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

COST Action TD1105

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Carbon nanomaterials for AQC gas sensors

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Outline

- Carbon nanomaterials: current issues
- Latest developments in carbon nanomaterial gas sensors
- Conclusions

Carbon nanomaterials: Current Issues

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***

Latest developments Electrospun carbon nanofibers

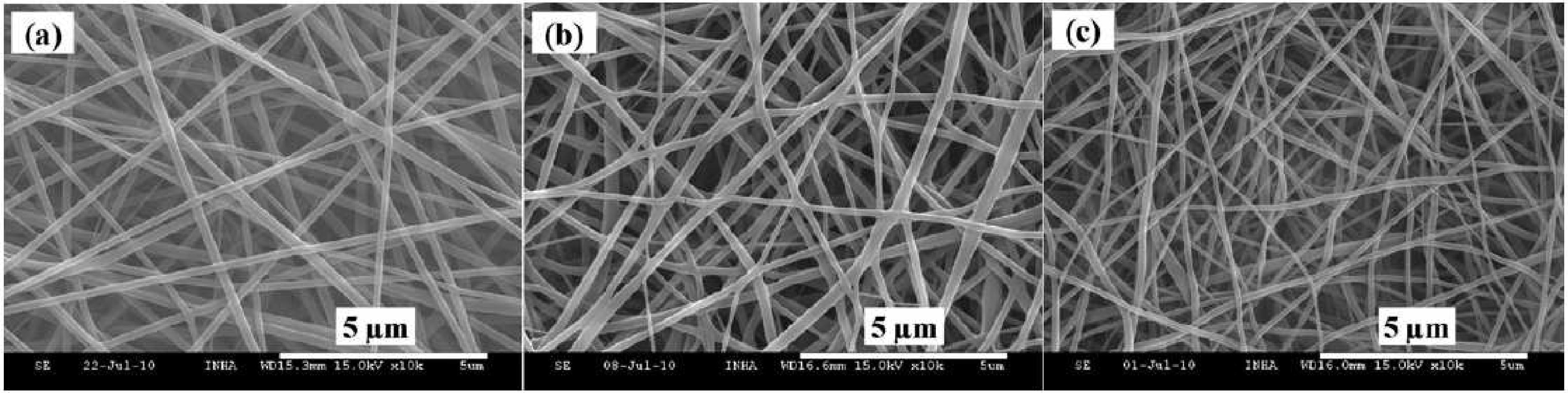

Fig. 1. SEM microphotographs of electrospun (a) pure PVP nanofibers, (b) PEDOT:PSS/PVP nanofibers, and (c) PEDOT:PSS/MWCNT—COOH/PVP nanofibers.

Room temperature detection of aromatic VOCs at ppm level

J. Choi et al., *Synthetic Metals* 162 (2012) 1513

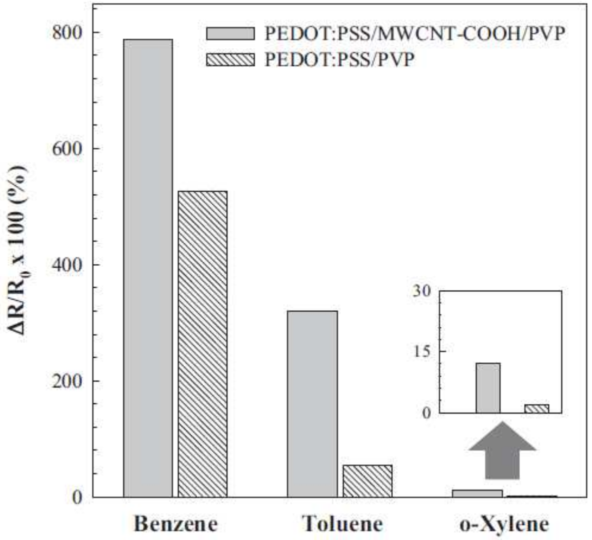

Fig. 4. Response magnitude of electrospun PEDOT:PSS/MWCNT—COOH/PVP and PEDOT:PSS/PVP nanofibers to the aromatic VOCs at room temperature.

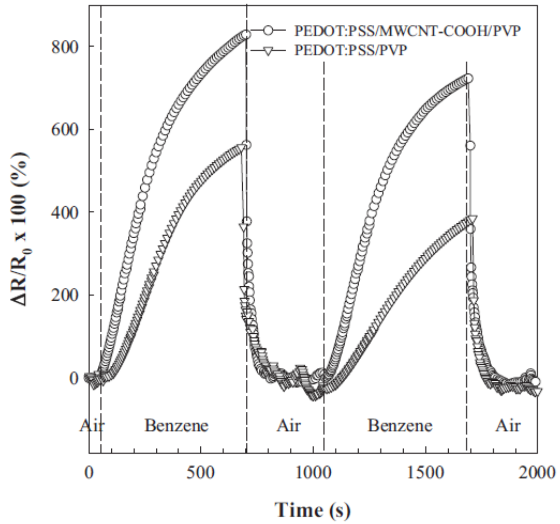

Fig. 5. Response of electrospun PEDOT:PSS/MWCNT—COOH/PVP and PEDOT:PSS/PVP nanofibers upon cyclic exposure to benzene vapor at room temperature.

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Latest developments Flexible CNT sensors

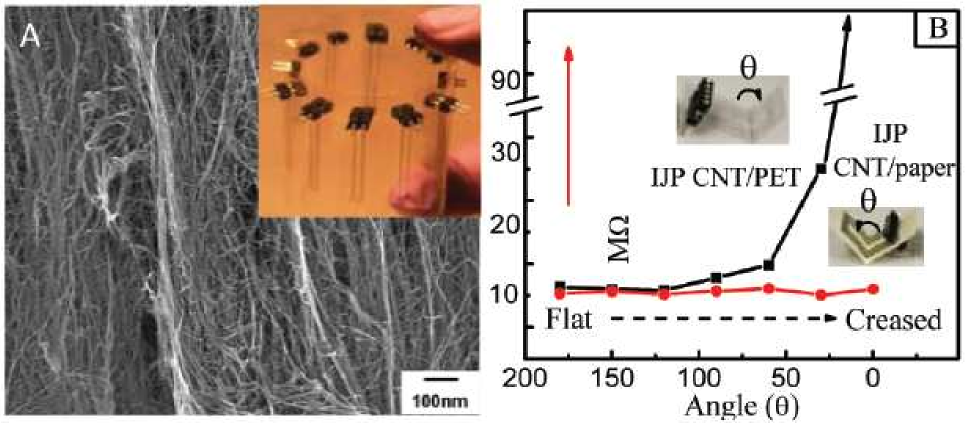


Figure 1. (A) Field-effect SEM image of inkjet-printed CNTs on PET (CNT/PET). The inset shows an array of 10 inkjet-printed CNT/PET sensors. (B) Plot of resistance vs bending angle for CNT/PET and CNT/paper sensors.

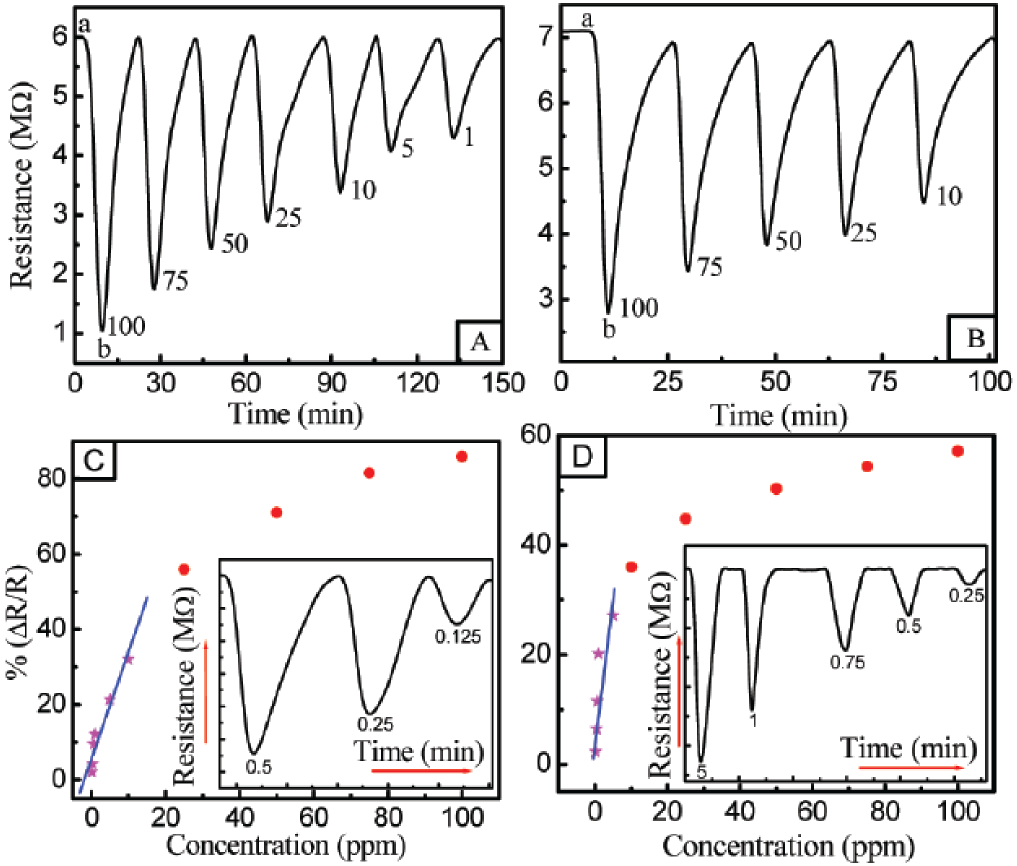
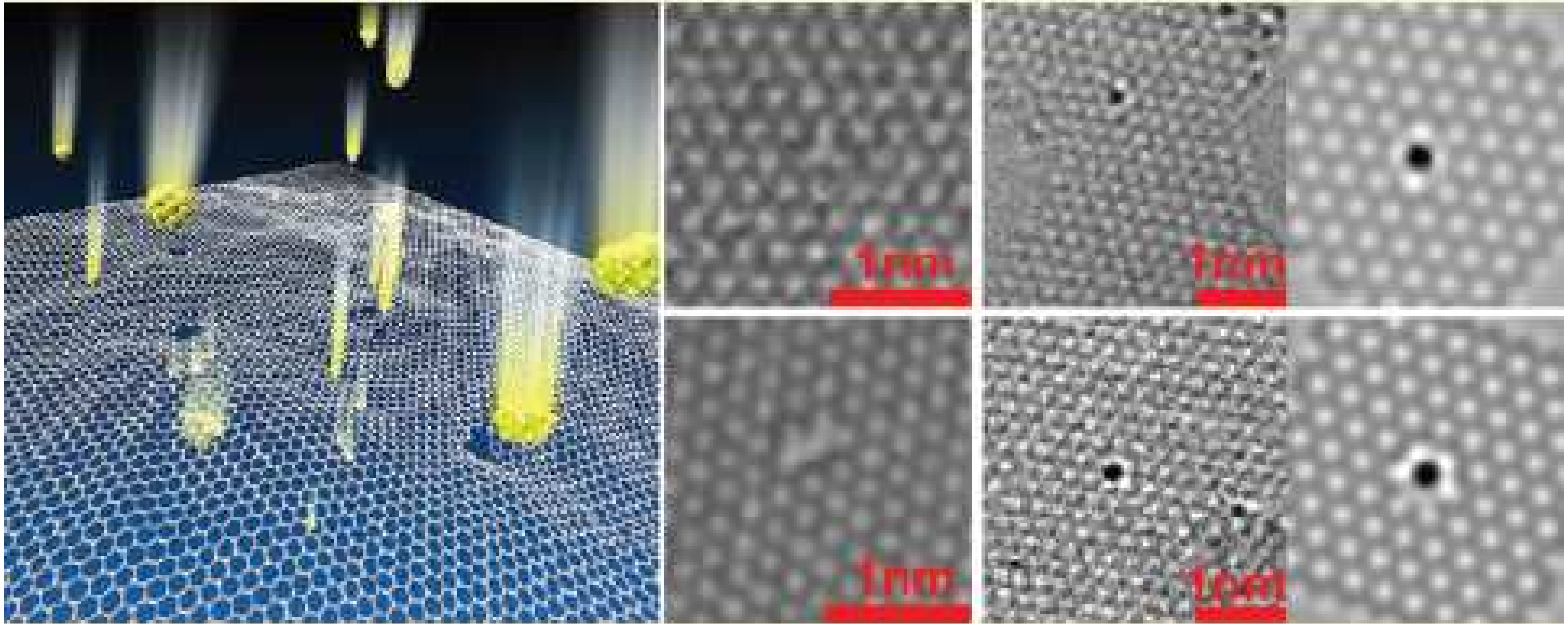


Figure 2. (A, B) Plots of resistance (R) vs time for successively decreasing concentrations of NO_2 vapor for inkjet-printed (A) CNT/PET and (B) CMT/paper films. NO_2 vapor was present at point "a" and removed at point "b". Numbers on valleys represent the vapor concentrations in ppm. (C, D) Plots of $\Delta R/R$ vs concentration for inkjet-printed (C) CNT/PET and (D) CNT/paper films. The insets show plots of resistance vs time at low concentrations.

Room temperature detection of NO_2 at ppm-ppb level

A. Ammu et al., *JACS* 134 (2012) 4553

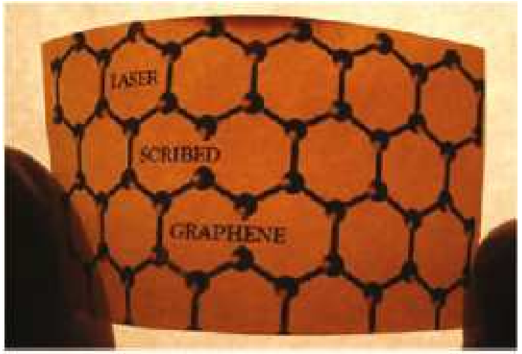
Latest developments Single atom substituted graphene

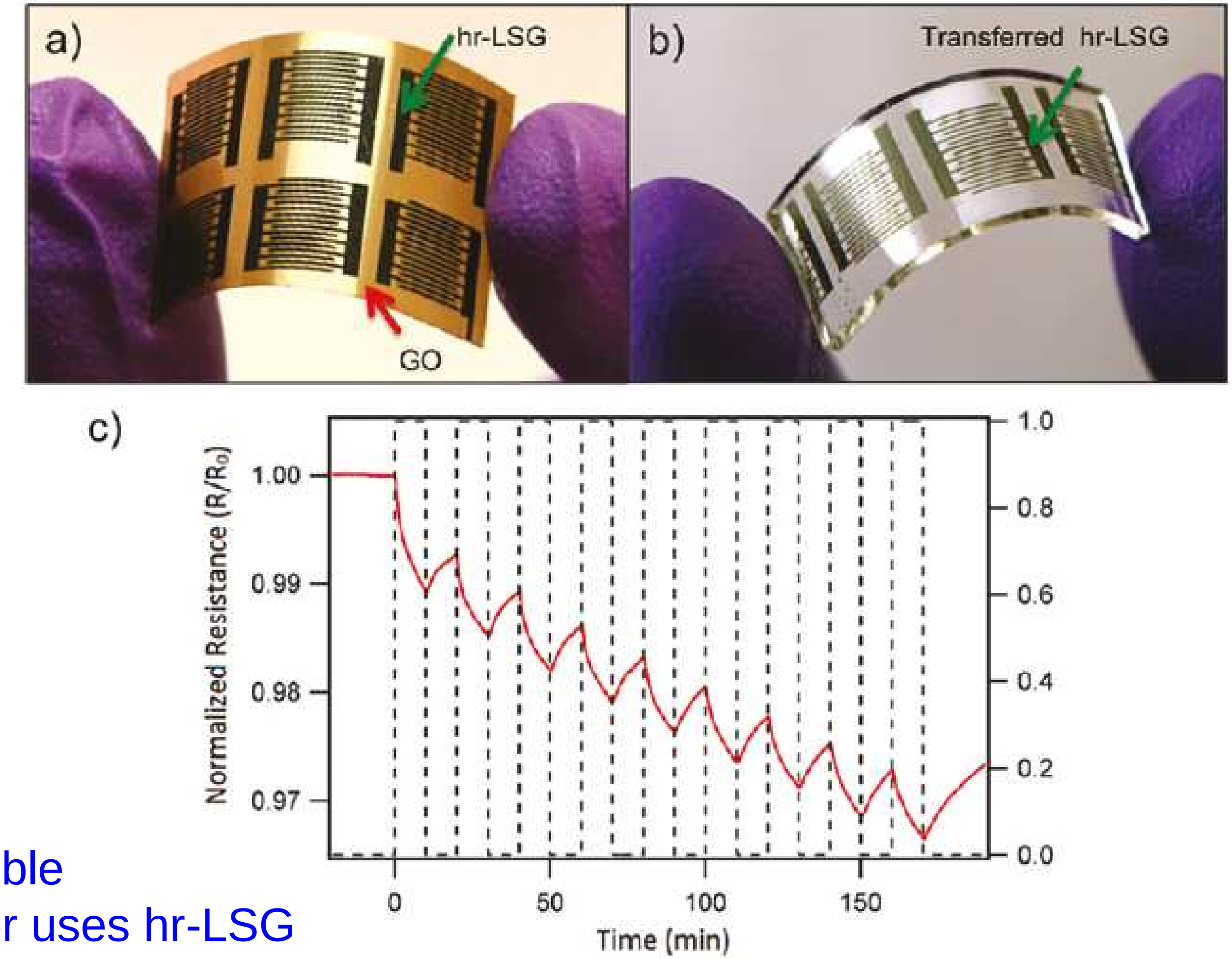


1. Create vacancies by high-energy atom bombardment (Au). Monovacancies, bivacancies selectively created by confining the kinetic energy of incoming atoms
2. Vacancy filling with different dopants (N, B, Pt, Co, In) by ion beam or sputtering

H. Wang et al., *Nano Lett.* 12 (2012) 141

Latest developments Laser scribed graphene





LSG is produced and patterned (mask less) from direct laser irradiation of graphite oxide films under ambient conditions

NO_2 detection using all-organic flexible interdigitated electrodes. The sensor uses hr-LSG as the active electrodes and marginally laser-reduced graphite oxide as the detecting media. The NO_2 concentration is 20 ppm in dry air gas.

V. Strong et al., *ACS Nano*, 6 (2012) 1395

Latest developments Pristine graphene transistor

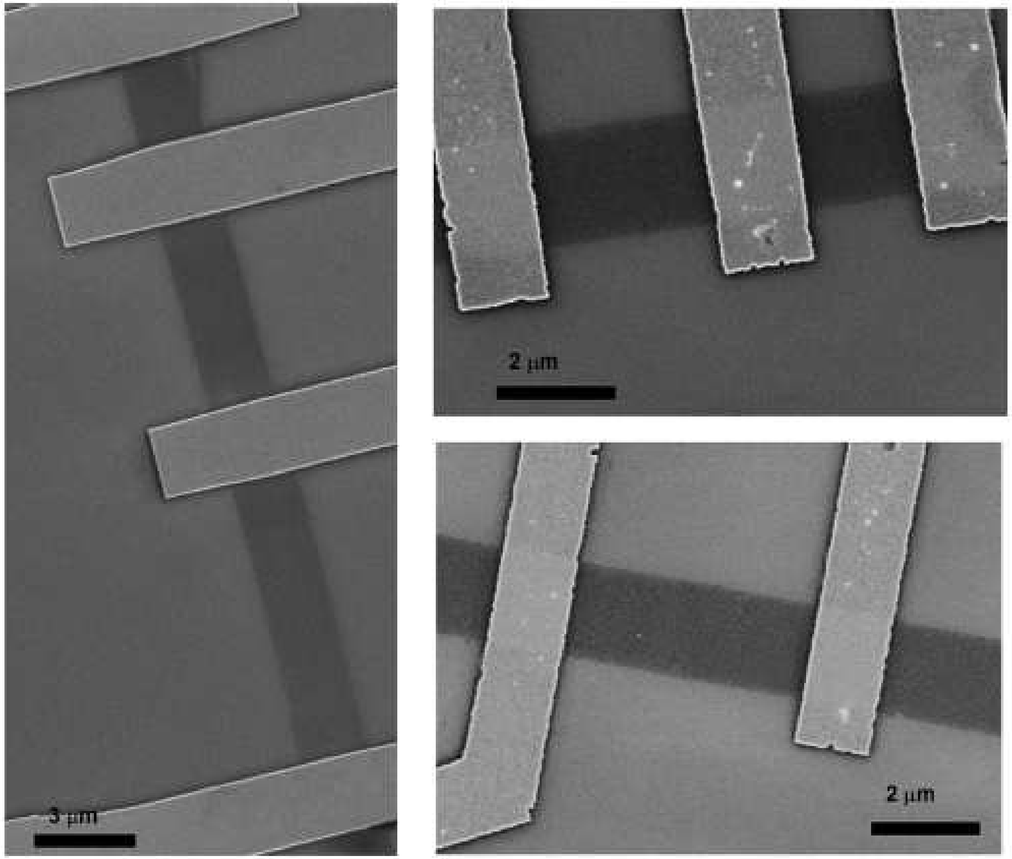
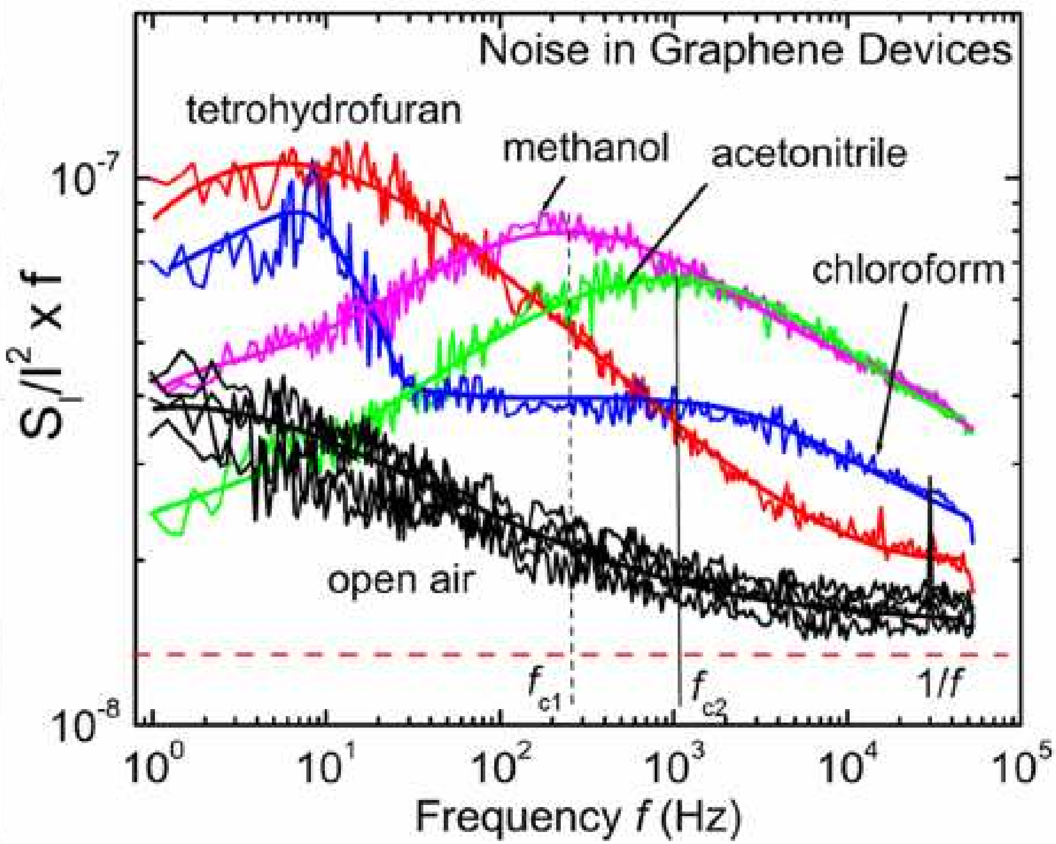


Figure 1. Scanning electron microscopy images of back-gated graphene devices with different number of top electrodes. In the



The low-frequency noise spectra of graphene is affected by vapors of different chemicals by inducing Lorentzian components with distinctive features.

S. Rumuantsev et al., *Nano Lett.*, 12 (2012) 2294

Latest developments Polycrystalline graphene ribbons

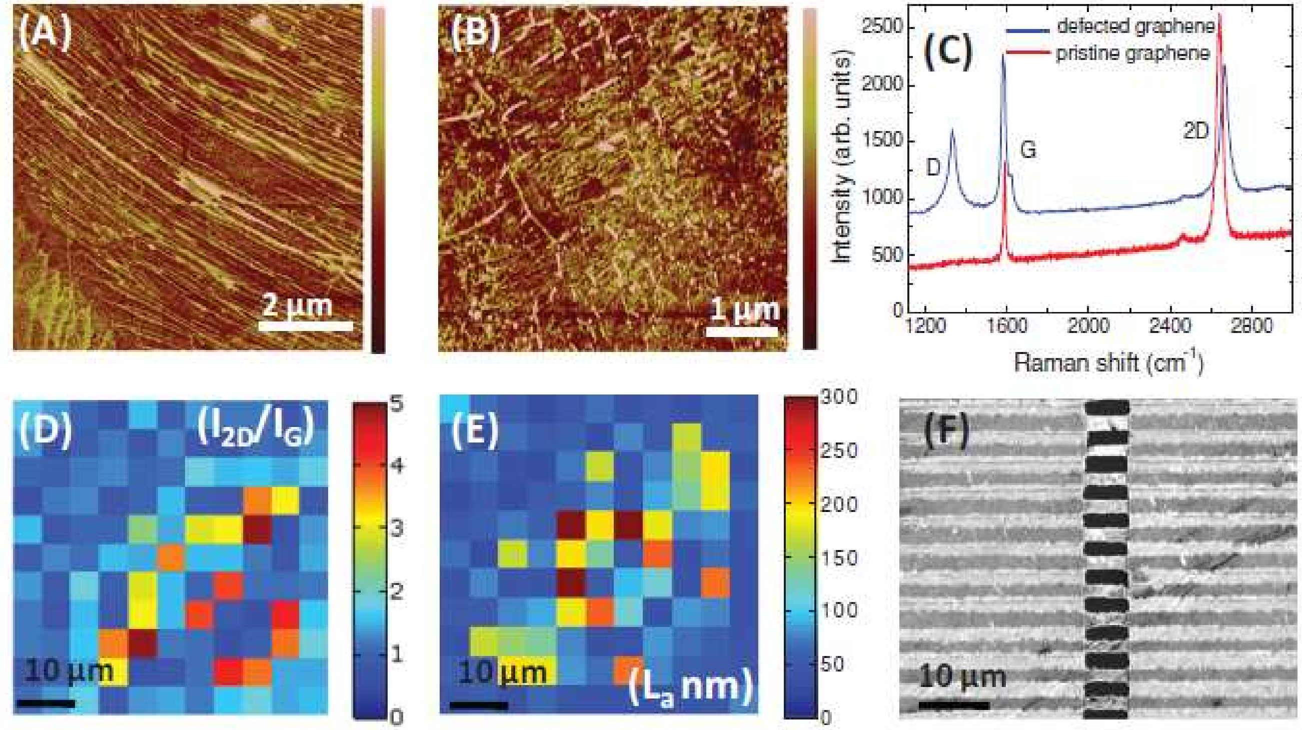
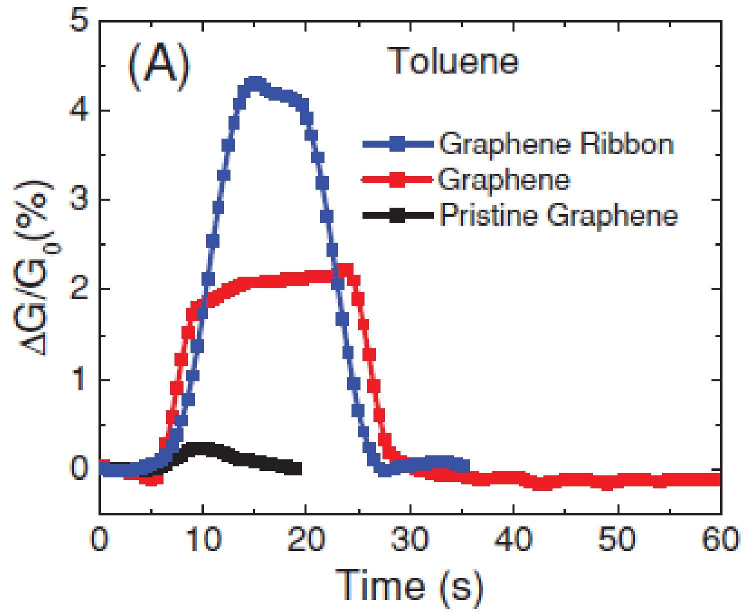


Figure 1. (A and B) AFM images of CVD graphene used for sensors, color scales are 10 and 5 nm, respectively, (C) Raman spectra of pristine and CVD-based "defective" graphene samples, (D) map of I_{2D}/I_G ratio indicating our CVD process produces mono to few layer graphene, (E) map of crystallite size indicative of 30 to >300 nm distance between line defects with an average L_a ~ 80 nm (see text), and (F) Scanning electron microscopy image of CVD graphene ribbons.



Cutting graphene in ribbons the width of which is comparable to the dimensions of line defects increases sensitivity to ppb levels.

A. Salehi-Khojin et al., *Adv. Mat.*, 24 (2012)
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Conclusions

- 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