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

COST Action TD1105

WGs and MC Meeting at Cambridge, 18-20 December 2013

CARBON NANOMATERIAL BASED SENSORS FOR AIR POLLUTION MONITORING

Eduard Llobet

Sub-WG Leader: Carbon nanomaterials

University Rovira i Virgili / Spain

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Reminder from Rome WGs Meeting in 2012

Carbon nanomaterials (CNMATs) show interesting properties for trace detection of ambient pollutants BUT:

- There is a need for cost-effective, scalable production methods that retain the essential properties of such materials …
- … and for tailoring surface properties via functionalization
- Contacting CNMATs is non-trivial (e.g. material contamination, which affects response, reproducibility…)
- High-quality vs low-quality CNMATs dilemma
- The advancement of applications of carbon nanomaterials is hampered by their biopersistence and pro-inflammatory action *in vivo*

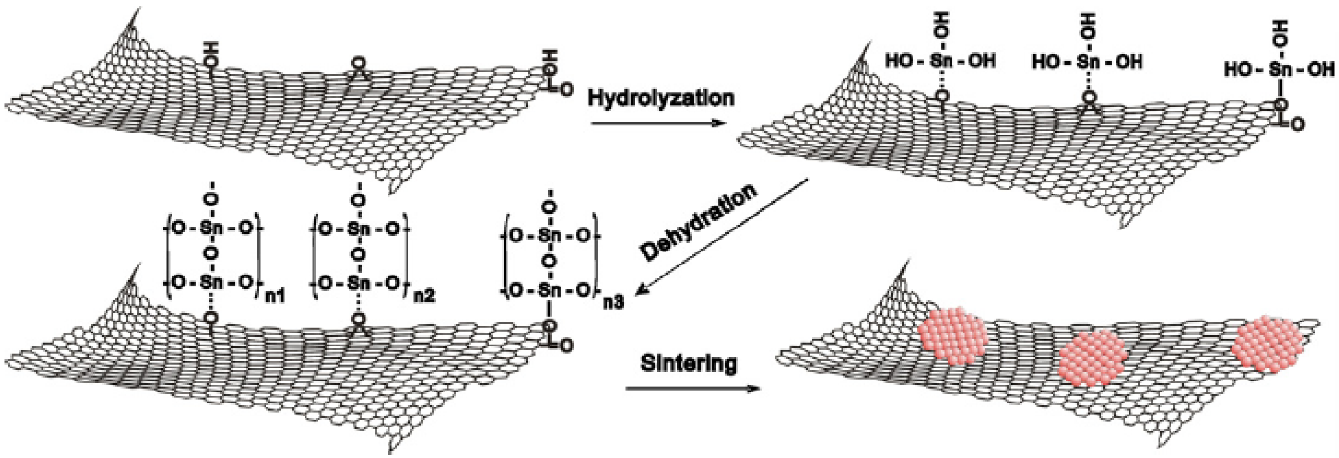
Reminder from Rome WGs Meeting in 2012

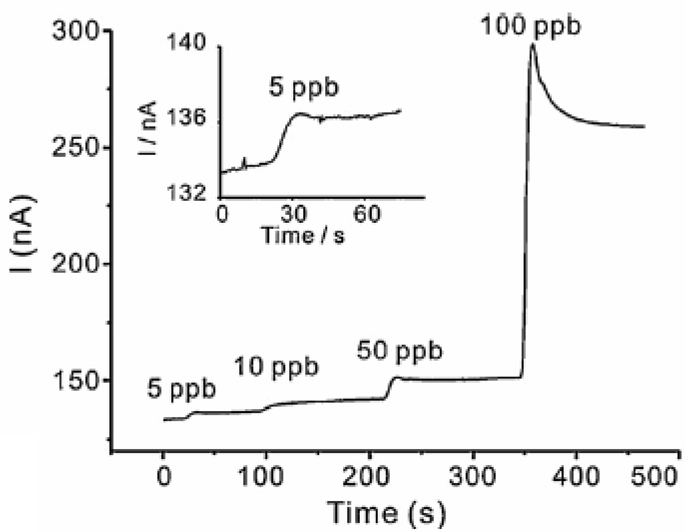
- Single atom substitution brings about accurate control of surface properties of graphene
- Electrospinning of carbon nanofibers or laser scribed graphene are scalable techniques for producing unexpensive AQC sensors for mass market applications
- The previous techniques are well adapted for producing sensors on flexible substrates
- The analysis of low-frequency noise in carbon nanomaterials and, particularly, in graphene can be of interest for increasing selectivity

From Dec 2012 to Dec 2013 some 900 journal papers published on:

(graphene OR carbon nanotube OR carbon nanofibre) AND gas sensor

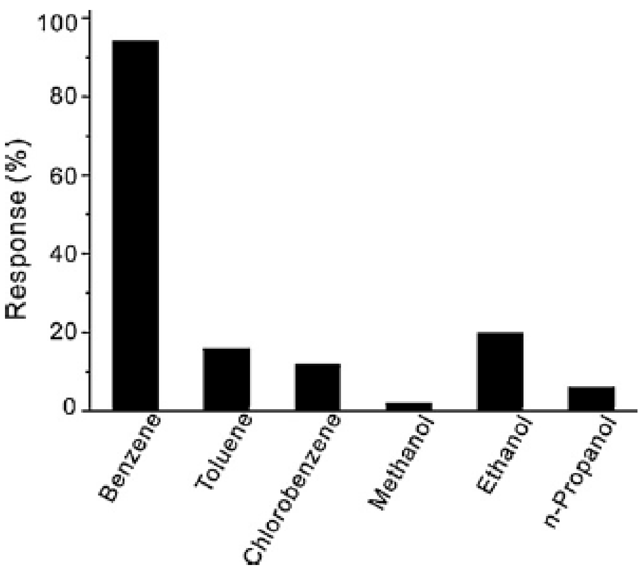
Latest developments SnO_2/graphene nanocomposite





RGO+5 nm SnO_2 NPs.
Working temperature: 210ºC
LOD for benzene: 5ppb

F.L Meng et al., Analytica Chimica Acta 736 (2012) 100



Latest developments S-G and EDA-G for detecting NO_2

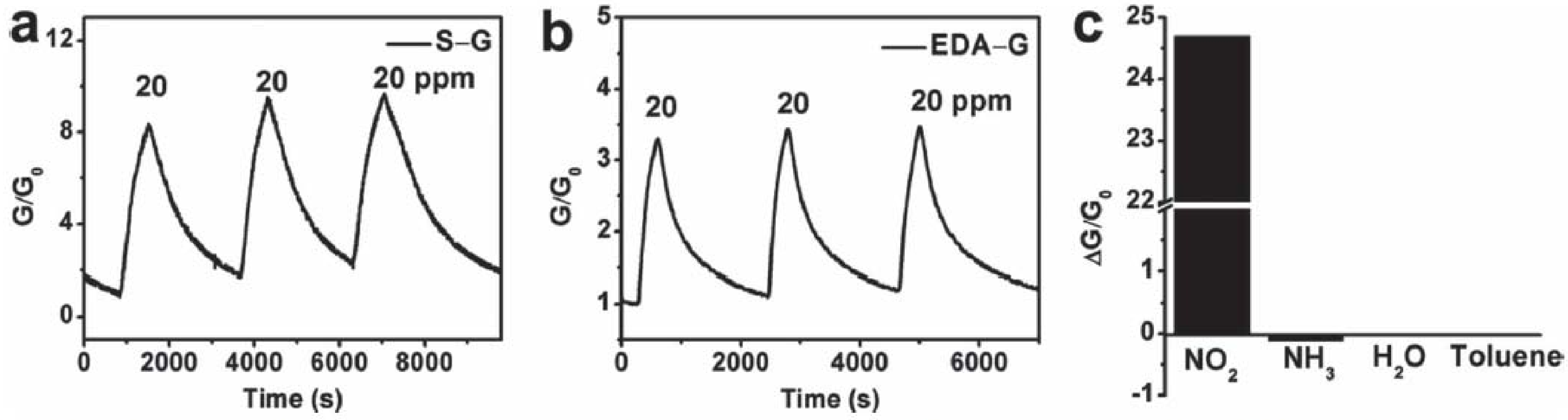
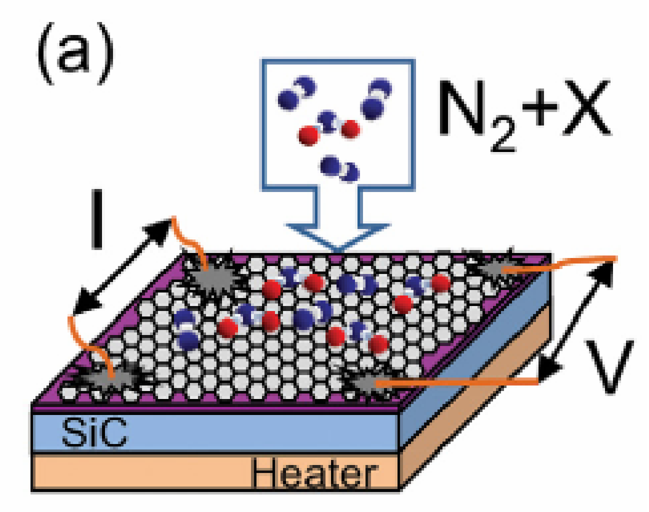


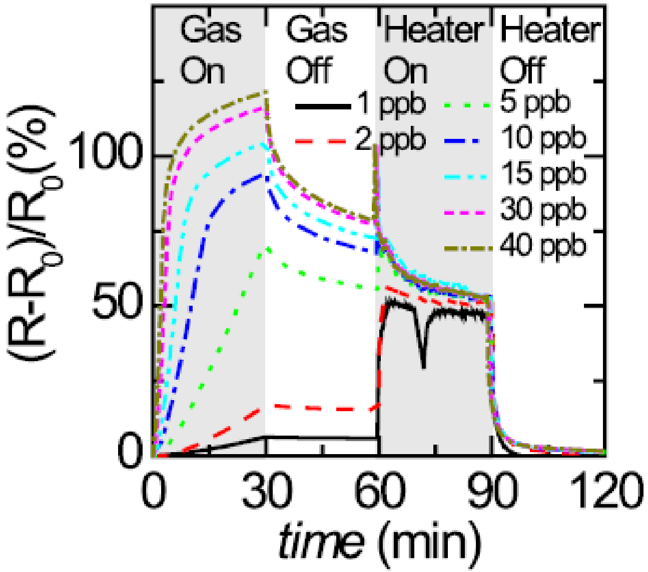
Figure 4. a) Conductance changes of an S-G-based sensor during 3 successive cycles of exposure to 20 ppm NO_2 for 10 min and N_2 flow for 30 min. b) Conductance changes of an EDA-G-based sensor during 3 successive cycles of exposure to 20 ppm NO_2 for 5 min and N_2 flow for 30 min. c) Response of an S-G-based sensor to 50 ppm NO_2, NH_3, H_2O, or toluene.

W. Yuan et al., Adv. Mater. 2013, 25, 766

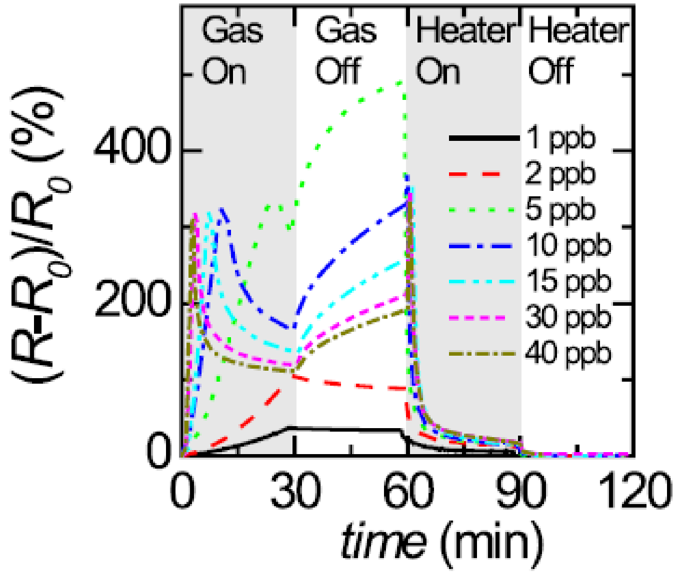
Sensing mechanism relies on changes in the electron withdrawing (donation) of sulphenil (EDA) groups upon adsorption of NO_2

Latest developments Epitaxial graphene gas sensor





Epitaxial Graphene



Quasi freestanding Epitaxial Graphene

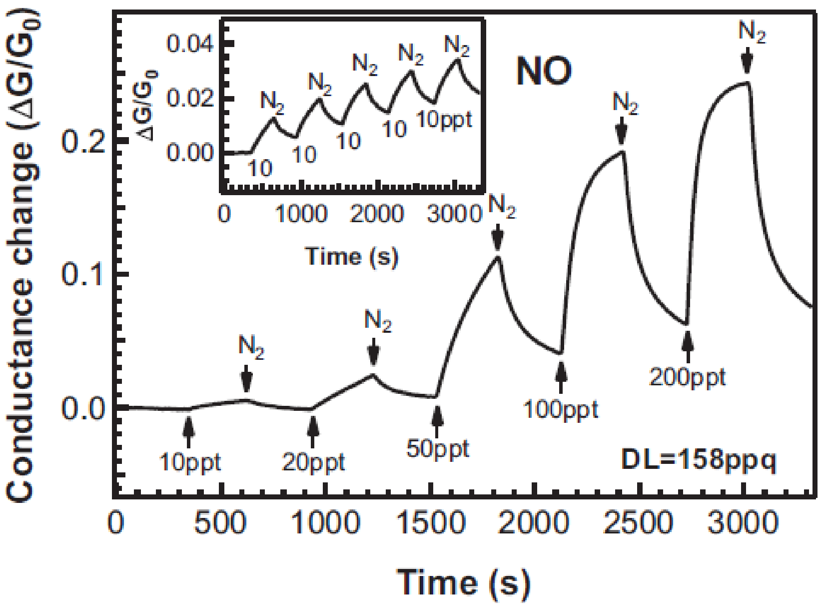
6-fold increase in sensitivity

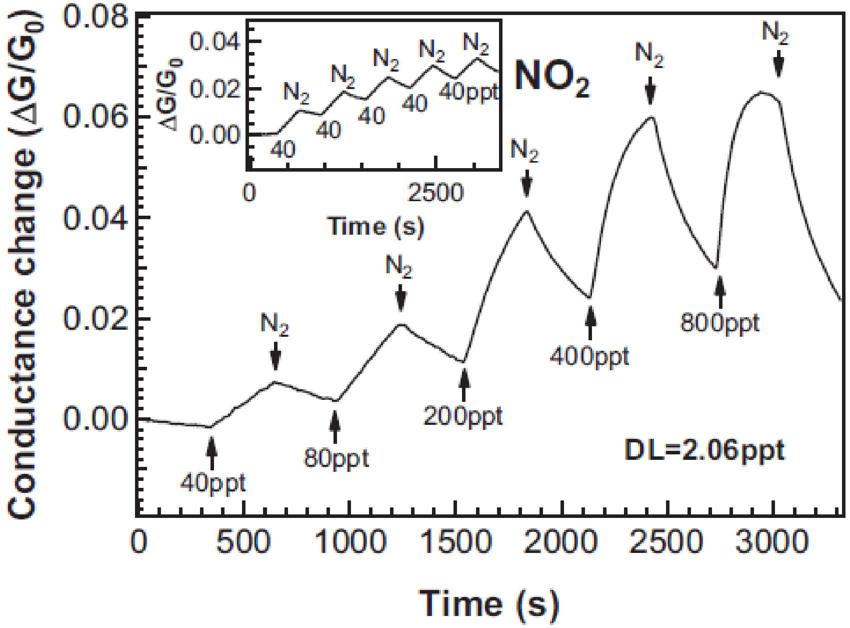
I. Yezhokin et al., APL. 103, 053514 (2013)

E_F close to Dirac point => Resistance heavily affected by surface doping

Heating at 150ºC needed for baseline recovery

Latest developments ppt sensitivity of UV-cleaned graphene



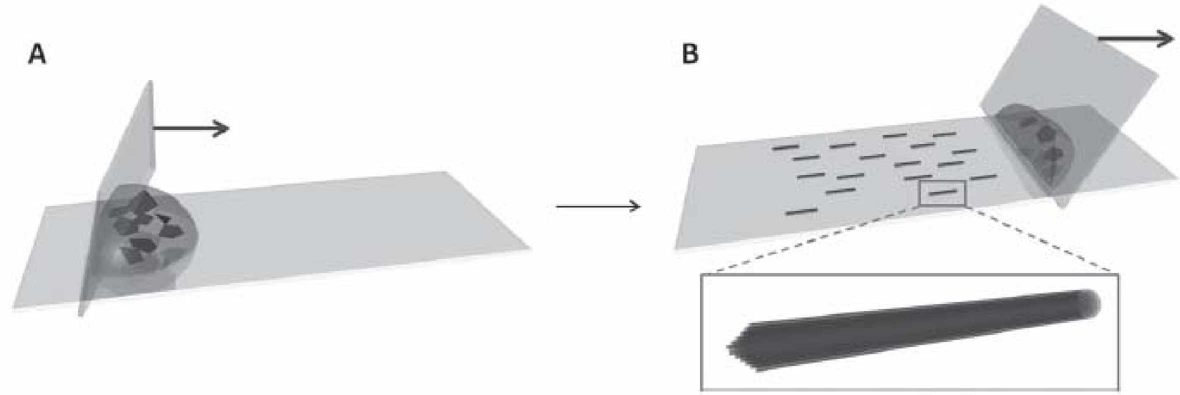


G. Chen et al., APL. 101, 053119 (2012)

Room temperature operation, UV light used for cleaning

Sensitivity possibly dominated by substrate defects! (B. Kumar et al. Nano Lett. 2013, 13, 1962)

Latest developments Graphene oxide scrolls



Scheme 1. Schematic illustration of molecular combing of graphene oxide (GO) water solution on a hydrophobic substrate. (A) A droplet of GO water solution is deposited and dragged by a cover slip. (B) GO scrolls form and are deposited behind the receding water meniscus.

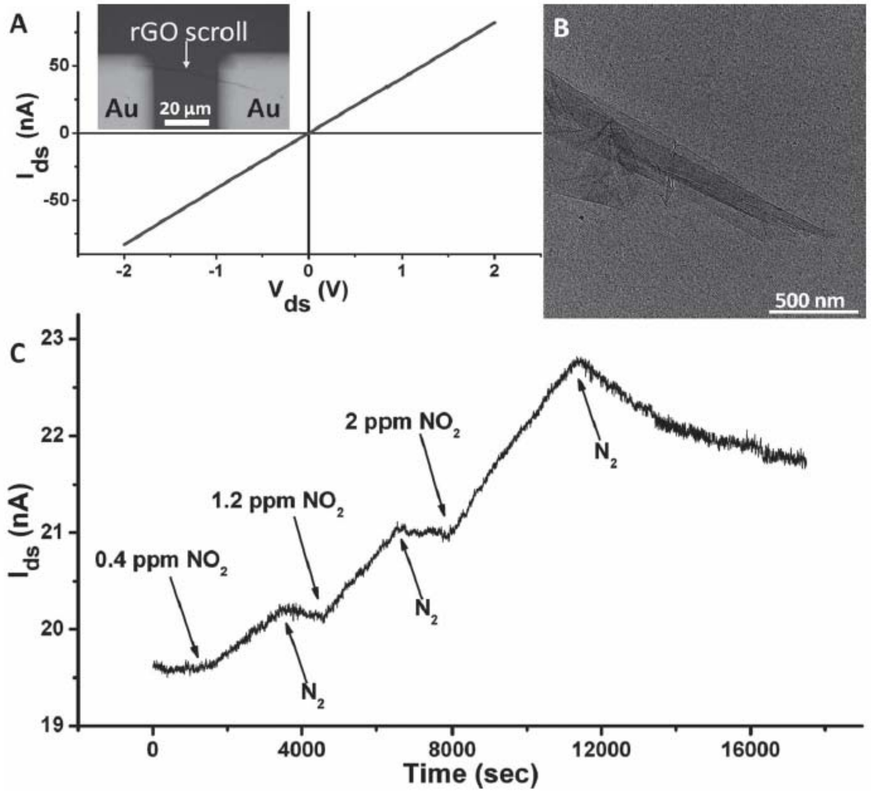
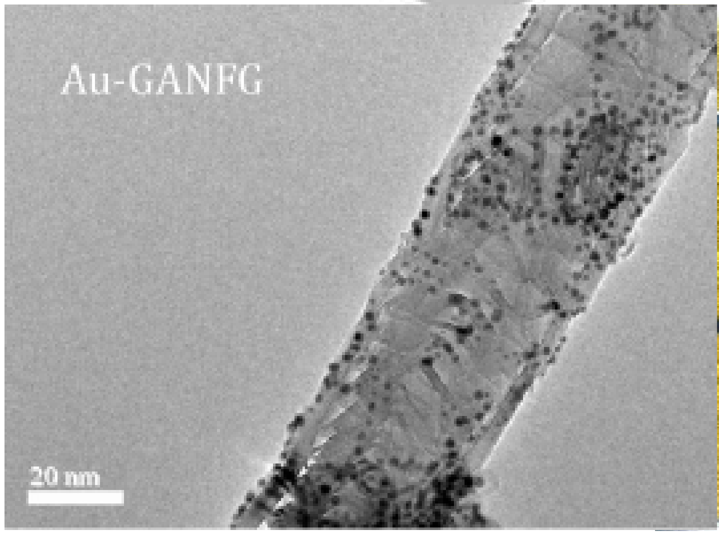
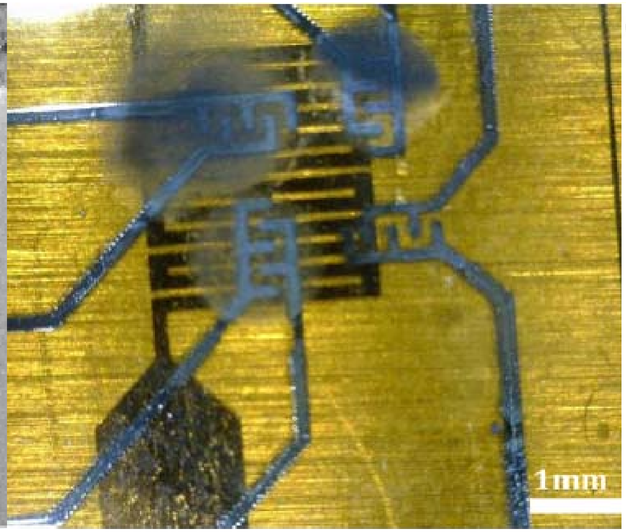


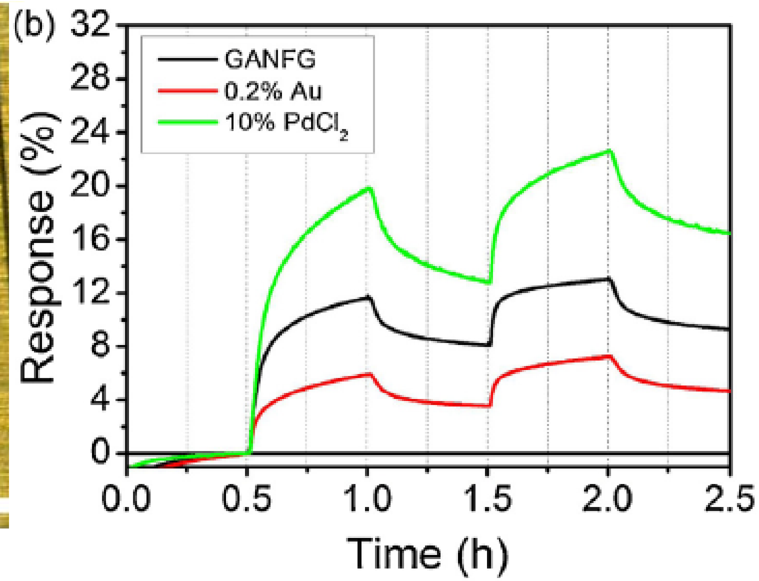
Figure 3. NO_2 gas sensor based on a single rGO scroll. (A) Plot of I_{ds} vs. V_{ds} of the single rGO scroll. Inset: Optical image of the fabricated single rGO scroll device. (B) TEM image of the GO scroll. (C) Real-time current response after exposure of the single rGO scroll device to NO_2 gas with increasing concentration.

H. Li et al., *Small* 2013, 9, No. 3, 382

Latest developments Au or Pd-doped carbon nanofibres





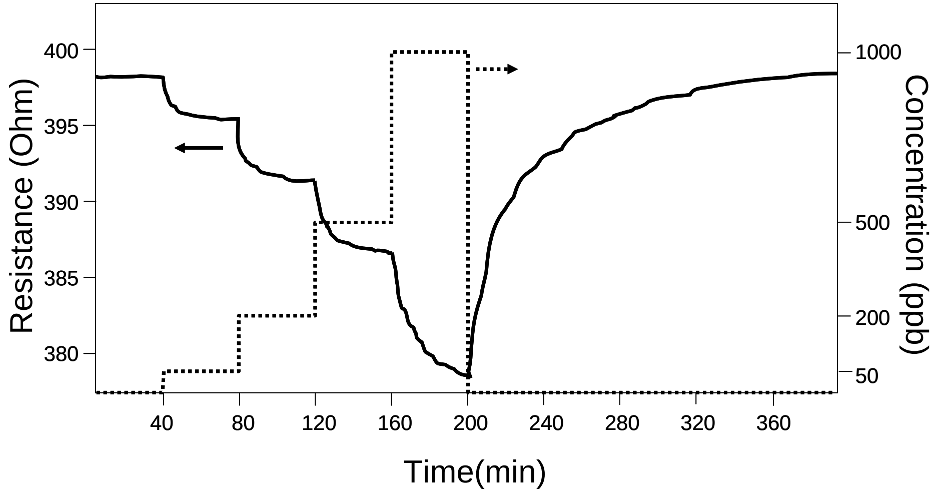


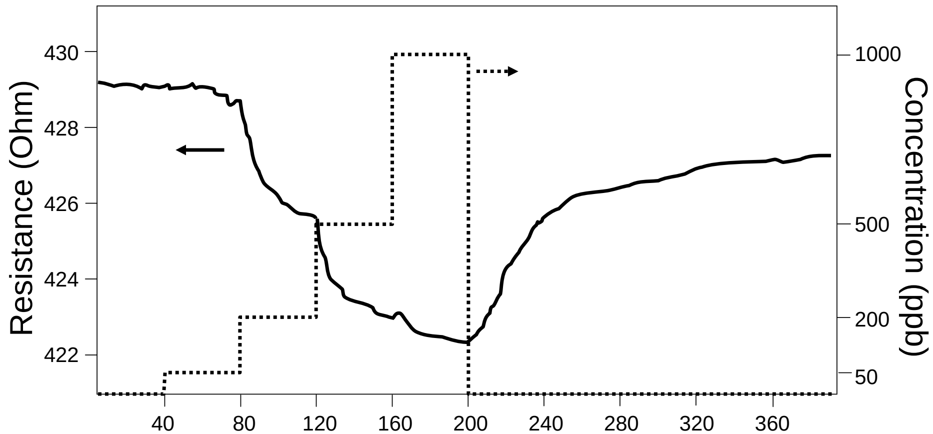
S. Claramunt et al., *SNB* 187 (2013) 401

Response (NH_3) and recovery (Air) of bare, Au and Pd decorated carbon nanofibre flexible sensors operated at room temperature.

Latest developments N or B-substituted CNTs

Response (NO_2) and recovery (Air) of N-doped (top) and B-doped (bottom) MWCNT sensors operated at room temperature.





Carbon 66 (2014) 662

Conclusions

- Response often dependent on substrate defects
- Room temperature detection but often UV light or heating necessary for baseline recovery
- PPB sensitivity (NOx, aromatics) but selectivity still an issue
- Funtionalisation is a key factor to achieve device-to-device reproducibility and boost selectivity
- Better understanding of sensing mechnisms also needed