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COST Action TD1105

3rd International Workshop *EuNetAir* on

New Trends and Challenges for Air Quality Control

University of Latvia - Faculty of Geography and Earth Sciences

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APPLICATION OF CHEMIRESISTIVE POLYMER FILMS IN AIR QUALITY CONTROL

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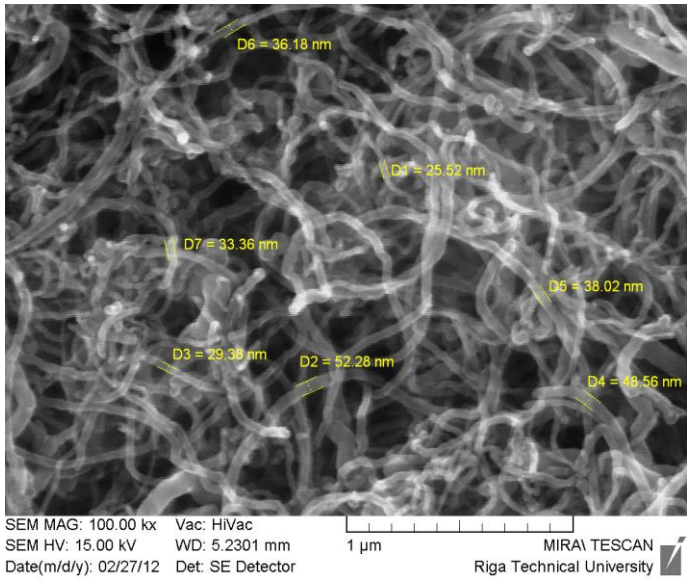
Outline

1. Materials
2. Sensor design
3. Production methods
4. Sensing mechanism
5. Conductive polymer based sensors
6. Non-conductive polymer based sensors
7. Conclusions

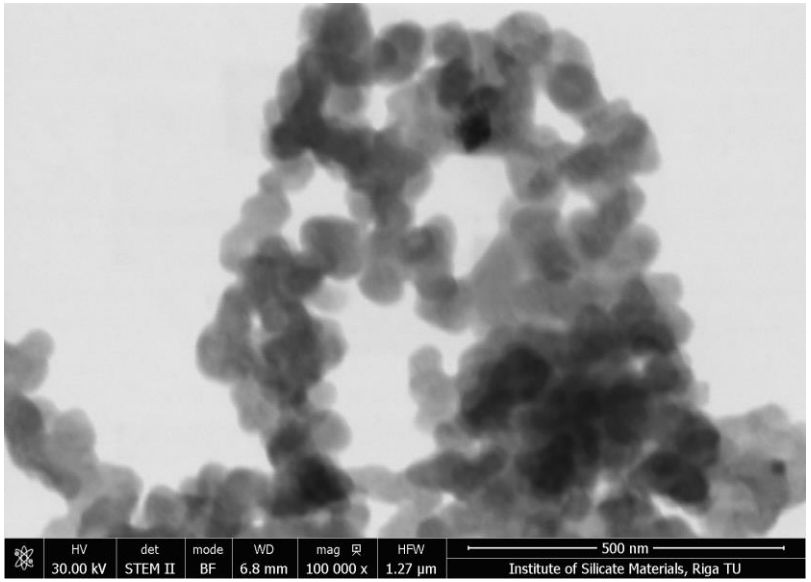
Materials

- Conductive polymers: polyacetylene (PA), polythiophene (PT), polypyrole (PPy), polyethylene dioxythiophene (PEDOT), polyaniline (PANI)
- Non-conductive polymers: ethylene-vinyl acetate, polyisoprene, silicon rubbers, polyurethane etc.
- Nano size filler:

Carbon nanotubes: MWCNT or SWCNT



Carbon black nanoparticles



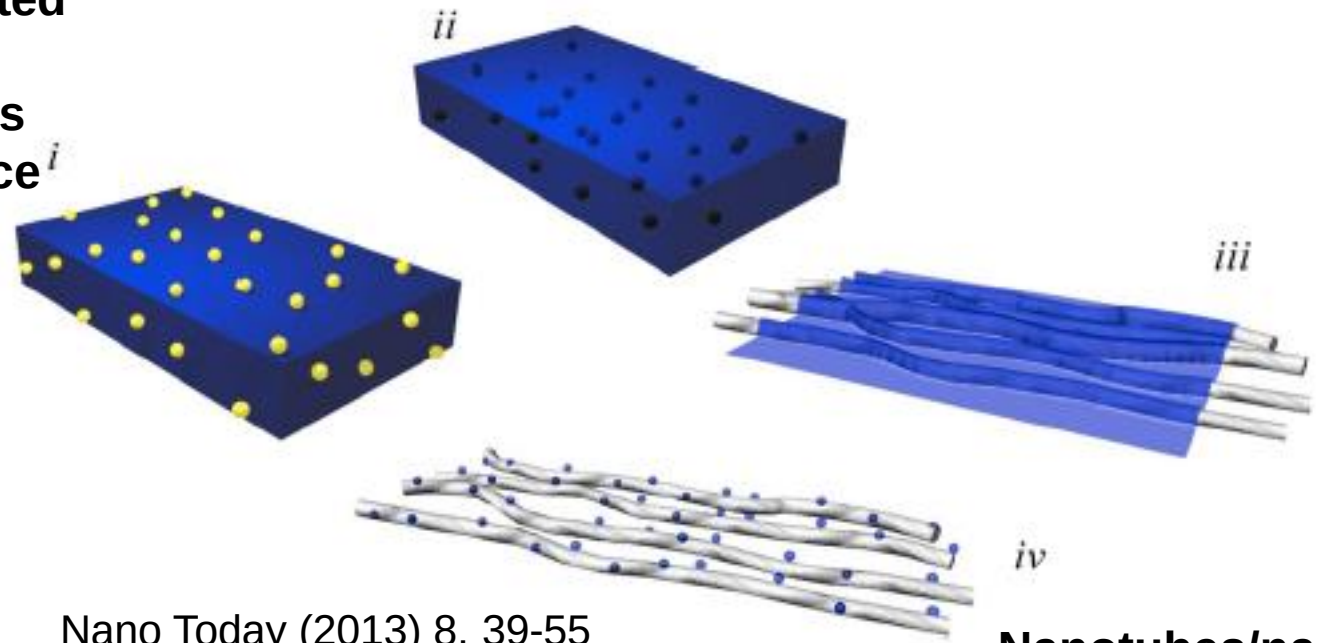
Metal nanoparticles

Au, Ag, Pt, Cu

Sensor design

Film, decorated with nanoparticles on the surface

Composite film



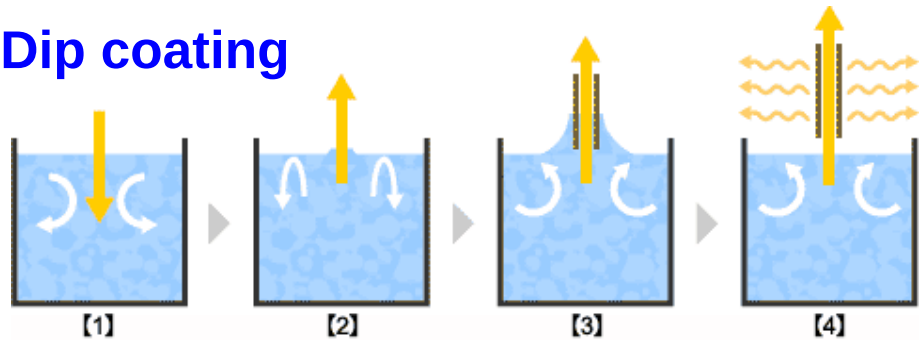
Nanotubes/nanofibres covered with conductive polymer

Nano Today (2013) 8, 39-55

Nanotubes/nanofibres decorated with nanoparticles

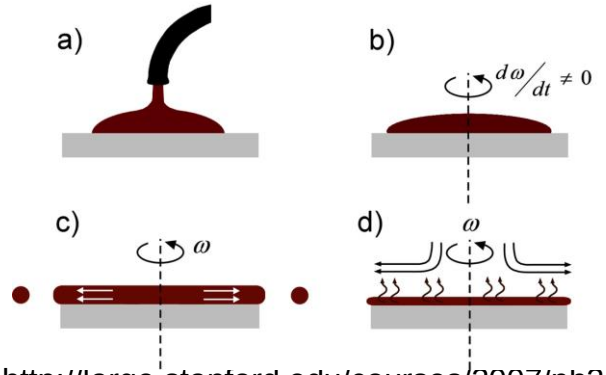
Production methods

Dip coating



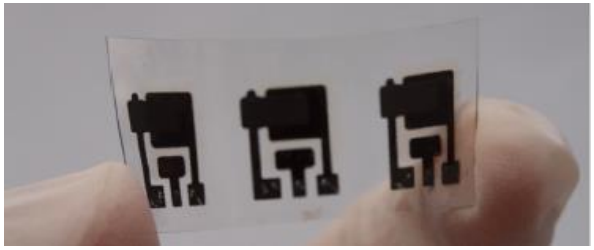
http://www.dip-coater.com/english/about_dip_coating.html

Spin coating



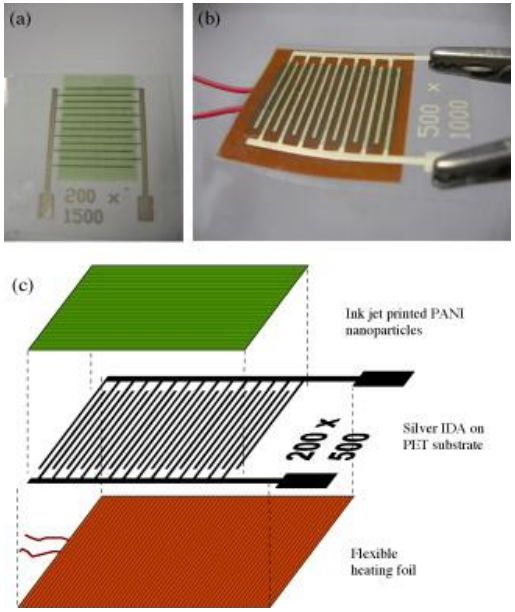
http://large.stanford.edu/courses/2007/ph210/hellstrom1/

Inkjet/screen printing



Sheet of fully printed sensors based on graphite paste

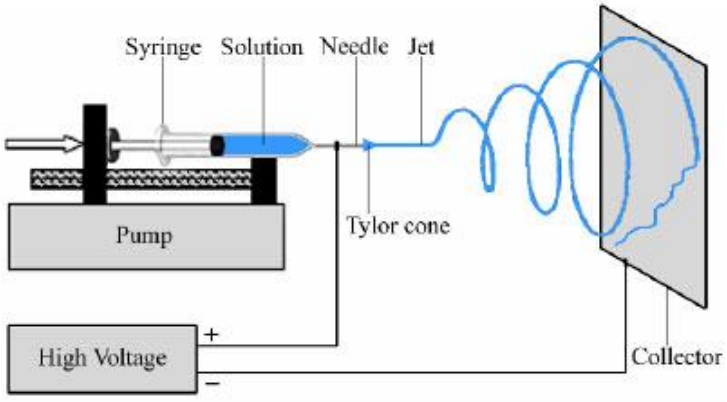
Sensors and Actuators B 209 (2015) 1084–1090



Inkjet printed PANI based sensor

Talanta 77 (2008) 710–717

Electrospinning



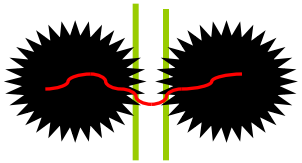
Braz. J. Chem. Eng. vol.26 no.1 São Paulo Jan./Mar. 2009

Sensing mechanism

Non-conductive polymer based sensors

$$R = \frac{L}{N}\left(\frac{8\pi hs}{3a^2\gamma e^2}\right)\exp(\gamma s_0)$$

$$\frac{R}{R_0} = \frac{s}{s_0}\exp[\gamma(s - s_0)] \qquad \left(\frac{R}{R_0} = \left[1 + \frac{\Delta l}{l_0}\right]\cdot e^{A\left(\frac{\Delta l}{l_0}\right)}\right)$$

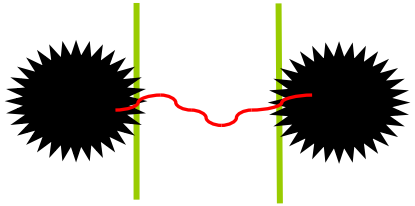


Conductive polymer based sensors

Swelling increases hopping distance between charges, electrical resistance increases

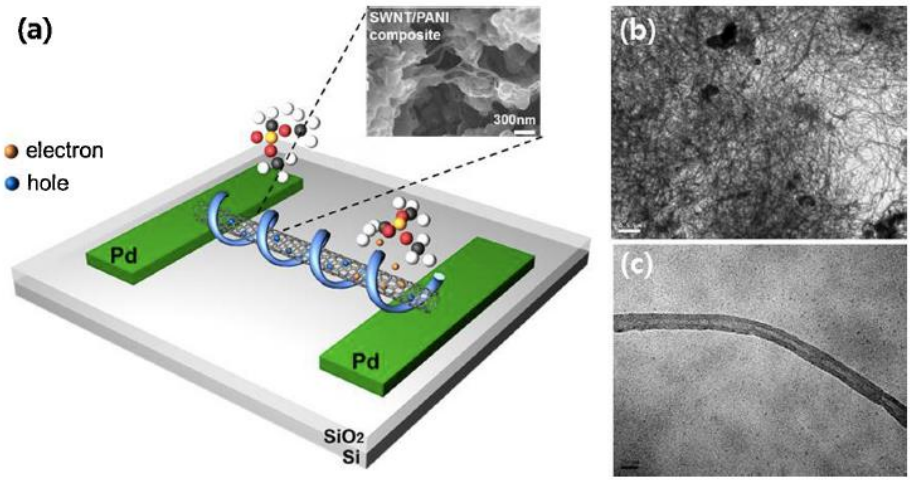
Electron donating gases (NH_3, H_2S) change conductivity of the sensor

$$\left(\frac{R}{R_0} = \left[1 + \frac{\Delta l}{l_0}\right]\cdot e^{A\left(\frac{\Delta l}{l_0}\right)+B\left(\frac{\Delta l}{l_0}\right)^2+C\left(\frac{\Delta l}{l_0}\right)^3+D\left(\frac{\Delta l}{l_0}\right)^4}\right)$$

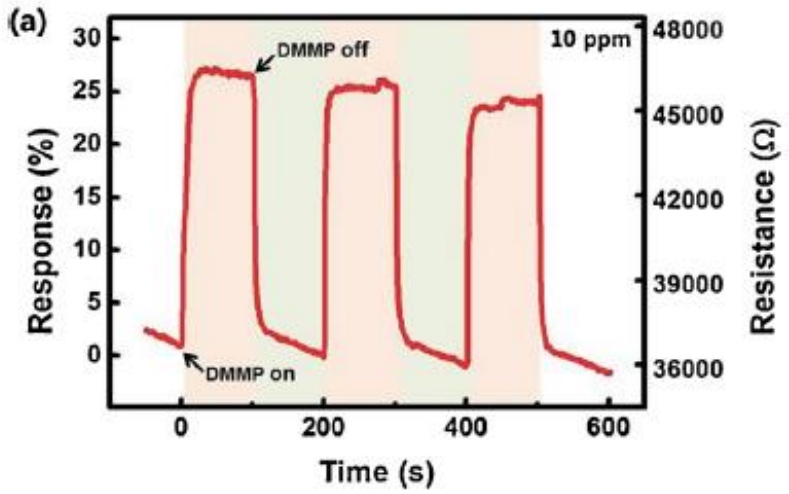


Sakale, Knite, Teteris
Sensors and Actuators A 171 (2011) 19-25

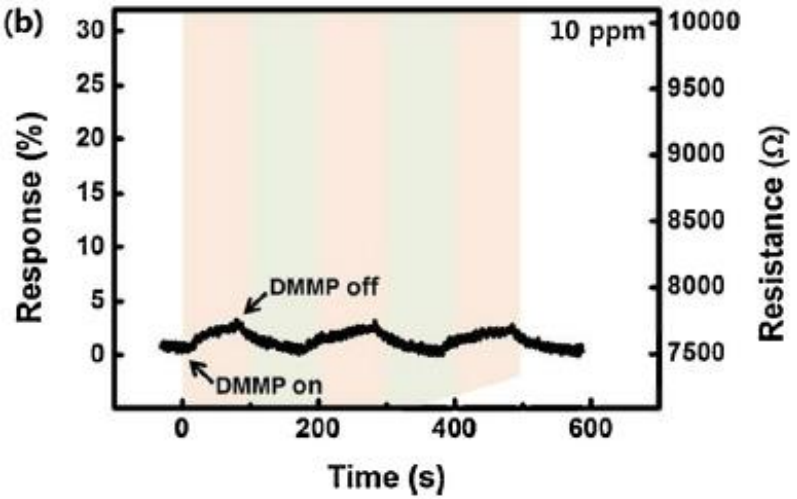
Conductive polymer based sensors I



Sensor material: single-walled nanotubes (SWCNTs) and polyaniline composite
Target analyte: nerve agent simulant gas dimethyl-methyl-phosphonate (DMMP) – electron-donating gas
Method of fabrication: drop casting
Sensing mechanism:
Majority of carrier (hole) density in both SWCNTs and HCl-doped polyaniline is decreased by the transferred electrons from DMMP.
Response time: 5.5s
Recovery time: 100s
Measurements performed at: 25°C, 28 ± 5% RH



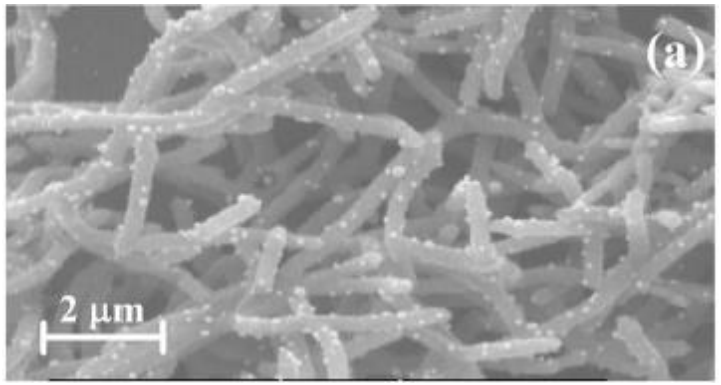
SWCNT-polyaniline composite sensor to 10ppm DMMP gas at room temperature.



Pure polyaniline sensor to 10ppm DMMP gas at room temperature.

Sensors and Actuators B 209 (2015) 444–448

Conductive polymer based sensors II



SEM image of PANI nanowires network functionalized with Au nanoparticles

Sensor material: PANI-Au nanowire network

Target analyte: H_2S - electron donating gas

Method of fabrication: electrodeposition

Sensing mechanism:

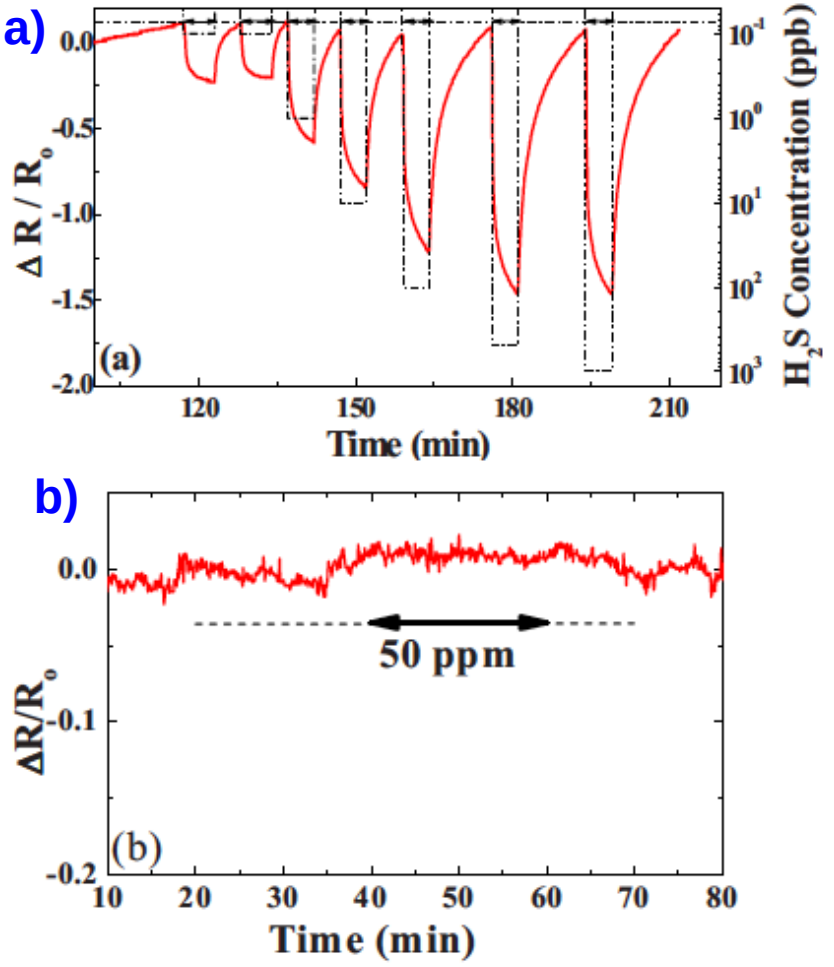
H_2S – weak acid/dissociate in ions (HS^-; H^+)

$H_2S + Au \rightarrow AuS + 2H^+$

Response time: < 120 s

Recovery time: < 300s

Measurements performed at: room temperature

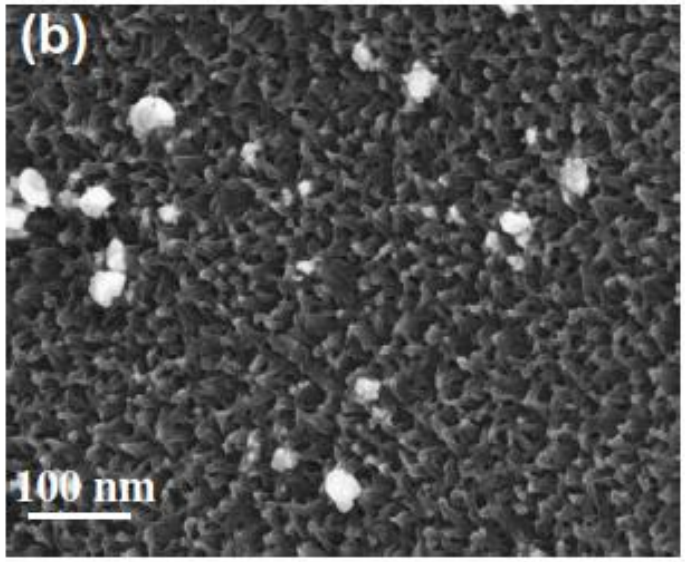


a) Response and recovery of PANI-Au nanowire network toward 0.1ppb, 1ppb, 10ppb, 100ppb, 500ppb, 1ppm of H_2S

b) Response of pure PANI to 50ppm of H_2S gas.

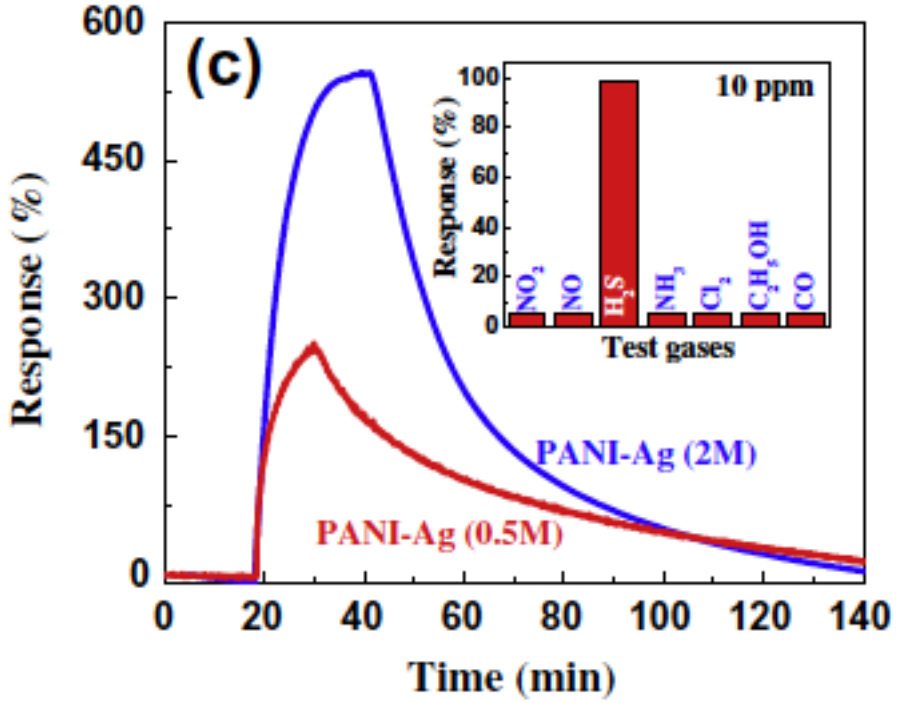
Applied Physics Letters 94, 083502 2009

Conductive polymer based sensors III



SEM image of PANI-Ag film. **Brush like surface!**

Sensor material: polyaniline–silver (PANI–Ag) nanocomposite
Target analyte: H_2S - electron donating gas
Method of fabrication: used special substrate, considerably increased surface area
Sensing mechanism: On the surface of Ag H_2S – weak acid/dissociate in ions (HS^-; H^+); new charge carriers H^+ are formed, conductance increases
Response time: 360 s (6min)
Recovery time: 5400s (90min)
Measurements performed at: room temperature

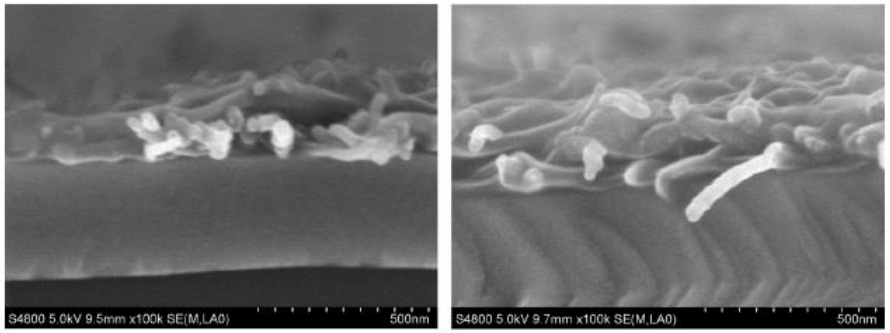


Comparative response curve for PANI–Ag (0.5 M) and PANI–Ag (2 M). Inset shows the selectivity histogram of PANI–Ag(0.5 M) at 10 ppm concentration of different gases.

Long recovery time!

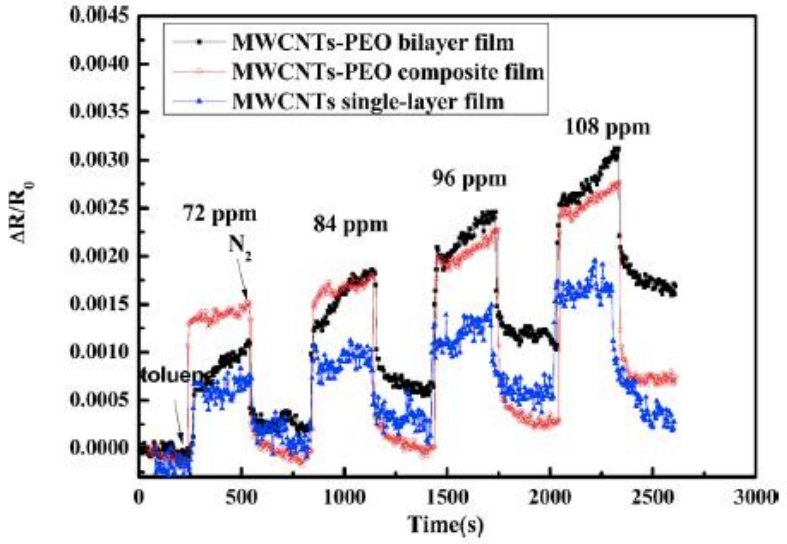
Organic Electronics 15 (2014) 71–81

Non-conductive polymer based sensors I



(a) (b)

SEM images of cross-section for MWCNT-PEO composite film (a) and MWCNT-PEO bilayer film (b).



Response curves to various toluene vapor concentrations.

Sensor material: MWCNT-polyethylene oxide composite

Target analyte: toluene

Method of fabrication: air-brushing

Sensing mechanism:

1. chemisorption (toluene CH_3 work as weak charge donors to MWCNT)
2. physisorption induced swelling

Response time: ~8s

Recovery time: ~8s

Measurements performed at: room temperature

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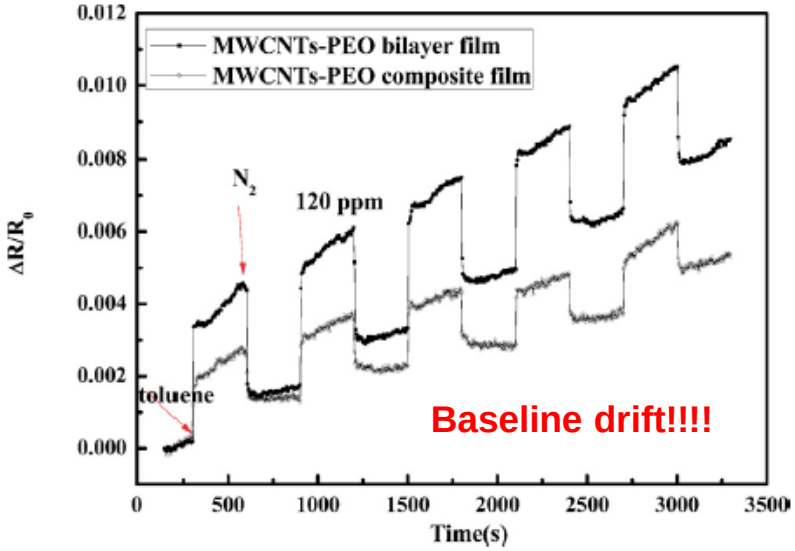
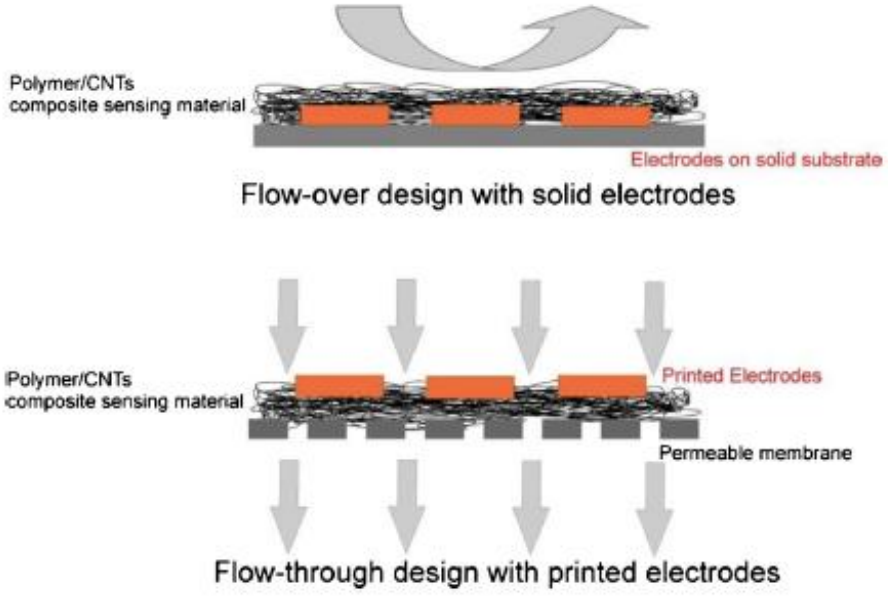
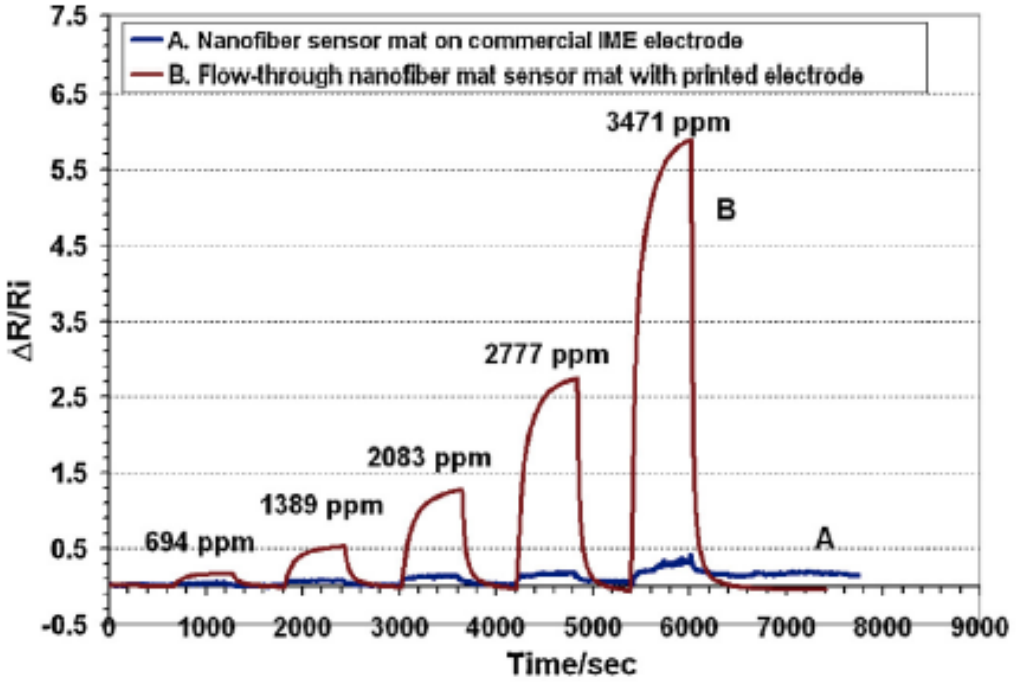


Response curves to 120 ppm toluene vapor, repeatedly 5 times.

Non-conductive polymer based sensors II



Schematic picture of electrode position.



Sensor response profile of a flow-through sensing mat with a printed electrode and a non-flow through sensing mat on commercial electrodes

Sensor material: SWCNT/PMMA composite

Target analyte: methanol

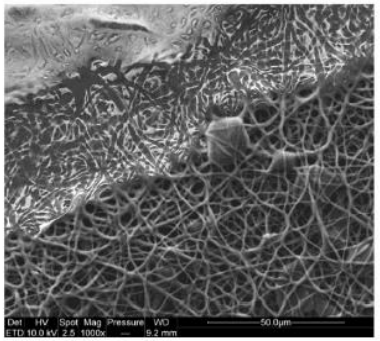
Method of fabrication: electrospinning

Sensing mechanism: physisorption induced swelling, SWCNT inter distance increase

Response time: ~200s

Recovery time: ~200s

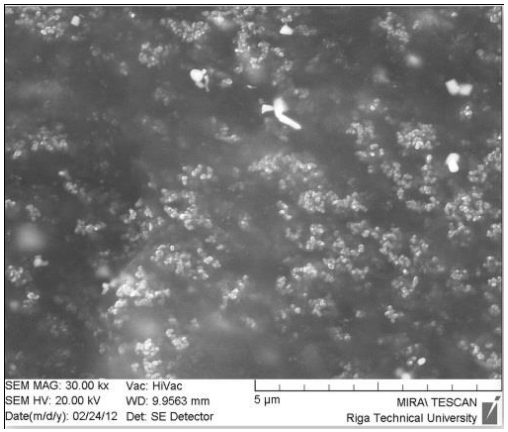
Measurements performed at: room temperature



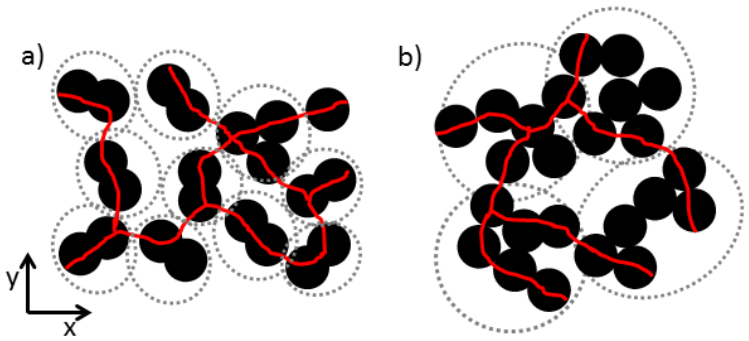
SEM image of electrode (silver ink) covered on nanofiber layers

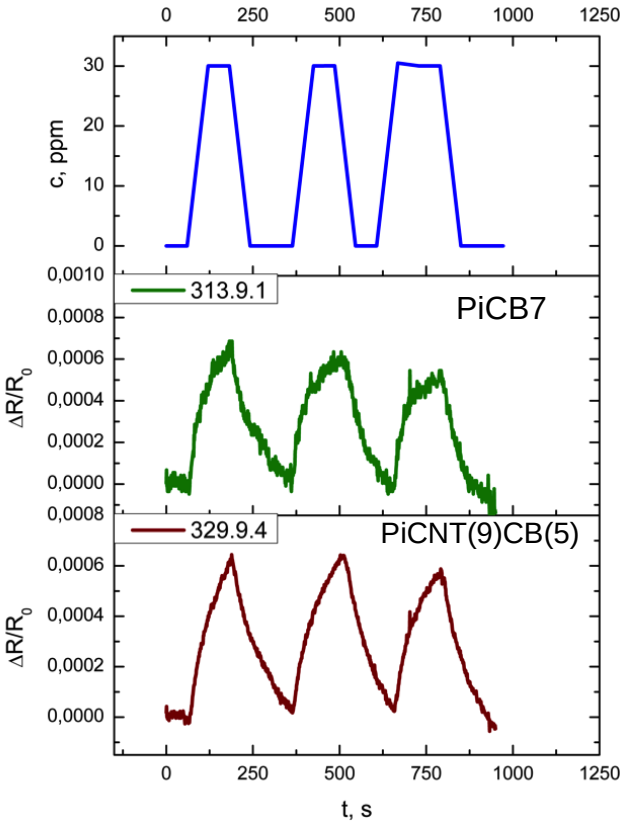
Sensors and Actuators B 186 (2013) 52-55

Non-conductive polymer based sensors III



SEM image of PiCB4.4





PNCC response to toluene 30ppm, exposure time 60s. Carrier gas N_2.

Sensor material: polyisoprene-nanostructured carbon composite (PNCC)

Target analyte: VOC

Method of fabrication: dip-coating

Sensing mechanism: absorption induced swelling, MWCNT/CB inter distance increase

Response time: 250s (200ppm toluene)

Recovery time: 250s (200ppm toluene)

Measurements performed at: room temperature

1) **Conductive network matters:**
   - **how many building blocks are in the network,**
   - **size and configuration,**
   - **uniform distribution**
2) **RH above 45% reduces response**
3) **face baseline drift**
4) **elastomer based matrix**

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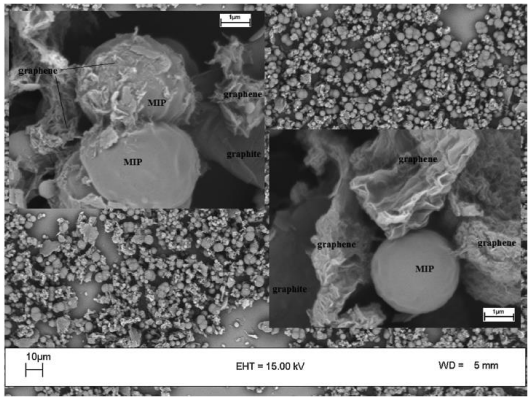
Non-conductive polymer based sensors IV

Molecularly imprinted polymers (MIP)



SEM image of graphene/graphite-

Sensor material: graphene/graphite-MIP/PMMA

Target analyte: nitrobenzene

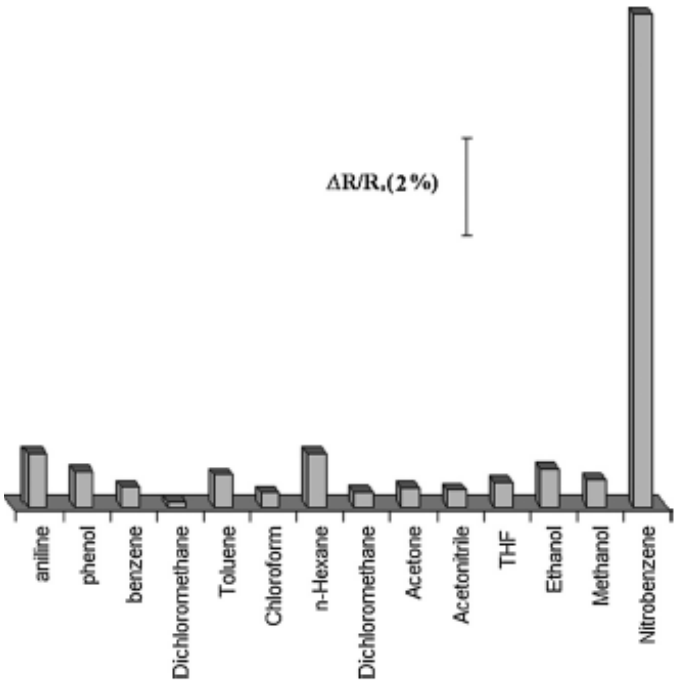
Method of fabrication: -

Sensing mechanism: physisorption induced swelling of MIP, conductive filler inter distance increase

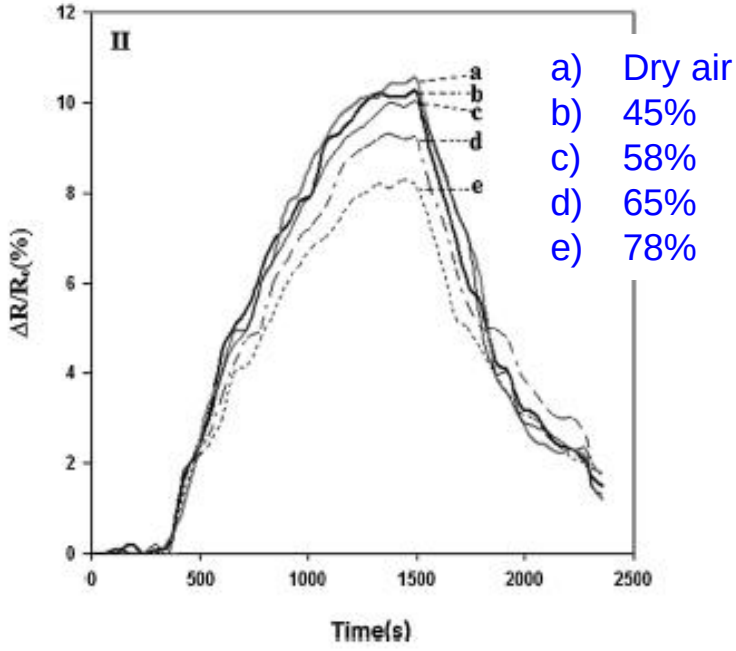
Response time: ~700s

(lowest c 1.25ppm)

Recovery time: ~750s



Sensor selectivity, VOC concentration 20ppm.



a) Dry air
b) 45%
c) 58%
d) 65%
e) 78%

Response to nitrobenzene 20ppm at various RH.

MIP improves selectivity!

Journal of Environmental Chemical Engineering 2 (2014) 1514–1526

CONCLUSIONS

- Chemiresistive polymer based sensors operate at room temperature.
- Easy & simple production. Potential for mass production by printing.
- Chemiresistive polymer films are sensitive. Can sense concentrations below regulated exposure limits.
- The trick is in details: surface area, electrode position, MIP, addition of fillers.
- OPEN problems:
  - long term performance,
  - recovery of the conductive polymer sensors,
  - baseline drift.

Thank you!