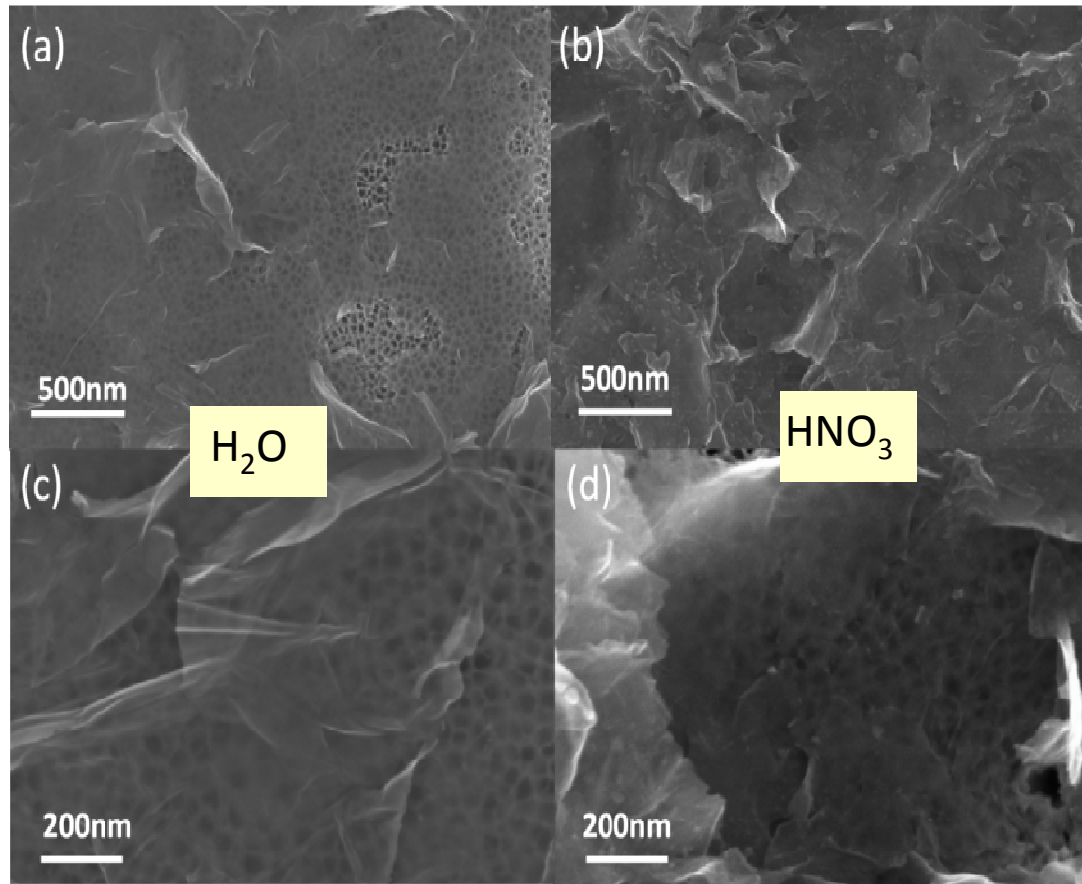
# SWCNT: humidity effect on different substrates



**Detection of 5 ppm  $\text{NO}_2$  using SWCNT on amorphous  $\text{TiO}_2$  substrate**

**Lower humidity to achieve recovery. 50% of the buffer gas was diverted through water bubbler. Relative humidity in the chamber rose to 52 %**

# Graphene

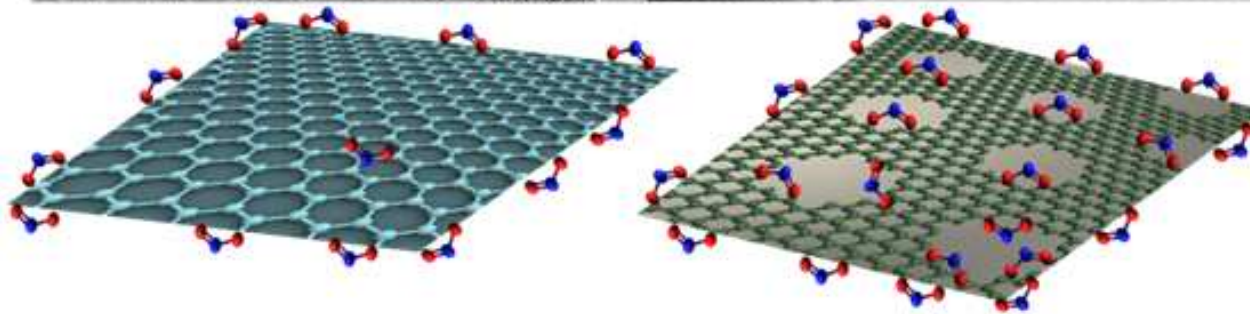
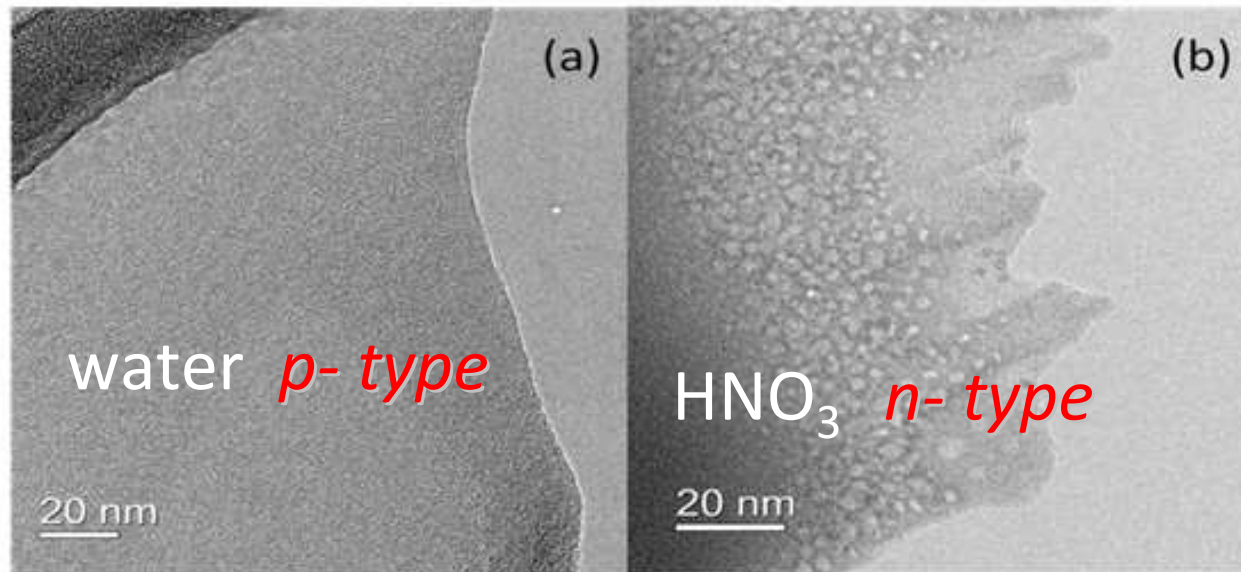


SEM images of sections of chemiresistors used for gas detection

(a), (c) preparations in pure water  
(b), (d) preparations in nitric acid

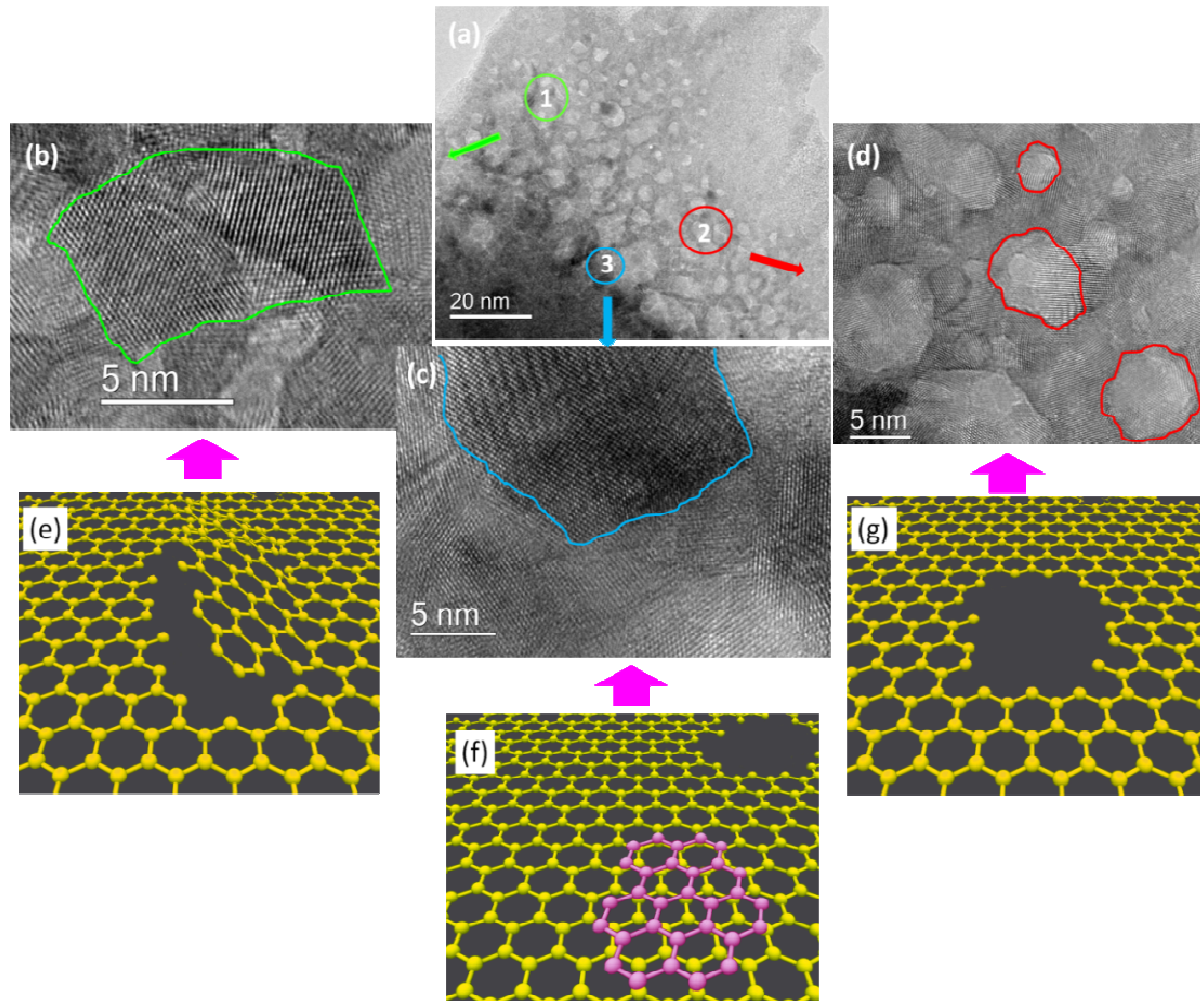
Whatman Anopore<sup>®</sup> membranes (~ 50 nm diameter pores) were used as substrate.

# Graphene



TEM images of (a) graphene flakes obtained from pure water dispersion (b) graphene nanomesh obtained from nitric acid dispersion. Schematics of NO<sub>2</sub> adsorption on graphene flakes and graphene nanomesh flakes are shown below the corresponding TEM images.

# Graphene

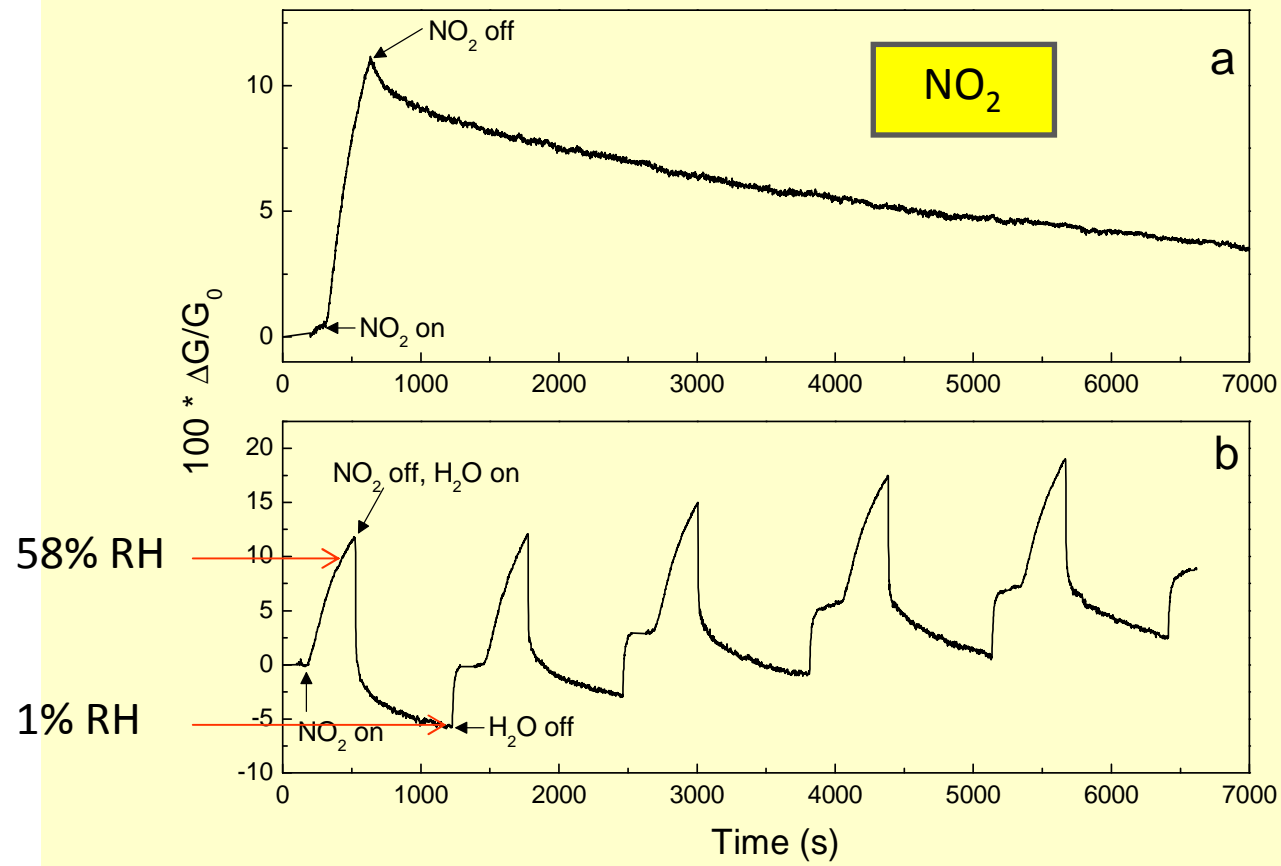


TEM and HRTEM images of graphene obtained from  $\text{HNO}_3$  acid dispersions and schematic interpretation of structures. (a) A section of regular TEM and (b) to (d) are HRTEM images of areas marked as 1, 2 and 3. (e) - (g) are schematic representations of the corresponding HRTEM images.

# Graphene sensor:

enhanced recovery using water vapour

**p-type response**



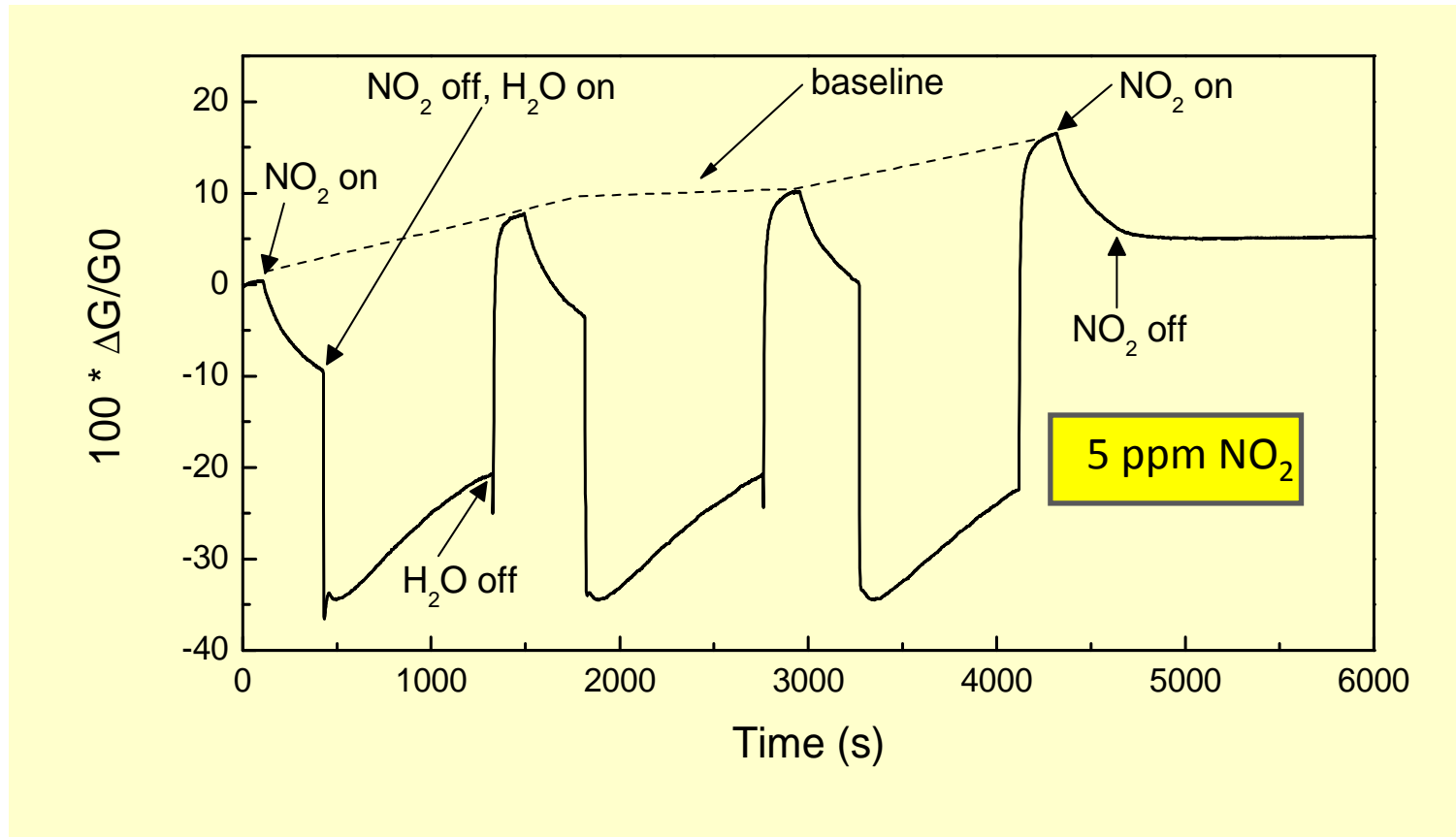
5 mins NO<sub>2</sub> 5 ppm  
Very slow  
recovery

5 mins NO<sub>2</sub> x 5  
+ H<sub>2</sub>O purging  
**Recovery  
dramatically  
reduced**



# Graphene: HNO<sub>3</sub>-treated

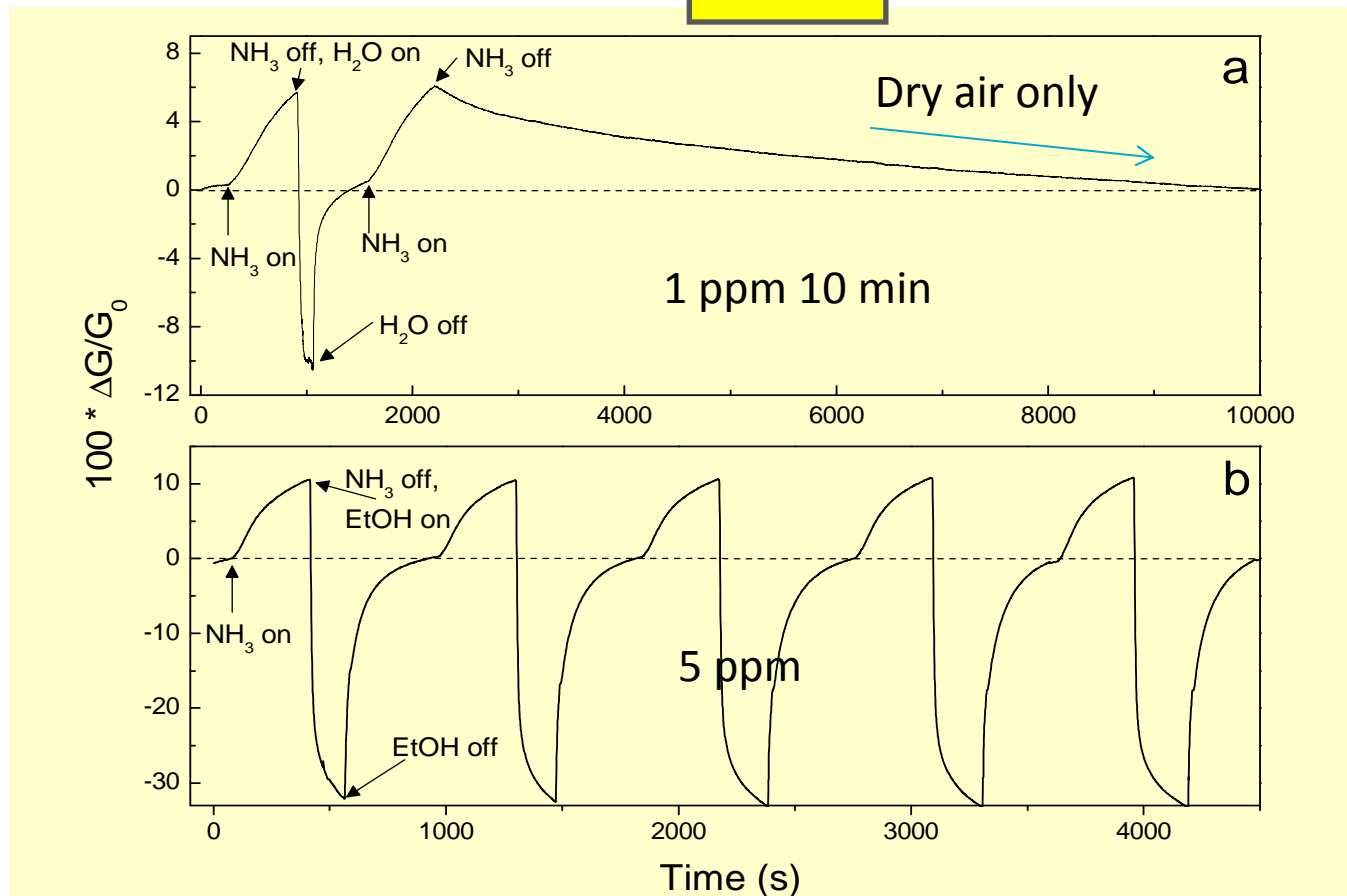
*n-type response*



The response of HNO<sub>3</sub>-treated graphene chemiresistor to 5 ppm of NO<sub>2</sub> (5 min exposure). The conductance decreases in response to NO<sub>2</sub> exposure confirming that acid-treated graphene behaves as an n-type semiconductor. There is an upward drift in baseline (marked by a dashed line) after each run. Four consecutive measurements are shown.

# Graphene: HNO<sub>3</sub>-treated

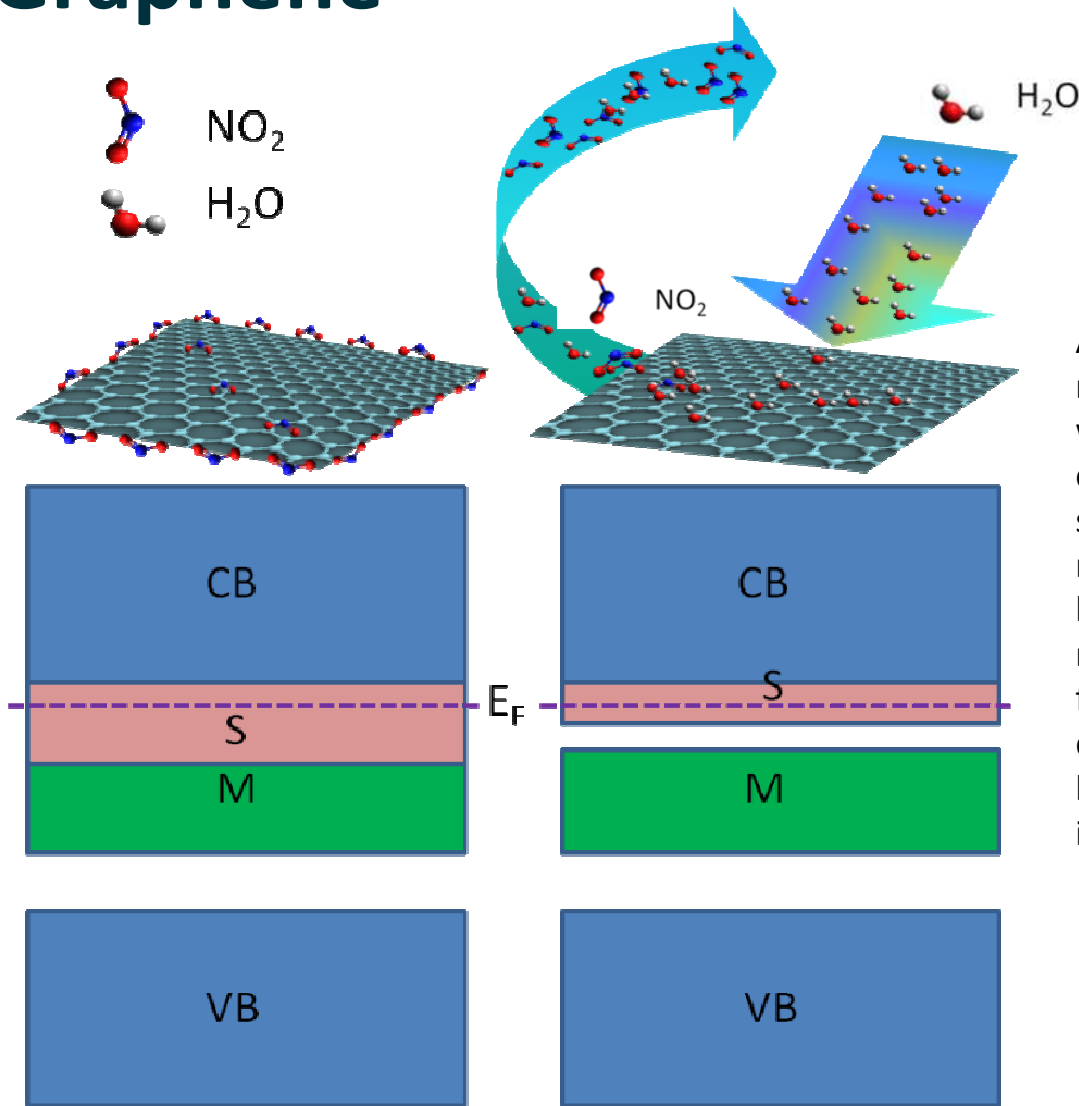
NH<sub>3</sub>



*Effect of H<sub>2</sub>O*

*Effect of EtOH*

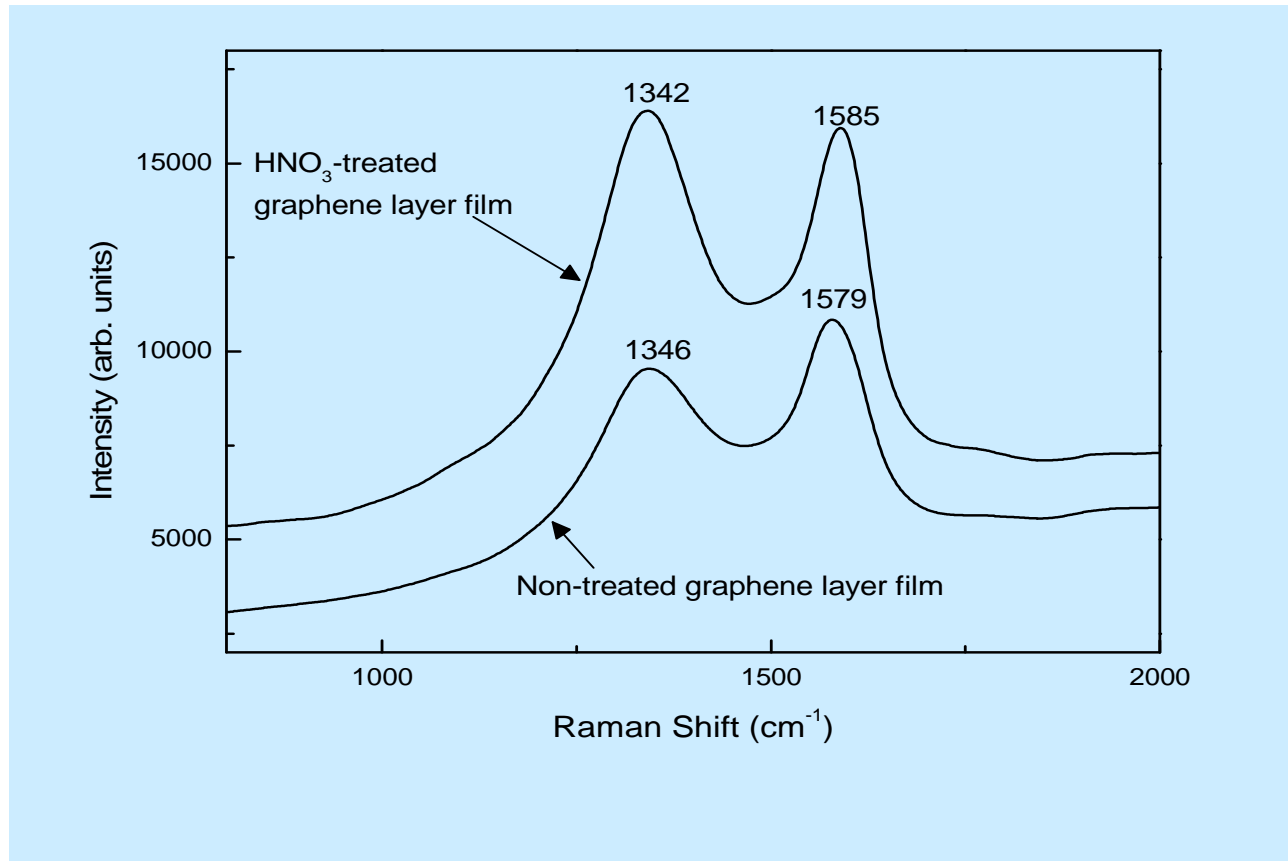
# Graphene



A schematic of a plausible mechanism of NO<sub>2</sub> removal from graphene flakes influenced by water vapour. The strong adsorption of NO<sub>2</sub> on graphene is due to overlap of molecular states (M) and substrate defects states (S) near the Fermi level ( $E_F$ ) with the conduction band (CB) of graphene. When water molecules are introduced, the electrostatic forces causes a movement of substrate defects states and the strong overlap between NO<sub>2</sub> orbitals with that of graphene is lost.

*Wehling et al Appl. Phys. Lett. (2008) 93, 202110*

# Graphene



Raman spectra for graphene. The increase in  $I_D/I_G$  ratio in the nitric-acid-treated samples is further evidence for increased defects in the structure

# Summary

- MW-Carbon nanotube yarns: simple robust sensor with enhanced response when acid-etched and coated with nanoparticles
- SWCNT recovery can be dramatically accelerated by using water vapour “purging”
- Graphene response is enhanced by acid treatment to form nanomesh structures. Water vapour accelerates recovery

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# Thank You

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