Nanomaterials for trace detection

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Outline

- Trace detection: many challenges
- Currently available technologies
- Nanomaterials: a few promises
- Medical applications
- Explosive and warfare agent detection
- Air Quality monitoring
- Outlook

Trace detection: many challenges

Water

-Heavy metals: Pb, Hg
-Endocrine disruptors
-Microbial pathogens
-Benzene, PCBs
- Warfare agents

Air

-Particulate matter

-SOx, NOx, O3, VOCs, CFCs, CH4, … explosives, warfare agents

Multimedia pollutants:
Heavy metals, VOCs, PCBs,…

-Heavy metals: Pb, Hg
-Benzene, Toluene, PCBs, Arsenic, TCE, TetraCE, Radon and other radioactive substances…

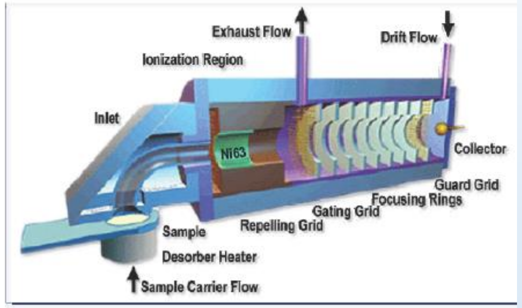
Soil

Medical applications

- Biomarker detection in breath and/or fluids

Currently available technologies

❖**Ion mobility spetrometry (GC-IMS)**



⇨most common technique used in commercial instruments for trace explosives detection
⇨strong reliability and sound performance favored applications in explosives detection
⇨Instrument formats range from small, hand-held devices to large, dedicated-site portal systems
⇨separates ions by how quickly they drift through a gas ⇨identification as possible explosives if drift time corresponds to known explosives

☑ Sensitivity to vapors at ppb level, without carrier gas
☑ near-real time detection
☑ Remote monitoring capability
☑ Wide range of volatile and semivolatile

👎 Not in situ detection
👎 Sensitive to pressure drifts and weather conditions
👎 Fairly expensive (5-7 k€)

❖**Mass spetrometry (GC-MS)**

⇨separation process occurs in high vacuum
⇨spectrum characteristic of the substance
⇨MS is a much more discriminating form of separation than IMS
⇨more engineering required

Constellation Technology corporation

☑ on site analysis of volatile compounds, weatherproof
☑ short time detection, discrimination and quantification (minutes)
☑ direct sampling system for on-site detection
☑ Wide range of products

☑👎 field portable but fairly large packaging and size (≅ 15 to 60kg)
👎 Not suitable for in-situ detection
👎 fairly expensive (100-200 k€)

❖**Surface Acoustic Wave (GC-SAW)**

⇨piezo-electric crystals with characteristic acoustic resonant frequencies
⇨when molecules adsorbed onto the crystal surface, the resonant frequency is changed
⇨respond to any molecule adsorbed onto the surface
⇨usually employed with a GC front-end but selectivity can also be introduced by a special coating

☑ fast response (≅10s)
☑Sensitivity (ppb-ppt)
☑Small and portable
☑Remote option

👎 not inherently selective
👎 Fairly expensive (16-20k€)

Z-Nose, Electronic Sensor Technlogy

❖**Chemiluminescence (GC-CL)**

⇨production and emission of light as a product of a chemical reaction

A + B —> products + lights

⇨example: Scintrex EVD 3500

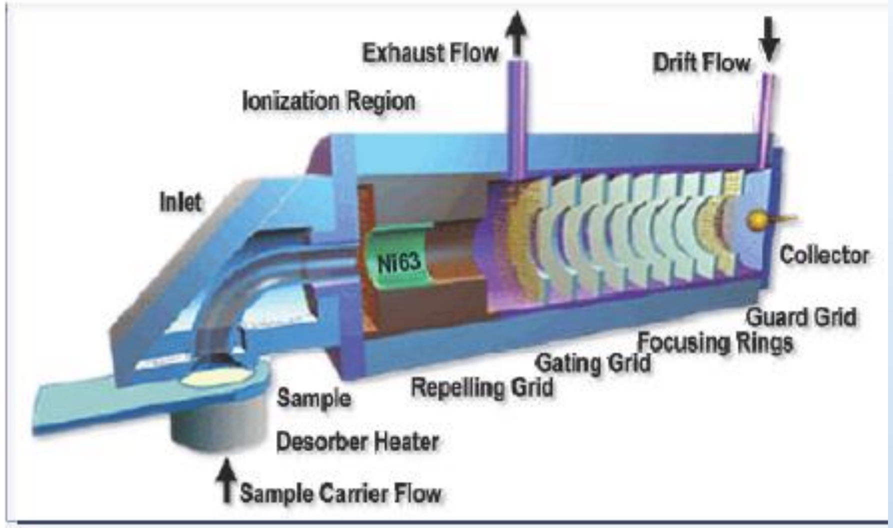
alternative chemiluminescent detection technique: reaction with luminol, a chemical which photoluminesces in the presence of certain oxidizers. For peroxide-based explosives as well as nitro-based.

☑short time detection
☑down to 1ppb for NO_2 compounds
☑weather sensitive (temperature, rain…)
☑non intrusive

👎 for specific targets
👎 expensive

Currently available technologies

❖Ion mobility spetrometry (GC-IMS)



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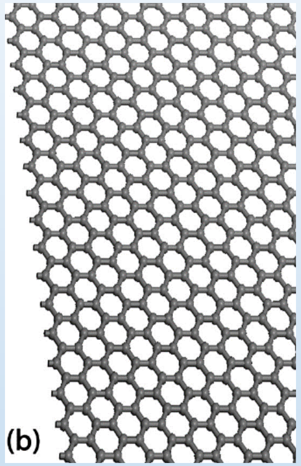
☑ short time detection
☑ down to 1ppb for NO_2 compounds
☑ weather sensitive (temperature, rain…)
☑ non intrusive

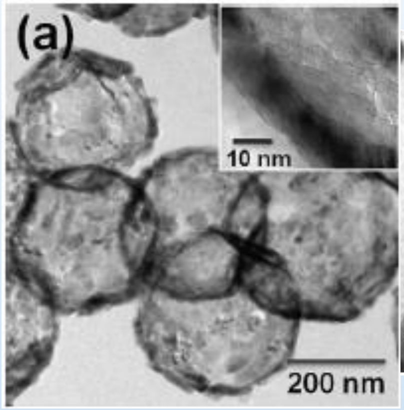
Trace detection: many challenges

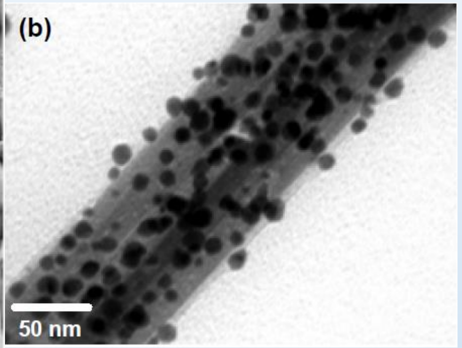
Continuous and ubiquitous monitoring sought

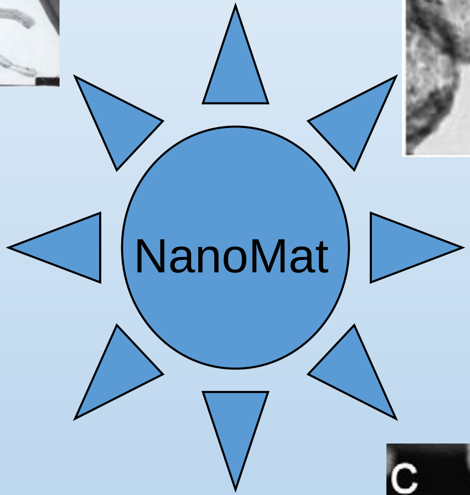
- High sensitivity for ameliorated LOD (ppb, ppt, ppq)
- High stability for reliability
- Selectivity
- Humidity and temperature compensation
- Reduced size
- Affordable cost
- Low power
- Distributed sensing

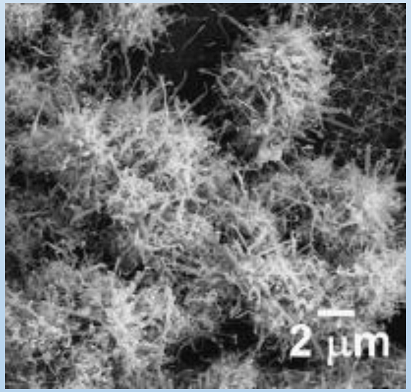
Nanomaterials: a few promises

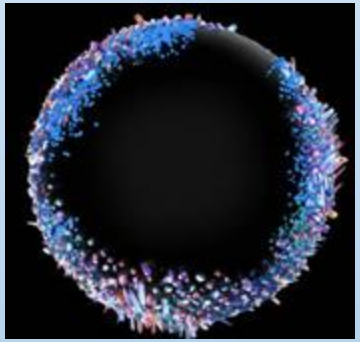


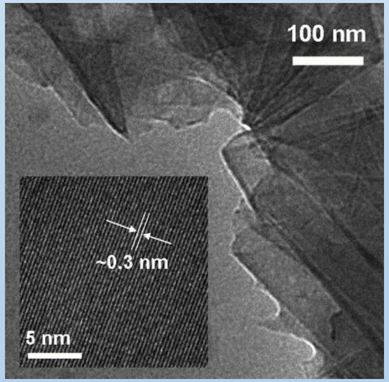


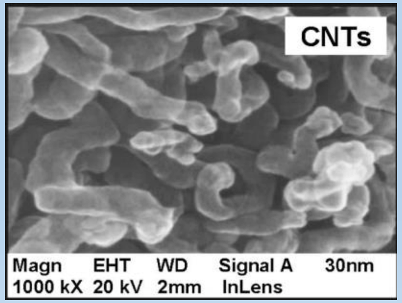


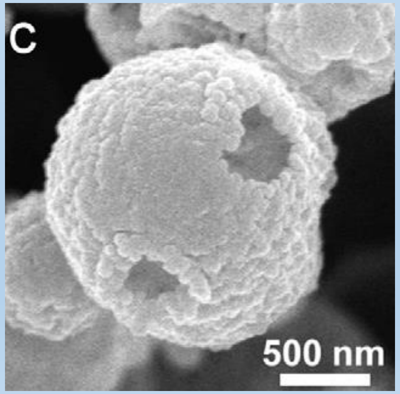


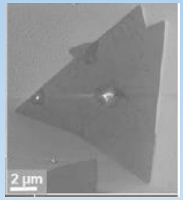




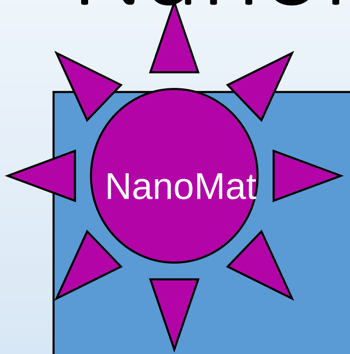








Nanomaterials: a few promises



- Low-dimensional structures have most of its atoms exposed to the environment

- Precise surface composition control

- Avoidance of grain boundary poisoning (such as in polycrystalline metal oxides)

- Some nanomaterials have high quality crystal lattice and show high carrier mobility and low noise

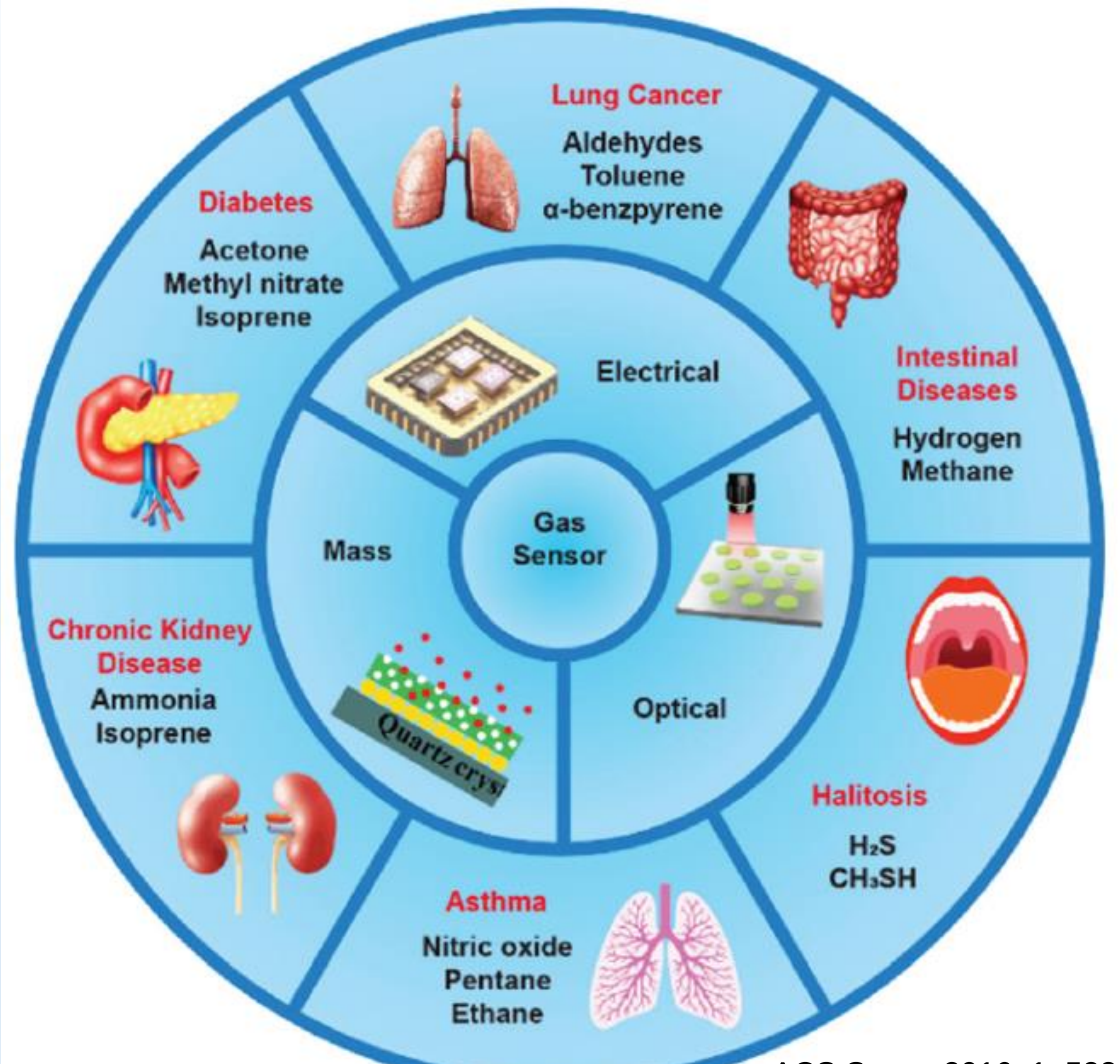
- Different techniques can be used both to create defects and graft functional groups to their surface

- Engineering of host-guest interactions or molecular imprinting for improved selectivity

- Fabricated by different methods, they are often amenable to making devices by conventional methods

- They are good model materials for computational chemistry studies

Medical applications: Breath diagnosis



ACS Sens., 2016, 1, 528

Nanosensors for:

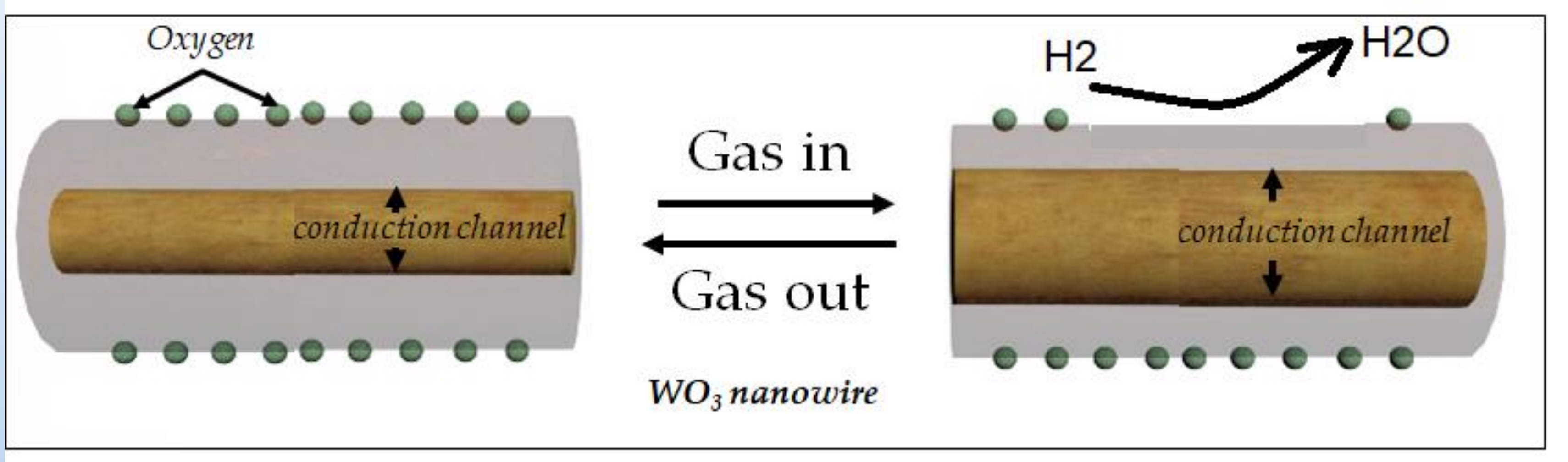
1. Untargeted analysis (e-nose approach)
2. Targeted analysis (highly specific sensors)

Specifications needed:

a) High selectivity
b) High sensitivity and low LoD
c) Fast response
d) Great stability

Medical applications: Breath diagnosis

Electrical: Chemoresistive (e.g. using MOX nanomaterials)



The exposure to gases that alter the equilibrium of surface oxygen species changes the width of the conduction channel in MOX nanowires.
Considering the existence of many NW to NW contacts in randomly oriented NWs, this leads to high changes in film resistance, i.e., high response upon exposure to gases.

Medical applications: Breath diagnosis (acetone)

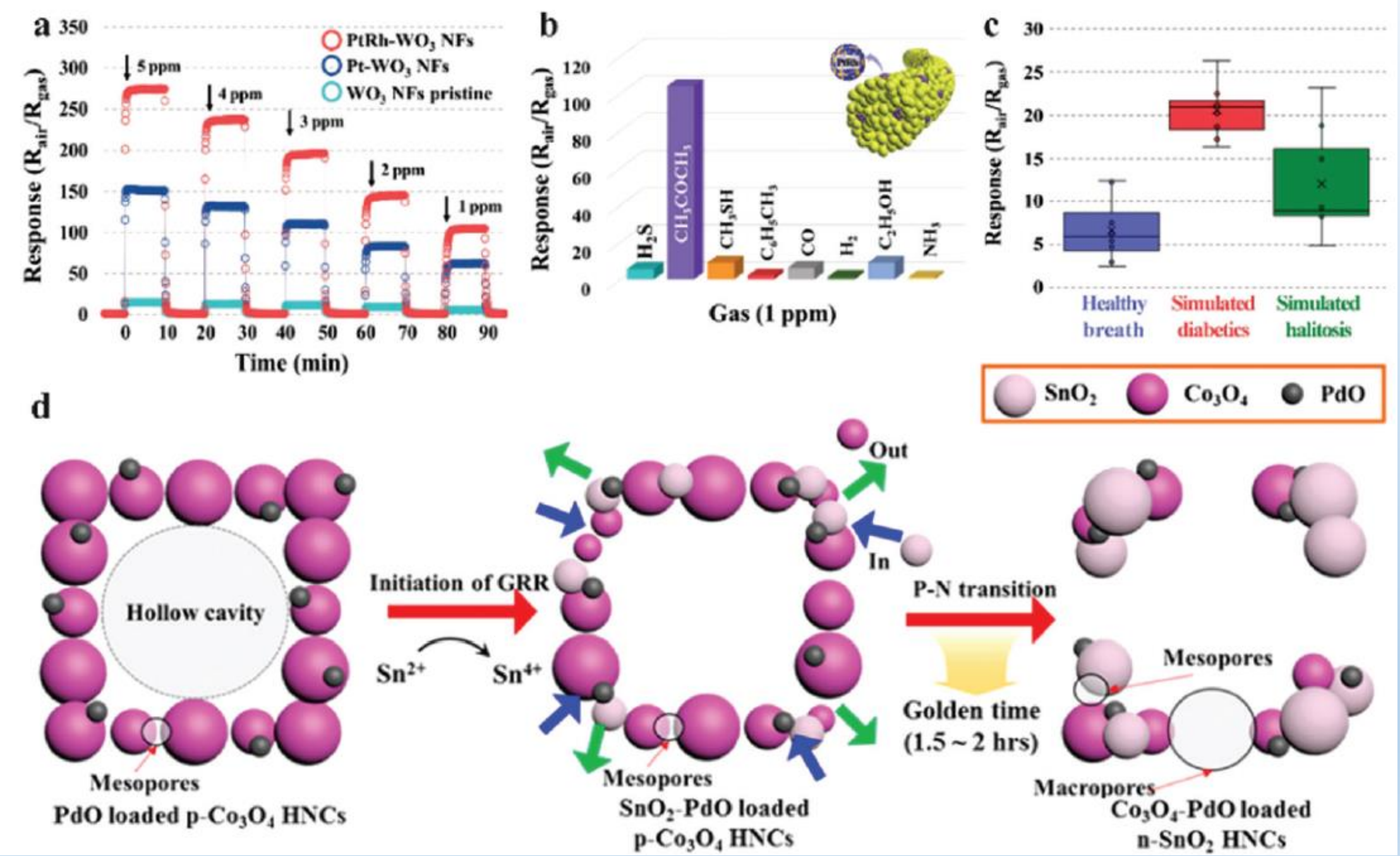
Chemoresistive detection

Catalyst NP supported on metal oxide NFs

Adv. Mater., 2017, 29, 1700737

Pd loaded cobalt oxide hollow cages synthesized using ZIF-67 galvanic replacement reaction used to substitute some cobalt oxide by tin oxide

J. Am. Chem. Soc., 2017, 139, 11868



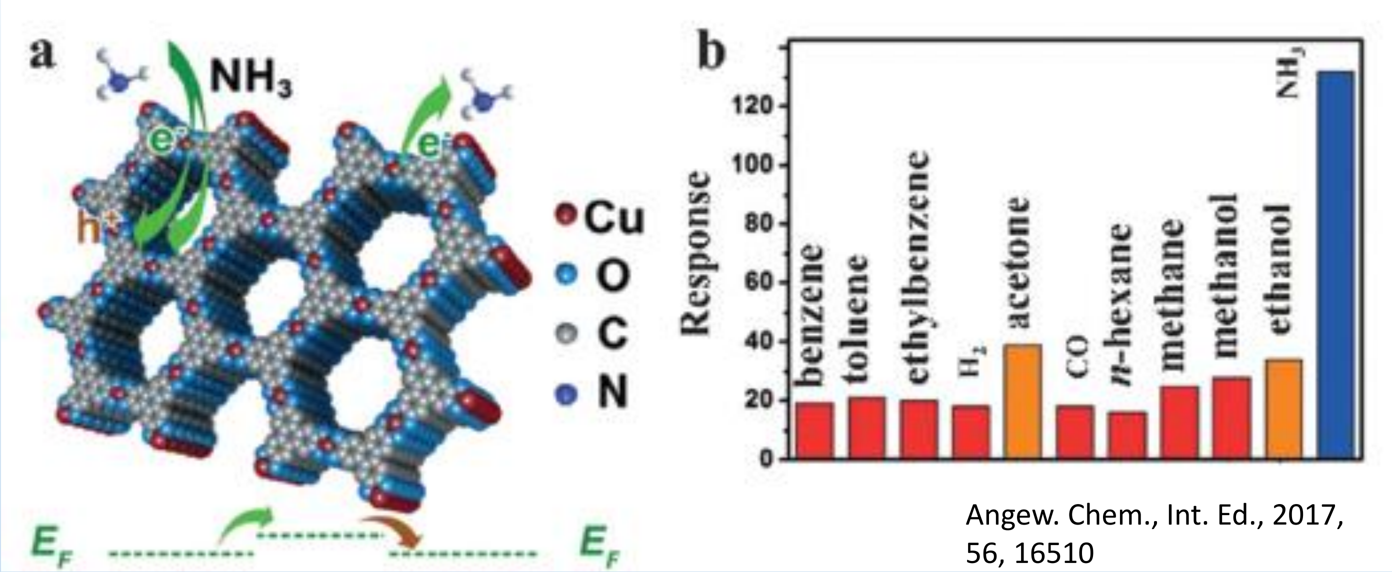
Medical applications: Breath diagnosis (acetone)

Materials	C/ppm	Response	Selectivity	T/°C	RH/%
Co-Doped ZnO nanofibres	5	5	4 (100 ppm)	360	25
Pd@ZnO nanosheets	50	30	1.9 (100 ppm)	340	25
Au/ZnO hybrid	5	15	1.7 (100 ppm)	270	NA
NiO-decorated ZnO	10	3.6	1.9 (100 ppm)	300	30
$ZnO/ZnFe_2O_4$ hollow cubes	5	9.4	2.4 (5 ppm)	250	NA
NiO/ZnO	1	1.3	2 (100 ppm)	275	30
ZnO nanosheets	5	6.7	2.5 (100 ppm)	300	40
$ZnO/ZnFe_2O_4$ nanocages	1	3.2	1.9 (100 ppm)	290	NA
$ZnO/ZnFe_2O_4$ microspheres	50	10	1.7 (200 ppm)	140	NA
ZnO supercrystals	20	25.4	4.3 (20 ppm)	340	NA
La/ZnO nanoplates	50	25	1.8 (200 ppm)	330	24
SnO_2 nanopolyhedrons	1	4	2 (100 ppm)	370	NA
SnO_2 nanowires	20	6	1.8 (50 ppm)	290	25
$PdO@ZnO–SnO_2$	1	5.1	3.4 (1 ppm)	400	95
$Si:WO_3$	0.6	3	2.5 (0.6 ppm)	400	40
RuO_2/WO_3	5	78	13 (5 ppm)	350	95
C-Doped WO_3	0.9	1.8	2.9 (0.9 ppm)	300	90
WO_3/Pt reduced graphene oxide	10	12.2	6 (10 ppm)	230	95
$Pt@WO_3$	1	62	31 (1 ppm)	350	90
TiO_2/In_2O_3	0.1	2.1	2 (10 ppm)	250	NA
Au/In_2O_3 films	5	43	9 (5 ppm)	340	22
In_2O_3/Au nanorods	0.1	1.3	3.6 (1 ppm)	250	94

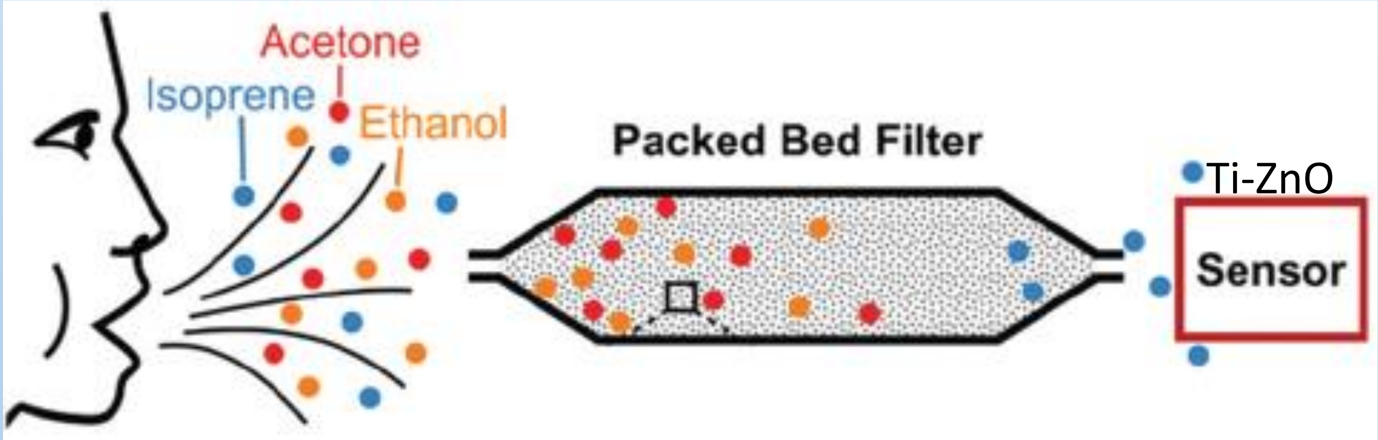
J. Mater. Chem. B, 2020, 8, 3231--3248

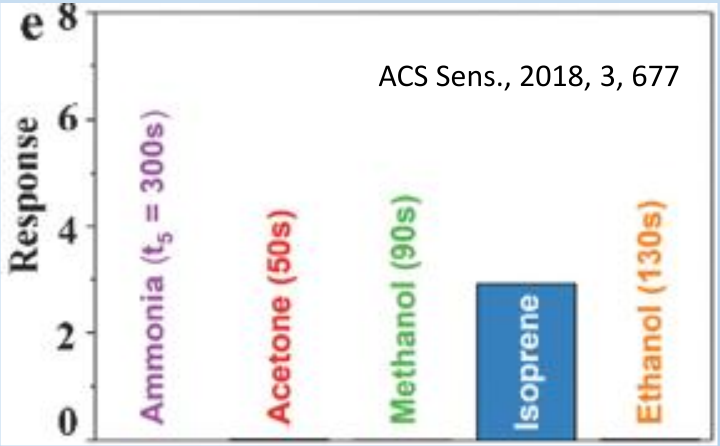
Medical applications: Breath diagnosis (ammonia/isoprene)

$Cu_3(HHTP)_2$
MOF thin films



Angew. Chem., Int. Ed., 2017, 56, 16510



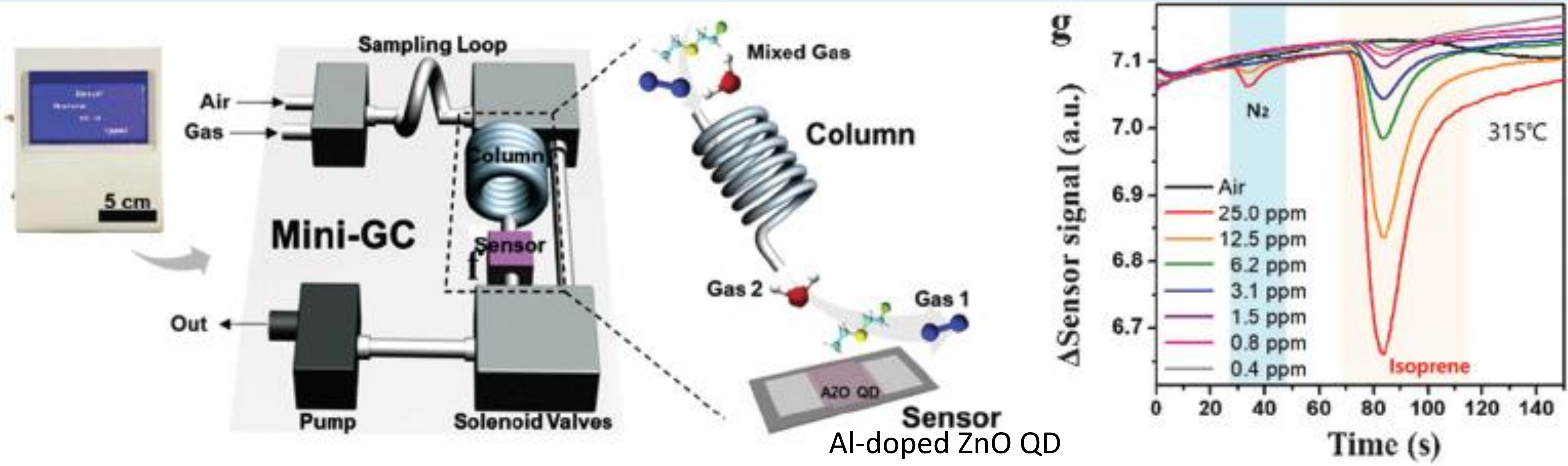


ACS Sens., 2018, 3, 677

Activated alumina, absorbs effectively hydrophilic compounds such as ketones, alcohols, and ammonia and not hydrophobic isoprene.

MINOS Sensoft

Medical applications: Breath diagnosis (isoprene)



mini-GC integrated with a ZnO QD sensor for selective isoprene detection in gas mixtures

Sens. Actuators, B, 2019, 290, 258

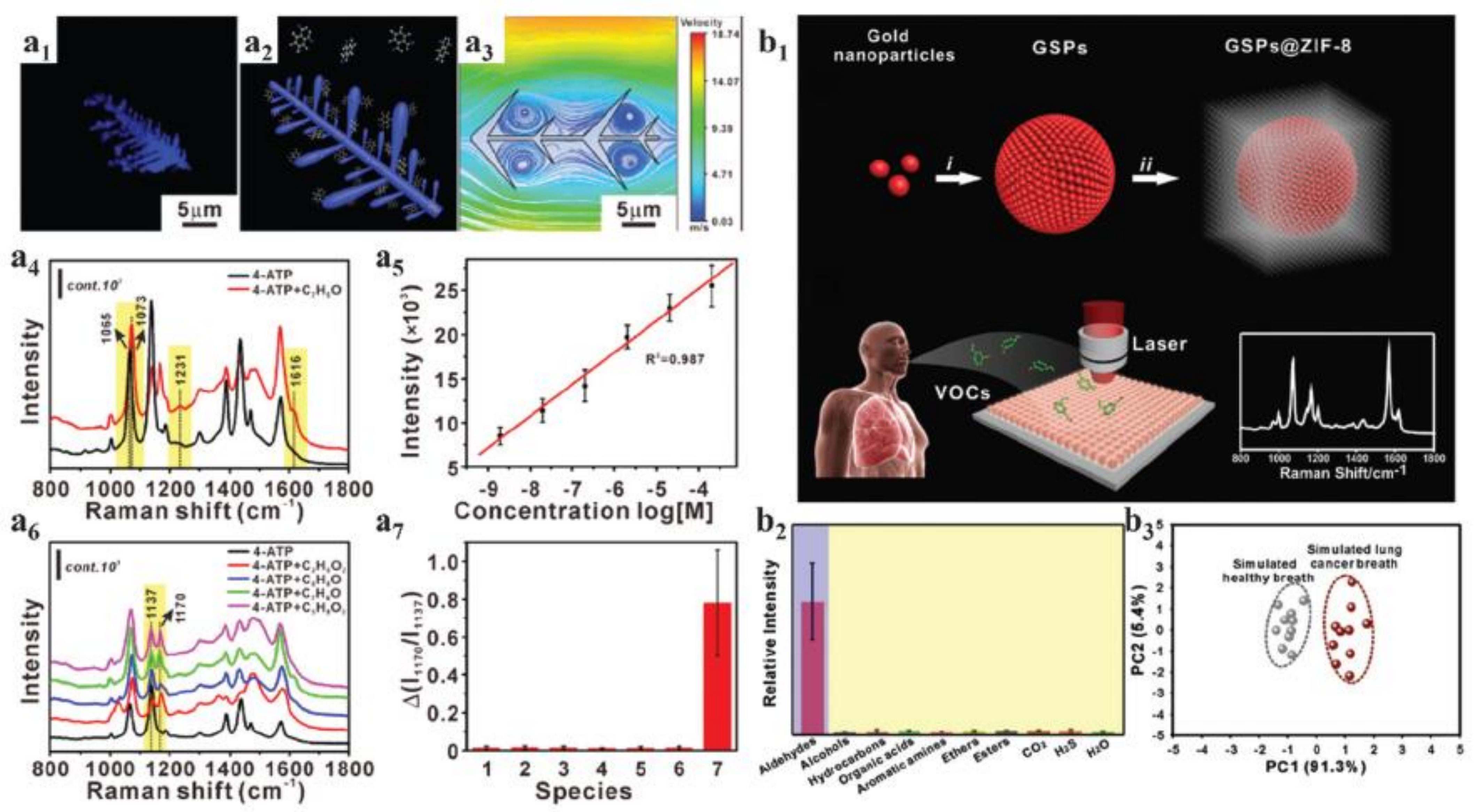
Medical applications: Breath diagnosis (aldehydes)

Silver dendrites for **SERS** detection of benzaldehydes

Anal. Chem., 2017, 89, 1416

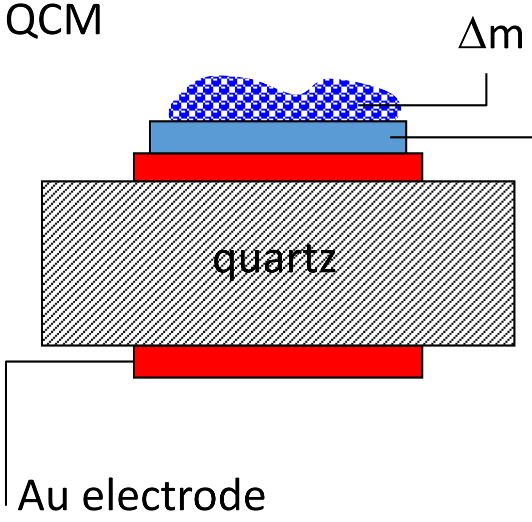
Gold superparticles coated with ZIF-8 for **SERS** detection of aldehydes

Adv. Mater., 2018, 30, 1702275



Medical applications: Breath diagnosis

QCM

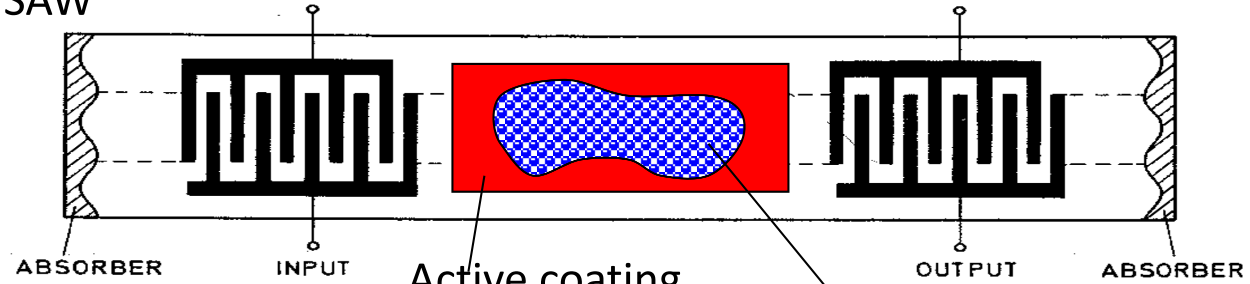


Polymer coating (active phase)

$$\Delta f = -2.3\times10^{6} f_o^{2} \Delta m/A$$

f_o (MHz), Δm (g), A (cm^2)

SAW



Active coating

Adsorbed gas molecules

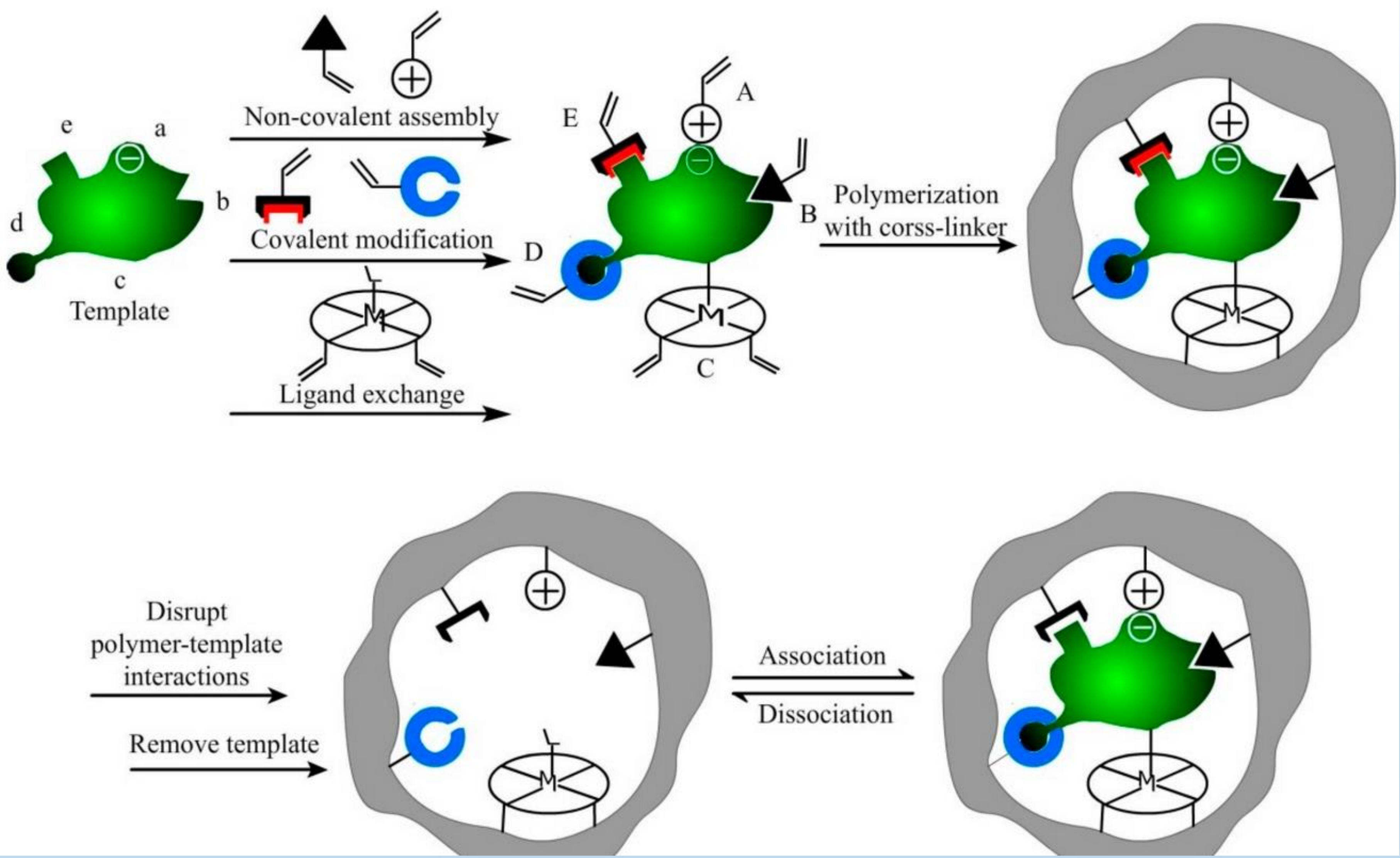
$$\Delta f = -k f_o^{2} \Delta(\rho_m d)$$

ρ_m: film density (varies with adsorption), *d*: thickness

Adapted from J.W. Gardner, *Microsensors*

Medical applications: Breath diagnosis

Molecularly Imprinted Polymers (MIPs)

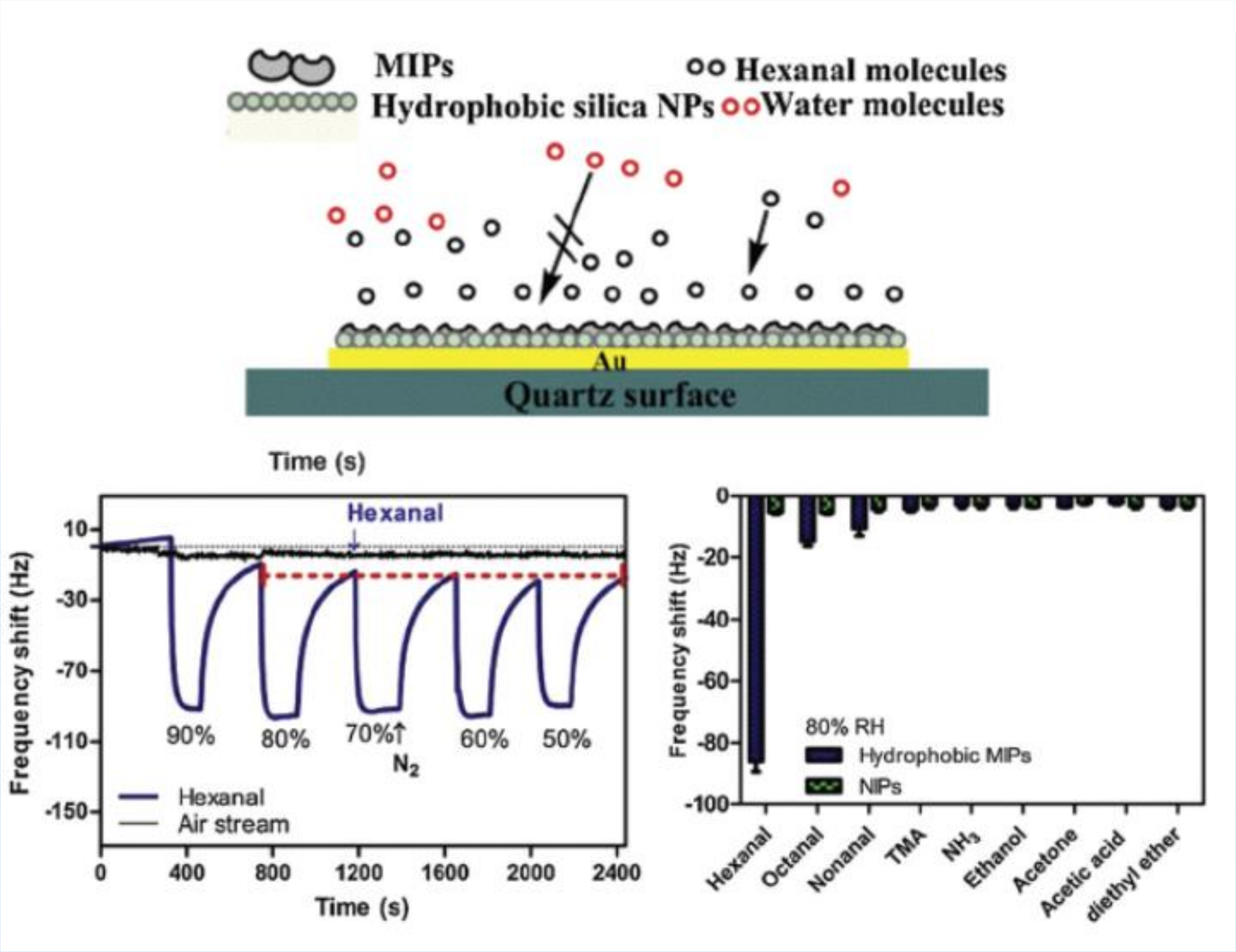


TrAC Trends Anal. Chem. 89 (2017) 146–162.

Medical applications: Breath diagnosis (hexanal)

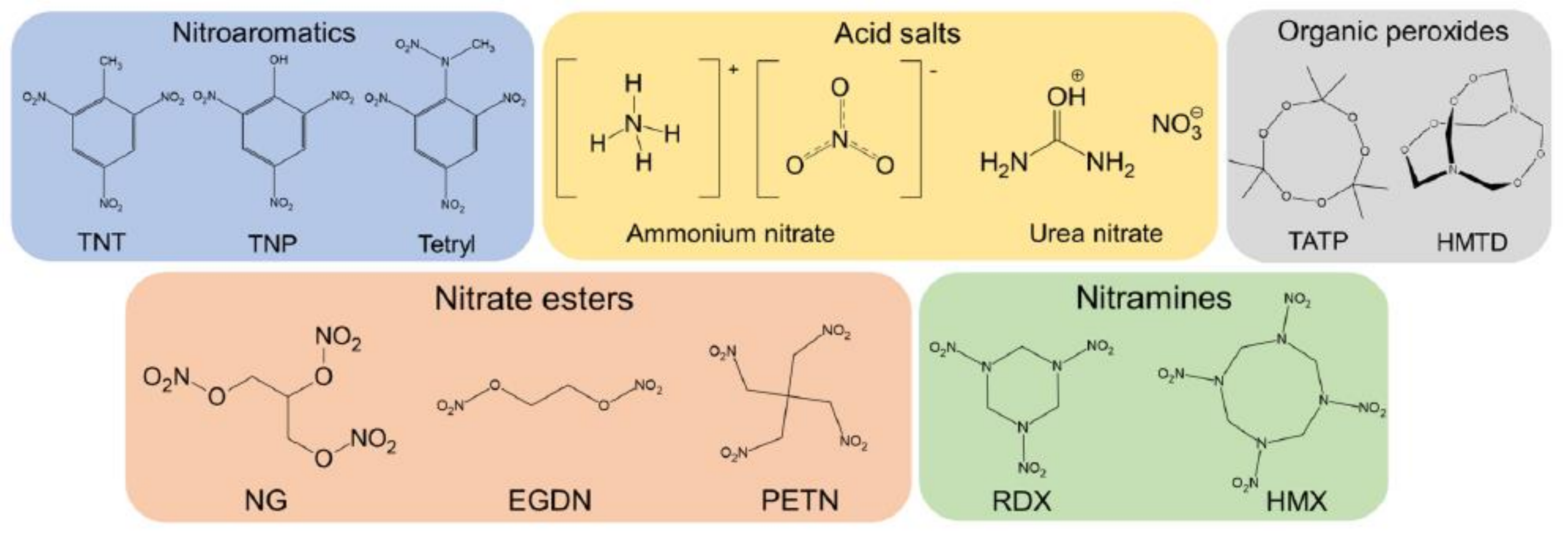
Polymer coated QCMs

MIP for Hexanal



Sens. Actuators, B, 2019, 291, 141

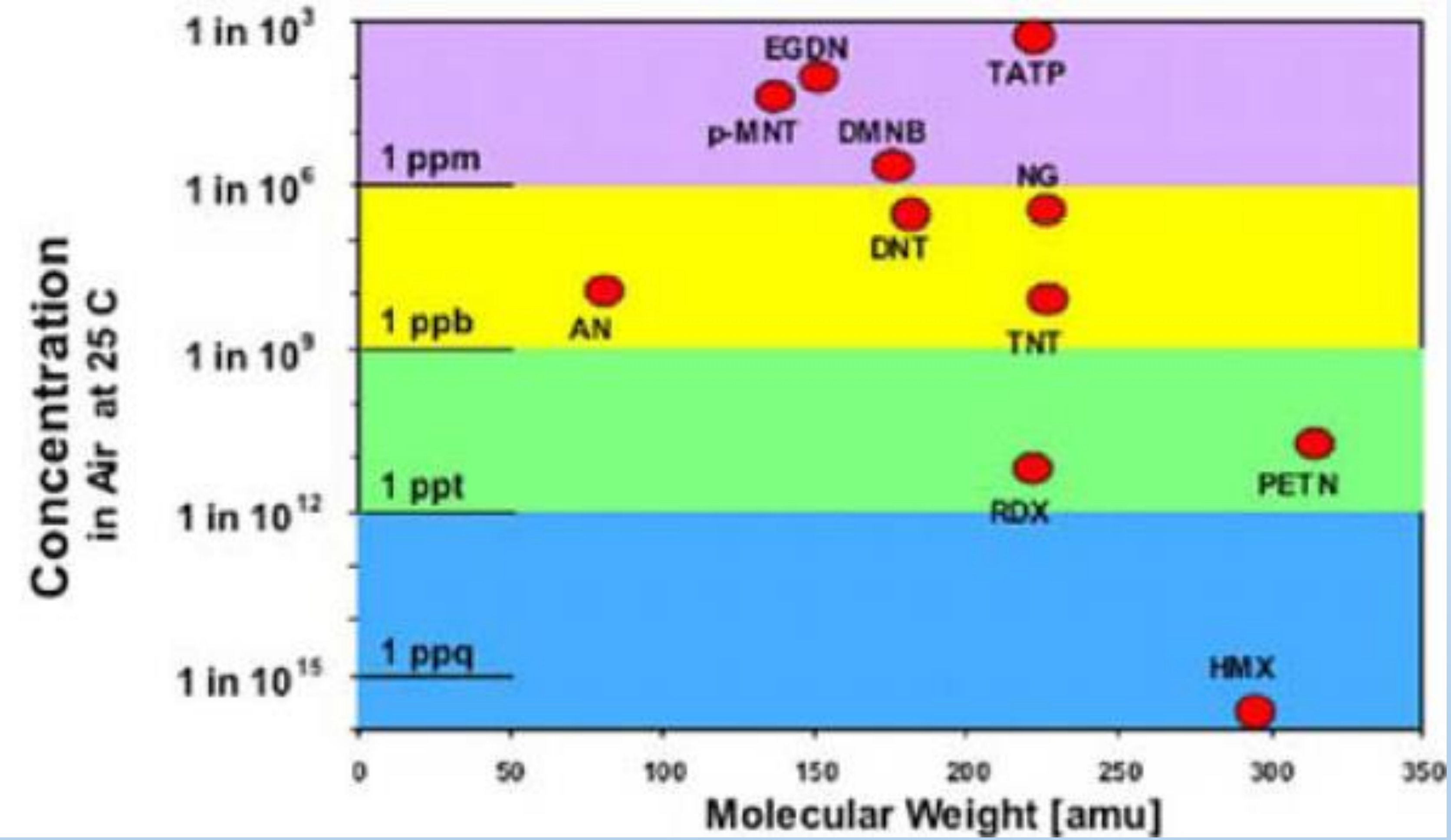
Explosive and warfare agent detection



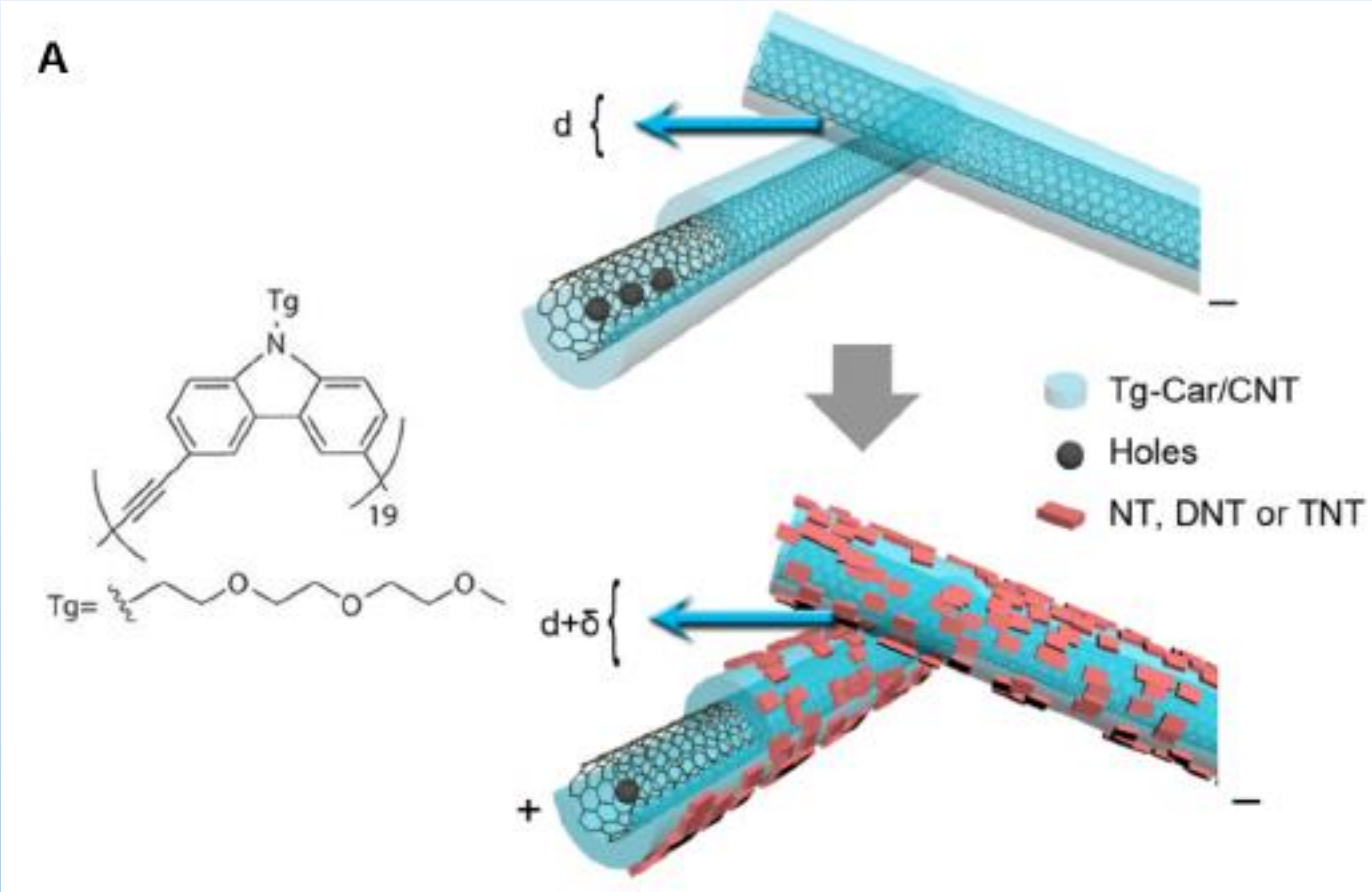
Classification of explosives by chemical groups: 2,4,6-trinitrotoluene (TNT), 2,4,6-trinitrophenol (TNP), 2,4,6-trinitrophenylmethylnitramine (tetryl), triacetone triperoxide (TATP), hexamethylene triperoxide diamine (HMTD), ethylene glycol dinitrate (EGDN), nitroglycerine (NG), pentaerythritol tetranitrate (PETN), 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX).

ACS Nano 2020, 14, 10804

Explosive and warfare agent detection



Explosive and warfare agent detection

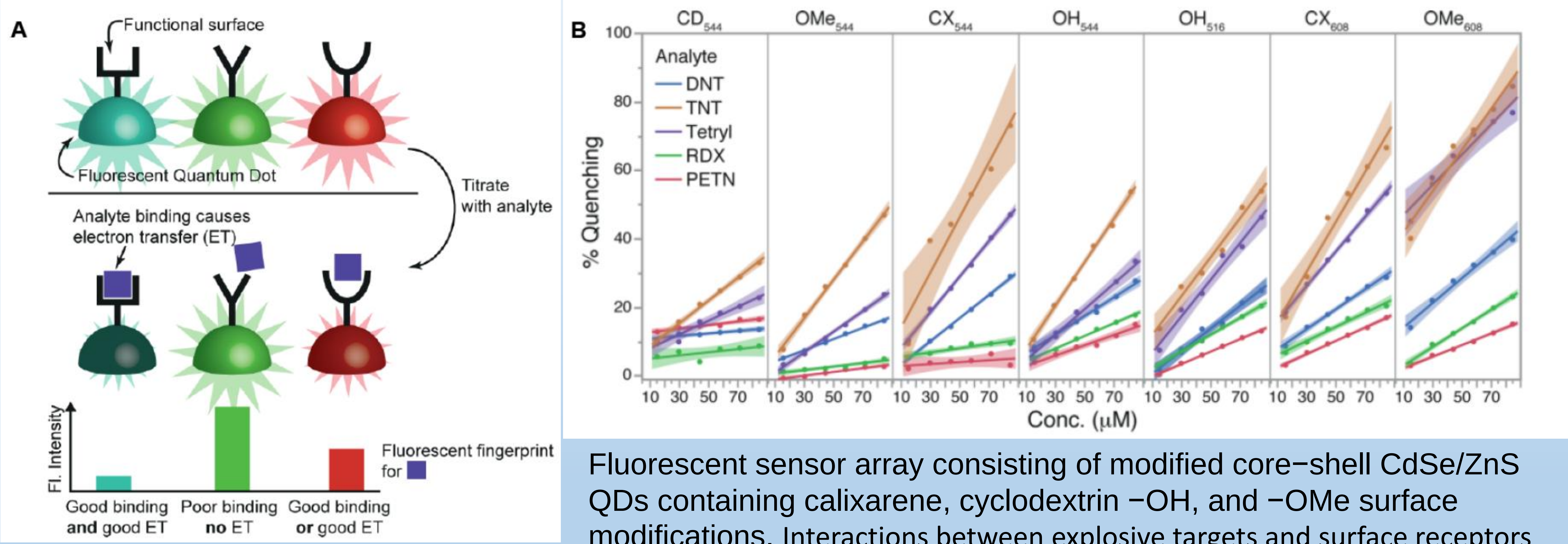


Surface functionlisation with an oligomer

ACS Appl. Mater. Interfaces 2015, 7, 7471

Explosive and warfare agent detection

optical sensing

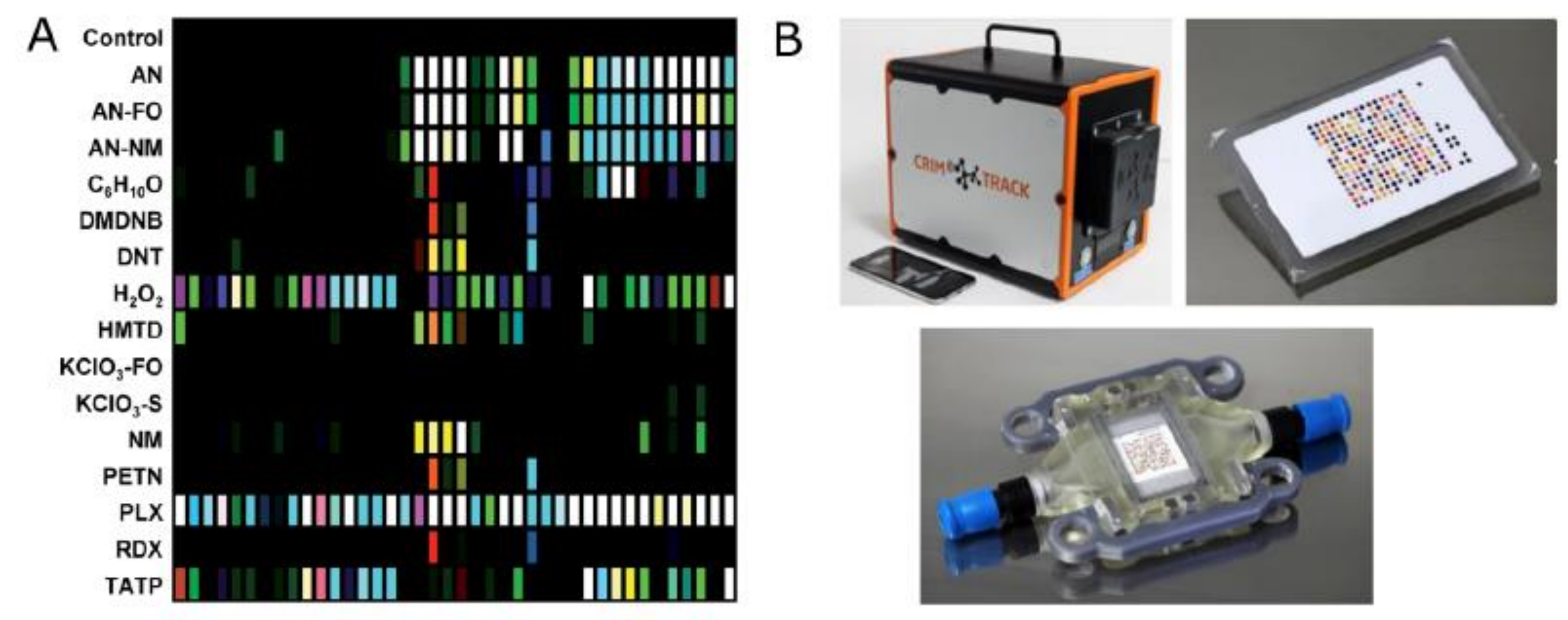


Fluorescent sensor array consisting of modified core−shell CdSe/ZnS QDs containing calixarene, cyclodextrin −OH, and −OMe surface modifications. Interactions between explosive targets and surface receptors occur through a combination of host−guest binding, electrostatics, and π−π stacking.

ACS Nano 2016, 10, 1139

Explosive and warfare agent detection

Colorimetric arrays



Anal. Methods 2014, 6, 2047

Arrays of:

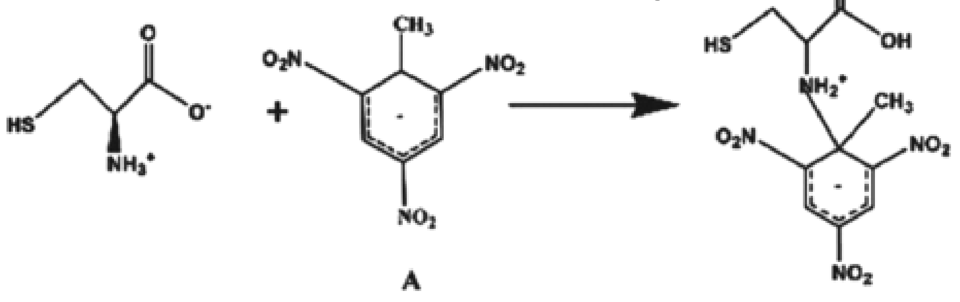
Functionalised nanoparticles

MOFs

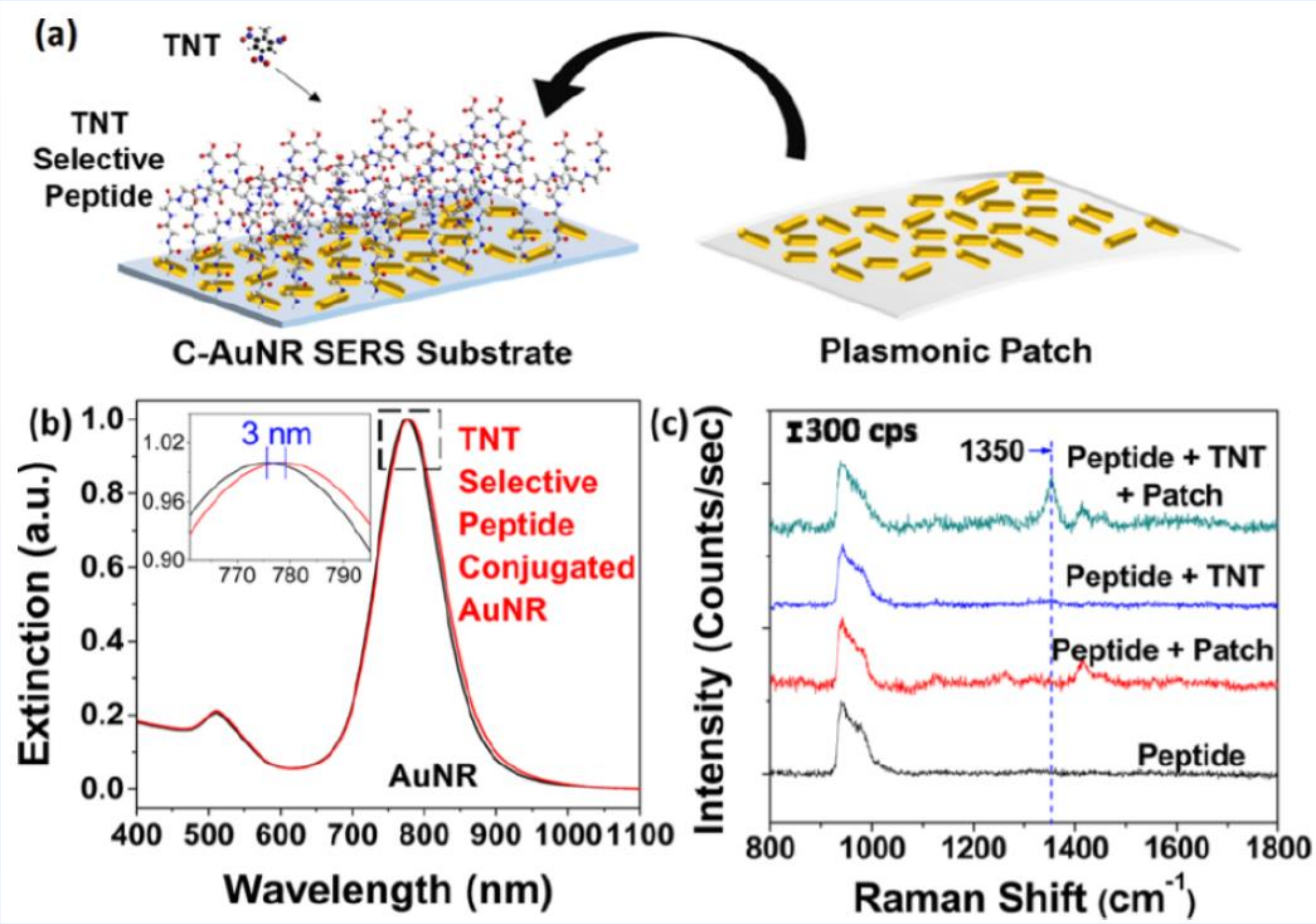
Polymers

Fluorescent molecules

Interaction between TNT and cysteine



Explosive and warfare agent detection



SERS "plasmonic patch" for the collection and analysis of explosives
(a) Schematic representing vapor detection of TNT via peptide-conjugated gold nanorods. (b) Characterization of bare and peptide-conjugated gold nanorods using UV−vis spectroscopy. (c) Raman data showing vapor-phase detection of TNT.

ACS Appl. Mater. Interfaces 2019, 11, 37939

Air quality monitoring

The main pollutants are: PM, SO_2, NOx, O_3, CO, CO_2, H_2S, NH_3, VOCs, PCBs

PM: Particles are deposited on collecting plates and back-up filters and subsequently quantified by gravimetry.

SO_2: A known volume is passed through an absorption solution containing hydrogen peroxide which oxidises SO2 to sulphate. The latter is determined by ion chromatography or titration. IR or UV absorption, UV fluorescence.

NOx: Chemiluminescence detection.

O_3: Sampling and UV absoprtion

CO_2, CO: NDIR spectrometry.

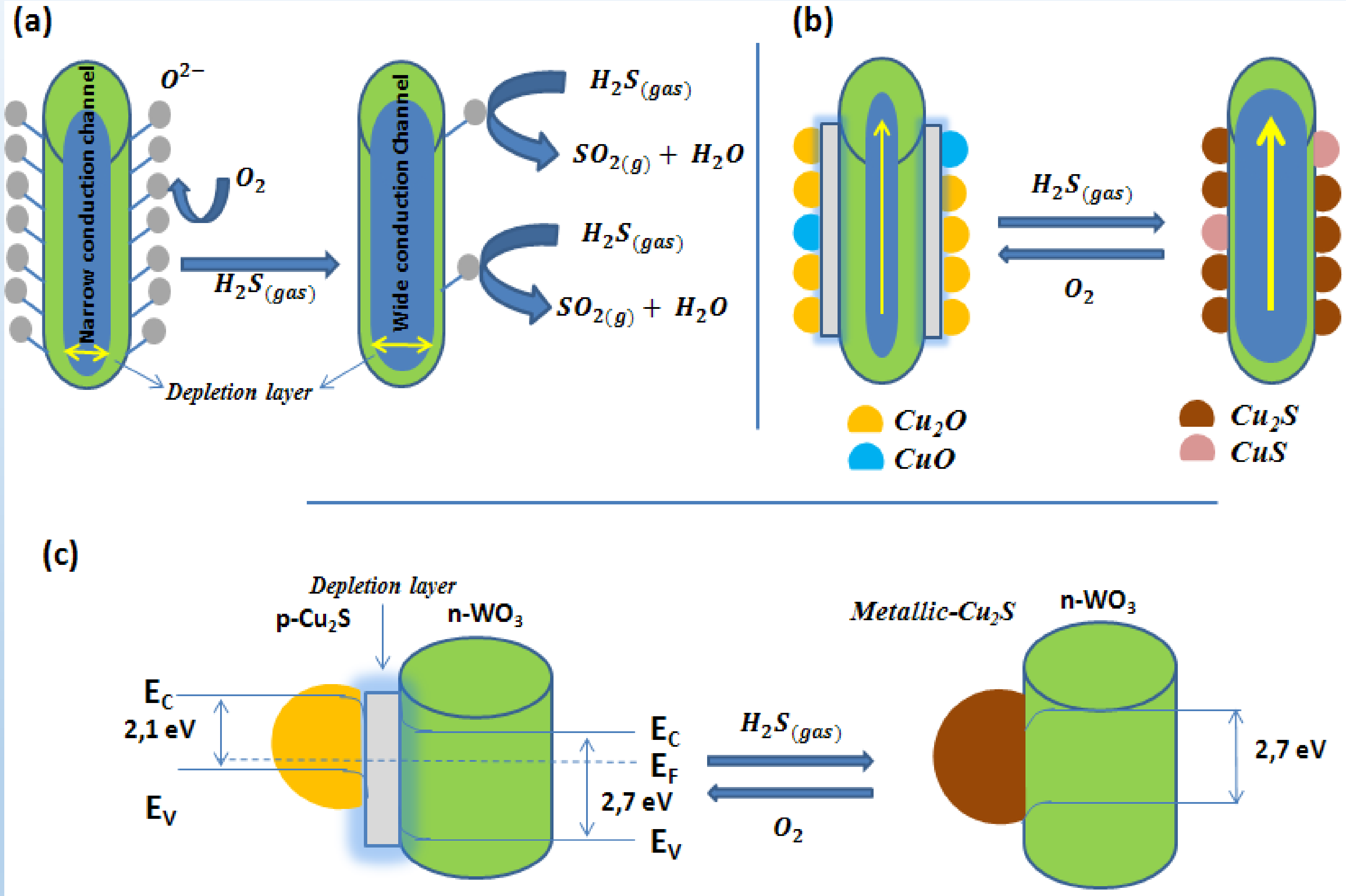
H_2S: A known volume is passed through an absorption solution containing an alkaline suspension and then analysed by colorimetry or spectrophotometry.

NH_3: Known volume is passed through an absorption solution of dilute sulphuric acid. The resulting ammonium in the absorption solution is determined by water analysis.

VOCs: Sampling by adsorption on sorbents, sample preparation by solvent extraction or thermodesorption, and analysis by gas chromatography. (TVOCs by FID or PID).

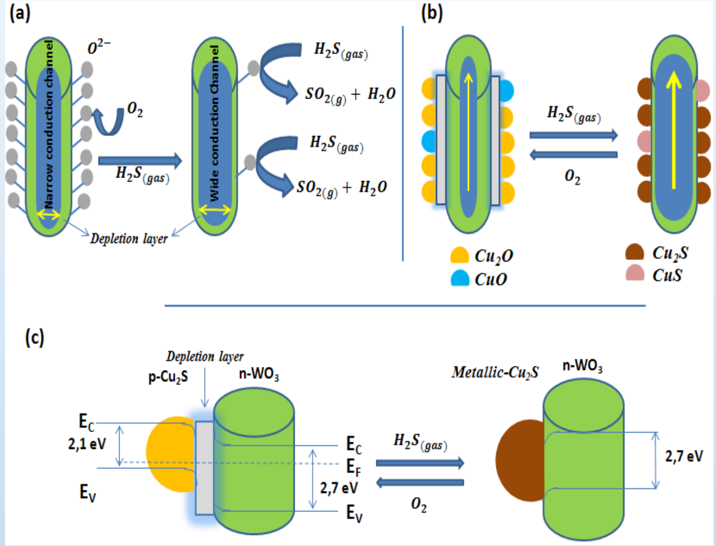
PCBs: Long term sampling and identification/quantification by isotope dilution GC-MS.

Air quality monitoring H_2S Chemoresistive

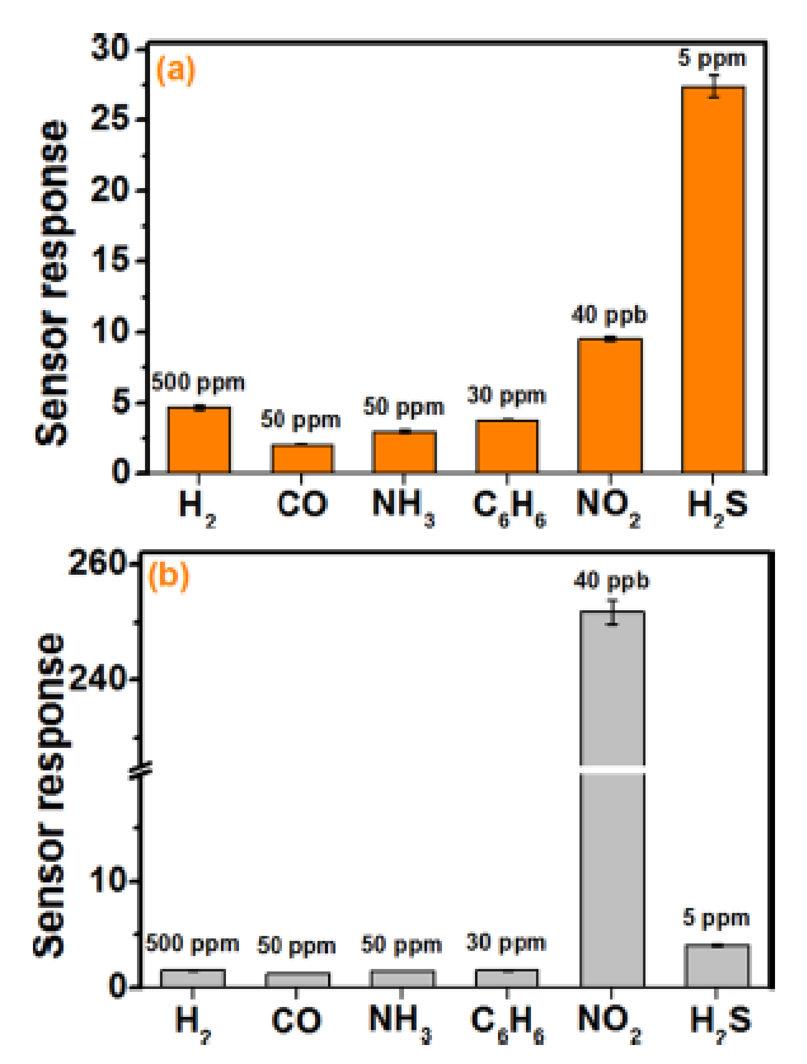


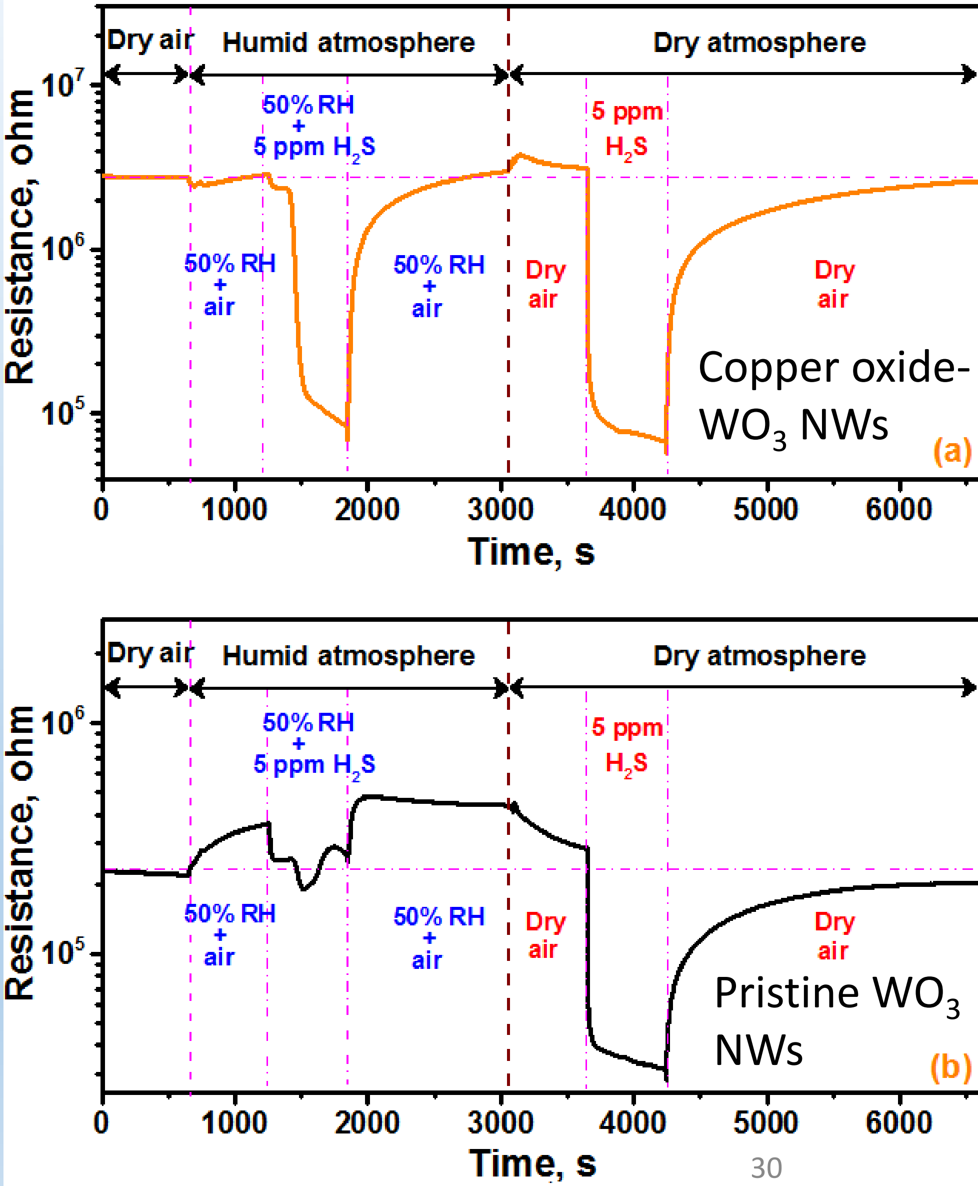
ACS Appl. Mater. Interfaces **2015**, 7, 6842

Air quality monitoring H_2S Chemoresistive

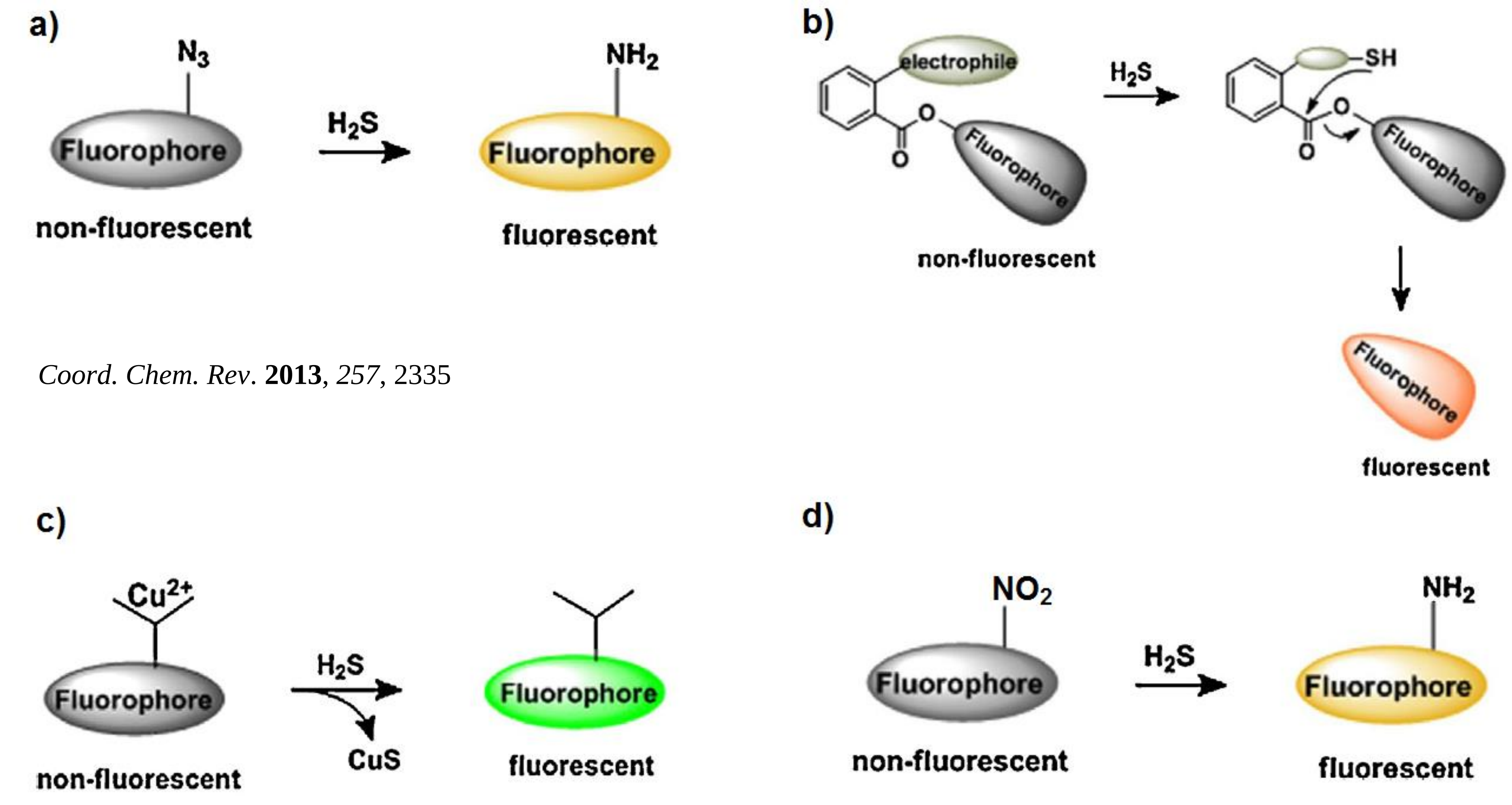


ACS Appl. Mater. Interfaces **2015**, 7, 6842





Air quality monitoring H_2S Optical

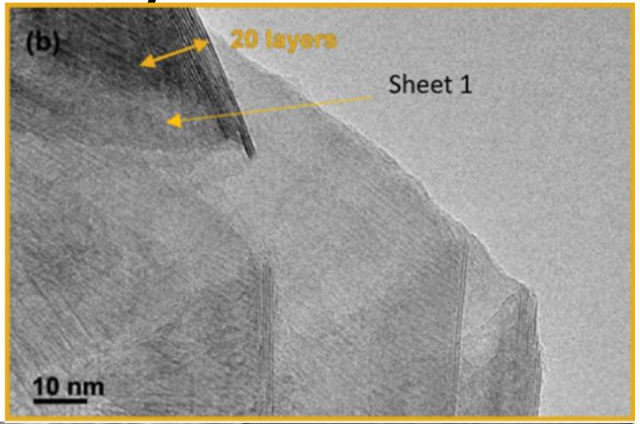


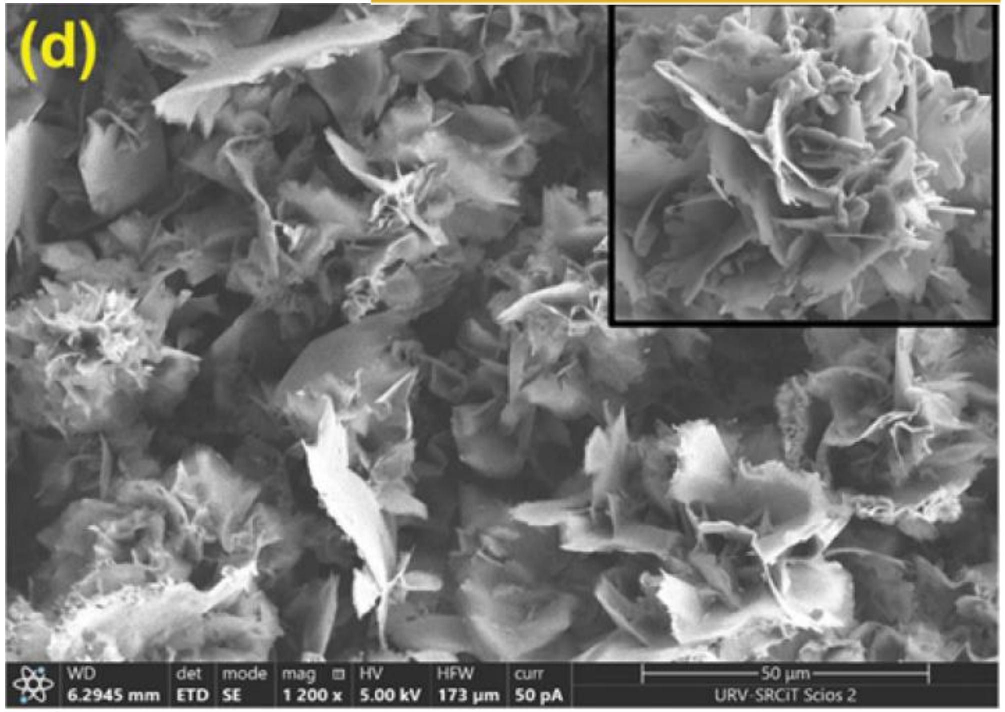
Coord. Chem. Rev. **2013**, *257*, 2335

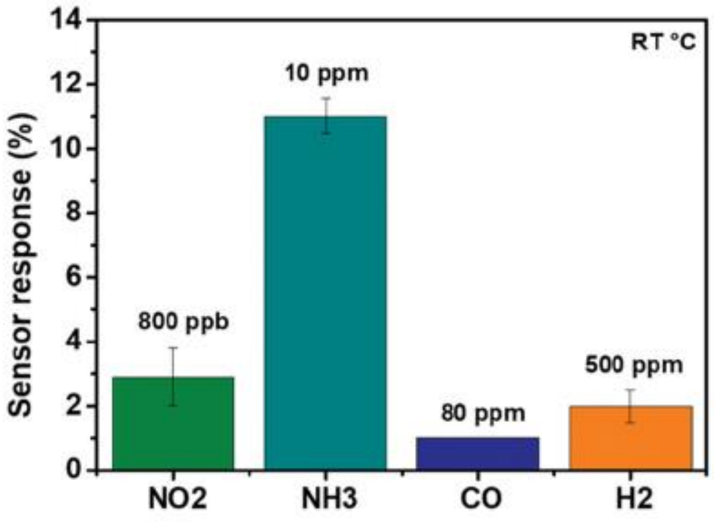
Reactions for the selective detection of H_2S employing fluorescent probes. Reduction of azides into amines by H_2S (**a**), nucleophilic addition of H_2S to the probe resulting in a cyclization process that generates a fluorescent molecule (**b**), H_2S mediates the precipitation of CuS (**c**), nitro to amine reduction (**d**).

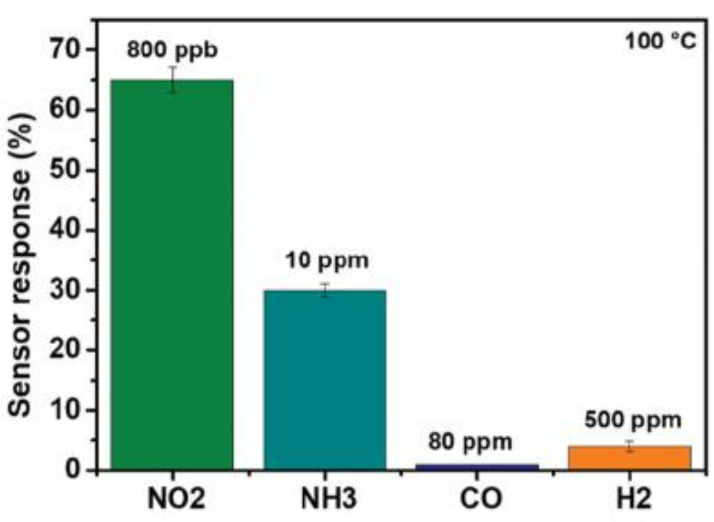
Air quality monitoring NO_2/NH_3 Chemoresistive

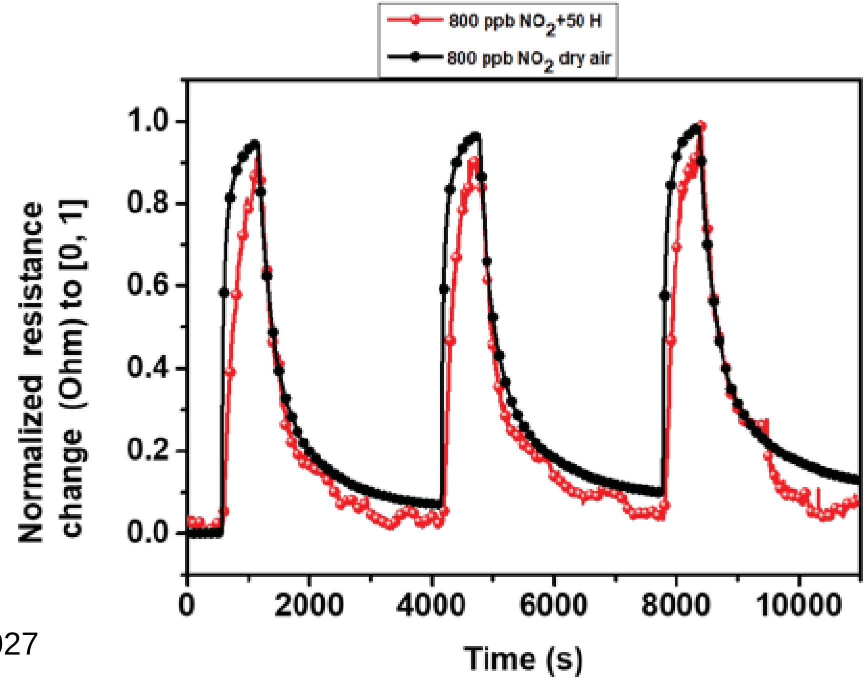
3D assembly of MoS_2 flakes











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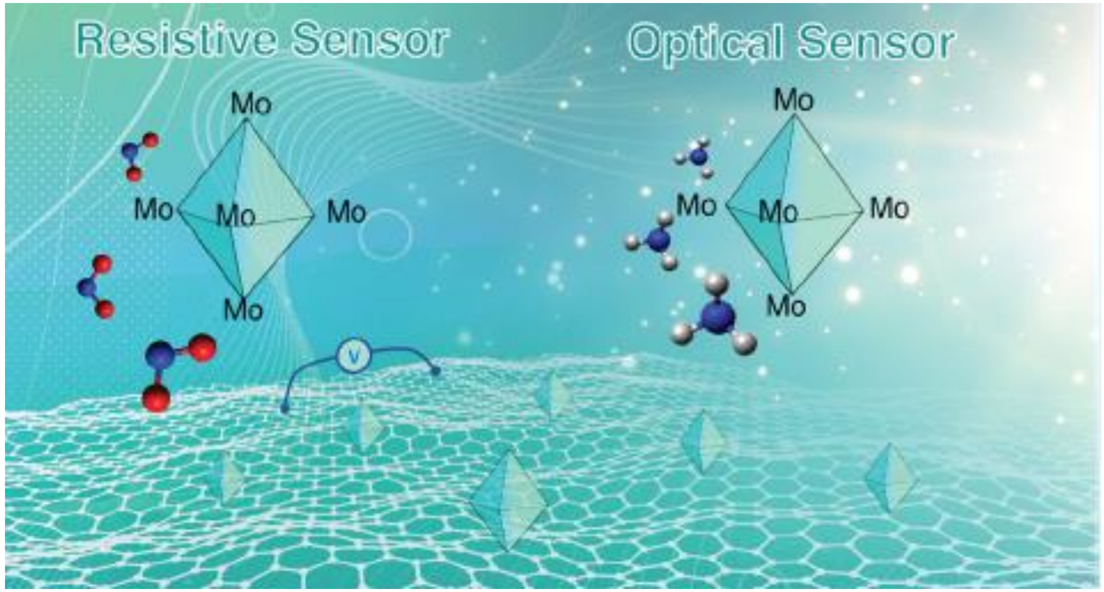
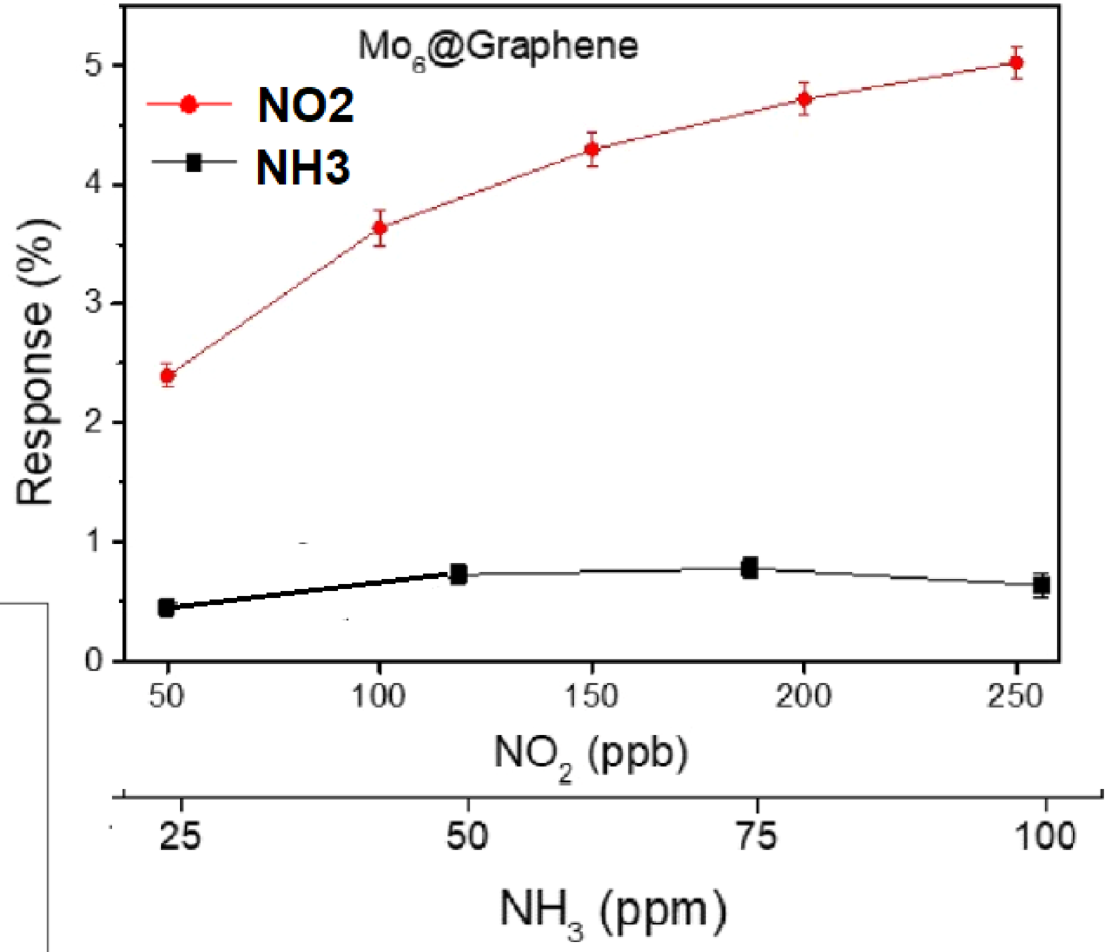
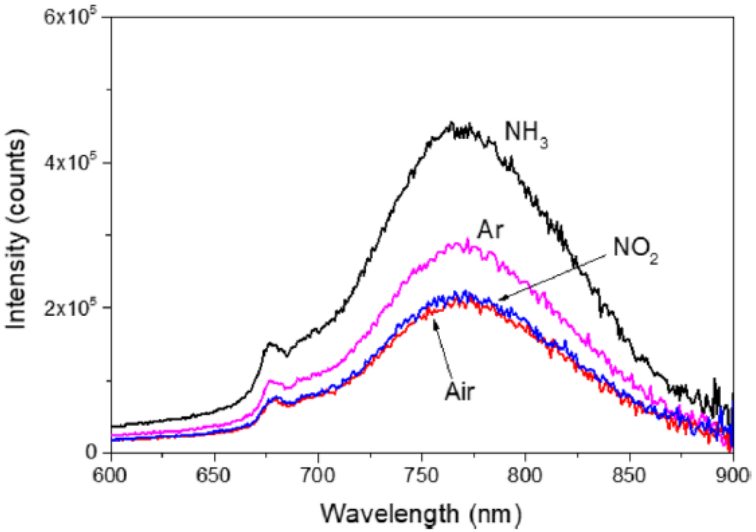
Air quality monitoring NO_2/NH_3 Chemoresistive/ optical



Chemoresistive @RT



Optical (PL @ RT)



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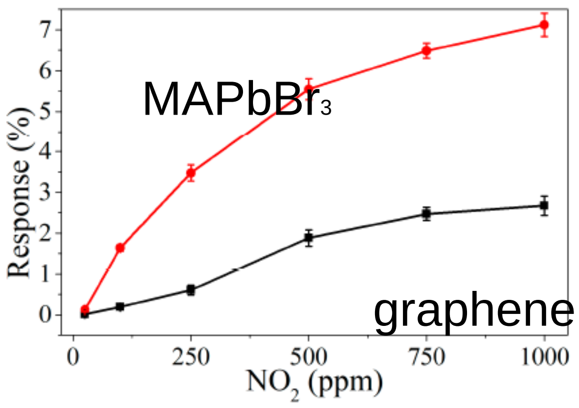
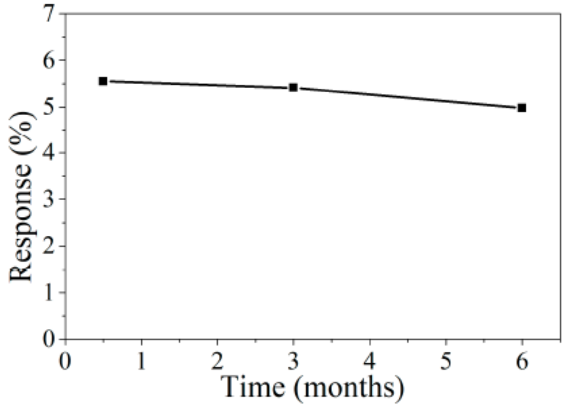
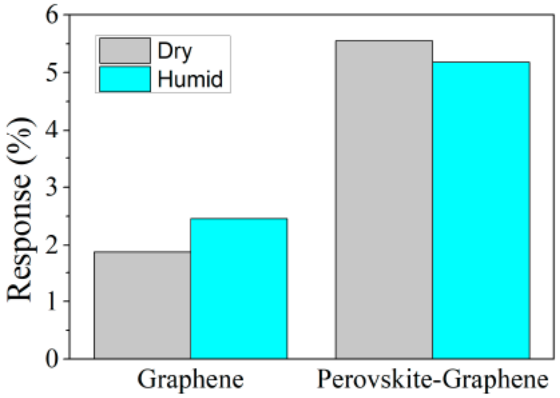
Air quality monitoring $NO_2/NH_3/H_2S$ Chemoresistive



(a)

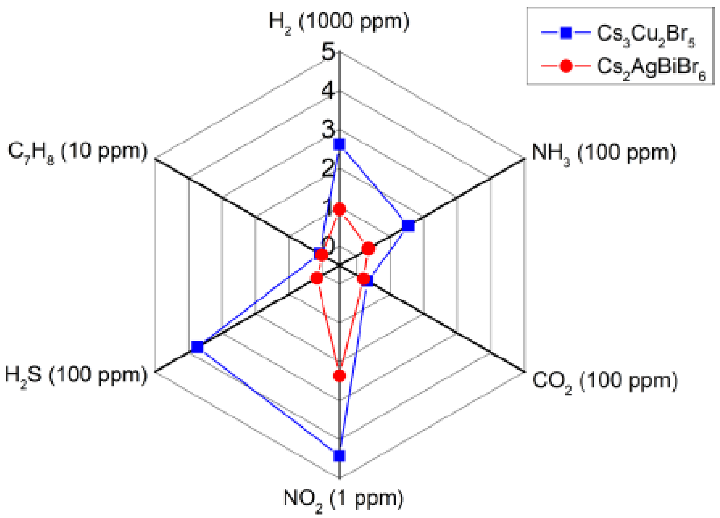


(b)



target gas	sample	sensitivity[a]	LOD	LOQ
NO_2	$Cs_3Cu_2Br_5$@graphene	7.57	8.5	28.2
	$Cs_2AgBiBr_6$@graphene	4.04	26.3	87.8
H_2	$Cs_3Cu_2Br_5$@graphene	3.08	24.4	81.5
	$Cs_2AgBiBr_6$@graphene	1.06	41.4	137.9
NH_3	$Cs_3Cu_2Br_5$@graphene	21.39	13.95	46.49
	$Cs_2AgBiBr_6$@graphene	1.24	43.52	145.08
H_2S	$Cs_3Cu_2Br_5$@graphene	75.44	13.6	45.3
	$Cs_2AgBiBr_6$@graphene	0.21	52.4	174.7

[a]Sensitivity expressed as % × ppb^{-1} for NO_2 and % × ppm^{-1} for H_2, NH_3, and H_2S gases (sensitivity is given by the slope of the calibration curves; the LOD and LOQ are expressed in ppb for NO_2 and ppm for H_2, NH_3, and H_2S).



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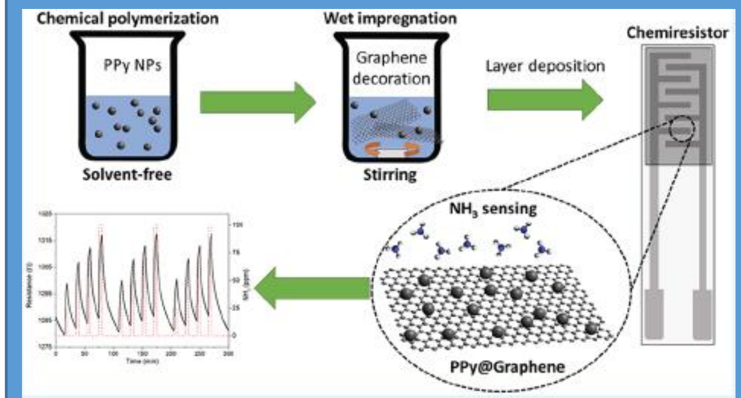
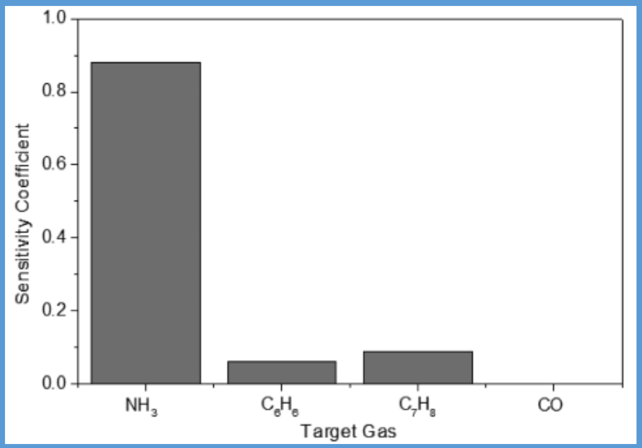
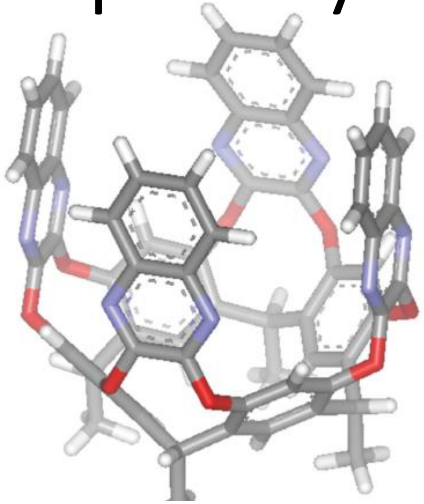


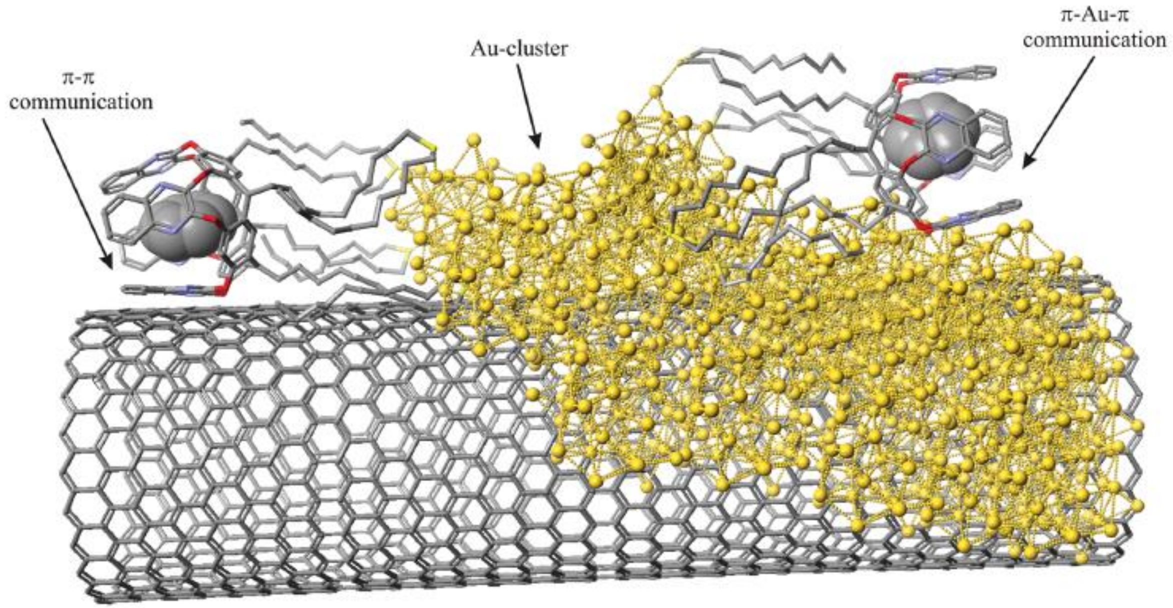


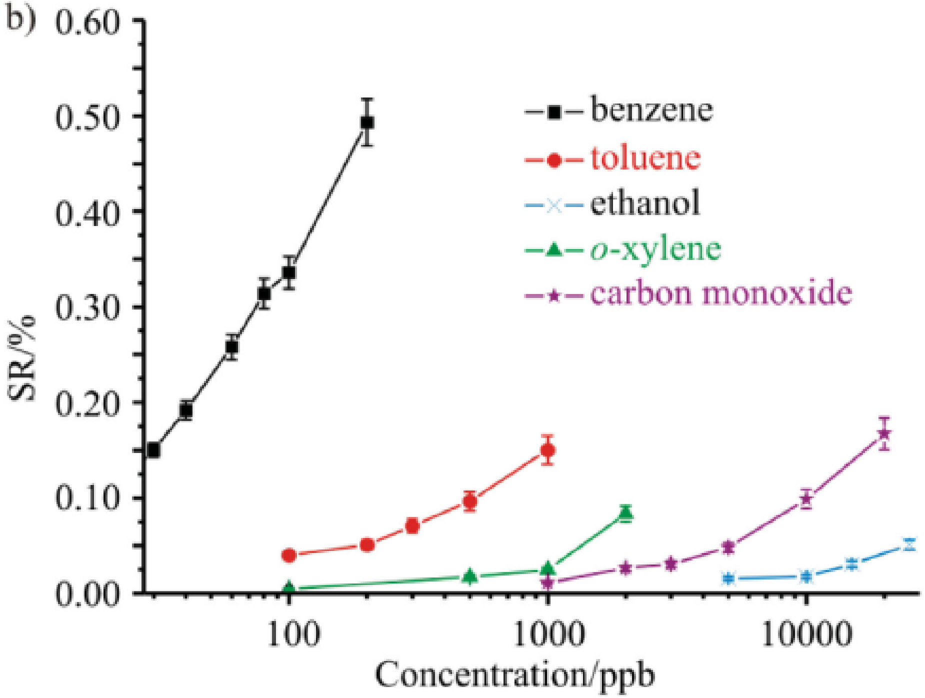
ACS Appl. Mater. Interfaces 2021, 13, 40909

Air quality monitoring C_6H_6 Chemoresistive



SAM of quinoxaline-walled thioether-legged cavitand





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Outlook

- Nanomaterials show interesting properties for trace detection: Higher response at moderate operating temperatures, even at R.T.
- There is a need for cost-effective, scalable production methods that retain the essential properties of such materials
- Functionalisation (surface engineering) is the way to increase sensitivity and minimize unwanted cross-sensitivity effects
- In some cases advancements towards molecular recognition have been achieved
- The need for separation and/ or pre-concentration cannot be ruled out for applications in which detection limits are low and the cost of false positives/negatives is high
- Integration in transducing substrates is a key issue

Thank you for your attention!