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

COST Action TD1105

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New Sensing Technologies for Air Quality Monitoring

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Emerging Sensing Materials for Air Quality Monitoring

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Plan

- Scientific context and objectives in the Action
- Research facilities available in ICMUB
- Current research activities in ICMUB
- Molecular materials:
  - Cavitands: Selective or not?
  - Solution processing: The example of phthalocyanines
- Polymers:
  - Dielectric materials
  - Conducting polymers
- Suggested R&I Needs for future research
• Background / Problem statement:

- Interest: The tuning of properties by molecular engineering
  morphology, roughness and specific surface, hydrophilicity or hydrophobicity, processability, electrical properties

- One way: to combine materials for improving chemosensing

AFM images (1 mm x 1 mm) of a pure HOGaPc film (left) and a hybrid film cellulose/HOGaPc film;

Langmuir 23 (2007) 3712-3722

• Brief reminder of MoU objectives:

  selectivity, low-cost: solution processing (e.g. printing techniques ...),
  low-power consumption (can operate at room temperature)
Research Facilities available in ICMUB

- Research Facilities:
- Synthesis
- Solution processing and secondary vacuum chamber
- Electrical and electrochemical measurement set-ups
- Workbenches: $O_3$ (generator/analyser, ppb range), $NH_3$ (ppm range), BTX (ppm range), humidity

Chemistry
Electrochemistry
Electronics
Current research activities in ICMUB

• Current research topics at the ICMUB:
  - New materials
  - New transducers

• Brief list of ongoing research topics of the ICMUB:
  - Humidity-insensitive ammonia sensors
  - Molecular Semiconductor-Doped Insulator (MSDI) heterojunctions as new conductometric transducers
  - New polymer/macrocycle hybrid materials
  - Electrochemical modification of electrodes

Molecular materials

Weak intermolecular interactions play a key role:

- From molecules to materials (structure and morphologies depend on these interactions)

- Between sensing materials and target gaseous species

They are Van der Waals, $\pi-\pi$, dipole-dipole, H-bonds, …

Structure and morphology are highly related to the processing techniques

Adsorption and desorption can occur at RT.
Molecular engineering

Ionic substituents → solubility in water

Withdrawing substituents → n-type materials

Long alkyl substituents → solubility in organic solvents
Cavitands

Selectivity?
Based on size, hydrophoby of the cavity, specific host-guest interactions


Selectivity?
Actually, in the case of BTX, R is correlated with the P_{sat}.
P_{sat}(X) < P_{sat}(T) < P_{sat}(B)
R(X) > R(T) > R(B)

Calixarenes

Resorcinarenes

$\begin{align*}
m = 1; 2; 3; 4; 5; 6
\end{align*}$
Cavitands

Covalently attached quinoxaline-bridged resorcin[4]-arene cavitands to gold nanoparticles anchored on oxygen plasma treated carbon nanotubes

Selectivity towards benzene

Solution Processing versus Vacuum Evaporation

Vacuum Evaporation

Submonolayer
Intermolecular interactions

Thick film
Intermolecular interactions

Solution Processing

STM image of LuPc₂ on vicinal Si
Different molecular orientations and adsorption geometries are pointed out

A sketch of the proposed adsorption geometry of type I molecule

LuPc₂ / PMMA (80/20 w/w) (polymethylmetacrylate):
by solvent-cast or spin-coating

The quasi-Langmuir-Shäfer Technique


Current increases under ozone

Y. Chen, M. Bouvet*, T. Sizun, Y. Gao, C. Plassard, E. Lesniewska, J. Jiang,
Dielectric polymers

Associated to capacitive or acoustic transducers, their response = f(dielectric constant)

- **Polyimide (PI)**, cellulose acetate, polycellulose acetate butyrate, polymethylmethacrylate and polyvinylpyrrolidone, **polyethylene-naphthalate (PEN)**

- Acrylamide-isoctylacrylate copolymers are prefered for CO$_2$ sensing

Specific effects:
- **swelling**
- **temperature** induces an increase of the motion of polymer chains segments, above T$_g$ (or for low T$_g$ polymers) diffusion of gases is higher

The interaction of polymers with VOCs can be described using **linear solvation energy relationship** (LSER) that takes into account dispersion, polarizability, dipolarity, basicity, acidity and hydrogen bonding interactions.

Conducting polymers

**Polypyrrole**

Partially oxidized = conductive form

**Partially oxidized Polyaniline**

- Generally associated with conductometric transducers;
- Sensitive to redox active species, e.g. NO\textsubscript{x} and NH\textsubscript{3}

Other conducting polymers

- Polythiophene
- Poly(p-phenylene vinylene)
- PEDOT

Layer by Layer Deposition of Conducting Polymers – Phthalocyanine Hybrid Materials

Cationic and anionic polyelectrolytes

Electrodeposited Polypyrrole-phthalocyanine hybrid materials

Electrooxidation of Pyrrole in the presence of sulfonated CoPc

PPy-sCoPc Hybrid materials

TPy-LiClO$_4$  PPy-sCoPc

Optical topomicroscopy

Scanning electron microscopy

Higher sensitivity to NH$_3$ of the hybrid material, with a weak effect of rh in the 20-80% rh range

Suggested R&I Needs for future research

- Research directions as R&I NEEDS:
  - to focus on the structure and morphology of sensing materials for a higher stability of the response of sensors (they depend on the processing techniques)
  
  - to study the compatibility with humidity (a key issue in AQM) The effect of rh on the response of sensors must be studied, not only at one particular value, but also in a broad rh range
  At RT, 100% rh \( \approx 22\,000\) ppm,
  but 100% rh at 20°C correspond to 73% rh at 25°C.
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