Carbon nanomaterials functionalized with macrocyclic compounds for sensing vapours of aromatic VOCs

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Abstract

Here we review the approach of employing macrocyclic compounds grafted to carbon nanomaterials for developing gas sensors and sensor systems, with special emphasis in the results achieved for selectively detecting BTEX compounds. In such an approach, carbon nanomaterials act as a transducing element able to collect and transport electronic charge efficiently, while the grafted macrocyclic compounds act as selective molecular receptors, implementing a receptor function. Strong and weak points of this strategy are identified and discussed. Despite a few weaknesses that still need to be addressed, these hybrid nanomaterials show good potential for being integrated in a new generation of inexpensive, hand-held analysers or wearable detectors for BTEX compounds with potential applications in workplace safety or environment monitoring

Keywords: BTEX; aromatic VOCs; gas sensor; carbon nanomaterials; macrocycle; cavitands; cyclodextrins; calixarenes.

1. Introduction

BTEX is a term describing a set of chemicals closely related to benzene. This set consists of benzene itself, toluene (i.e., methyl benzene), ethylbenzene and xylenes. BTEX are aromatic volatile organic compounds (VOCs). They are colourless, sweet-smelling liquids under normal temperature and pressure. However, their low vapor pressures imply that they can evaporate easily.

There are natural sources of BTEX compounds. For example, these appear in gas emissions from volcanoes and forest fires, are present in crude and can be found near natural gas and petroleum deposits. However, the main emissions of BTEX into environment are of anthropogenic nature. Primary releases of these compounds occur through emissions from combustion engines, mostly from vehicles, but also from aircraft and petroleum coke ovens. Incidentally, BTEX are also found in the smoke of cigarettes. Petrochemical industry is one of the main emission sources and BTEX compounds are among the most abundantly produced chemicals in the world. For instance, these compounds are created or used during the processing of petroleum products and the manufacturing of many chemical products such as paints, lacquers, thinners, solvents, adhesives or inks. The manufacturing of rubber and plastics, cosmetics and pharmaceutical products is also a source of BTEX.

Even though BTEX can be briefly bound to soils and sediments or be spilled in sea water, most releases eventually end up in the atmosphere (e.g. in land reclamation), where they may react with other pollutants and contribute to the formation of photochemical smog. As any other VOCs, BTEX compounds play also a role in the formation of ground level ozone which can damage crops and exacerbate respiratory conditions in humans (e.g. asthma).

The most common human exposure to BTEX compounds results from contaminated air breathing, particularly in areas of heavy motor vehicle traffic, petrol stations, motor vehicle repair stations, roadside works and through cigarette smoke. Exposure to BTEX at normal environmental concentrations, and even to higher concentrations over a short period of time, is unlikely to cause significant health damage. However long-term exposure to higher concentrations (usually only experienced in occupational settings) can be toxic to liver, kidneys, central nervous system and eyes. Table 1 shows exposure levels for BTEX compounds established by US safety and health administrations.

Table 1. Exposure levels to BTEX compounds as indicated by OSHA[1] and NIOSH[2], Jan. 2018.

Compound	**TWA[3]**	**STEL[4]**	**IDLH[5]**
Benzene	1 ppm	5 ppm	500 ppm
Toluene	100 ppm	150 ppm	500 ppm
Ethylbenzene	100 ppm	125 ppm	800 ppm
Xylenes	100 ppm	150 ppm	900 ppm

[1] OSHA: Occupational Safety and Health Administration (USA)

[2]NIOSH: The National Institute for Occupational Safety and Health (USA)

[3]TWA: time-weighted average. Employer shall assure that no employee is exposed to an airborne concentration of the pollutant in excess of the TWA value as an 8-hour time-weighted average.

[4]STEL: short-term exposure limit. The employer shall assure that no employee is exposed to an airborne concentration of the pollutant in excess of the STEL value as averaged over any 15 minutes period.

[5]IDLH: immediately dangerous to life and health exposure level.

BTEX compounds feature similar structures but quite different toxicological properties. Indeed, benzene is listed among the most harmful VOCs because it is recognized as a human carcinogen by the US Environmental Protection Agency and by the European Commission[1,2]. Long term exposures to relatively low concentrations of benzene over months or years lead to severe hemotoxic effects such as aplastic anemia and pancytopenia and to acute non-lymphocytic leukemia[3-7]. According to the Directive 2008/50/EC of the European Parliament and of the Council of May 2008, the limit value for the annual average exposure to benzene is 5 μg m^{-3} (1.6 ppb)[8].

Nowadays, several methods for detecting traces of BTEX in air are in use. Most of them involve pumping of the sample and subsequent analysis by employing colorimetric detector tubes or gas chromatography (GC-FID, GC-MS). These methods are bulky, expensive and do not allow implementation for a continuous monitoring of BTEX traces. In the last few years, pre-concentration methods and GC equipment have been improved in terms of miniaturization and with a limit of detection (LOD) reaching the ppb level for benzene[9-11]. However, such systems are still limited by their long response time, high power consumption and high cost. Alternatively, the use of portable photoionization detectors (PID) has been reported as well, but PID devices are not selective and give a total reading for VOCs. The only option to make PID more selective for BTEX in general and benzene in particular is to utilize a single-use, disposable and rather expensive filter at the inlet port of the device that would result in a dramatic cost increase of running benzene measurements. The industries in which normal activity may result in active exposure of their workers to BTEX compounds (specially to benzene), would clearly benefit from affordable, portable, highly sensitive and selective detectors able to run continuous measurements.

During the last decades, a great effort has been done aiming to investigate different strategies to improve the selectivity of chemical sensors. To reach that milestone, sensors have been equipped with bioreceptors employing specific antigen-antibody-type binding interactions (inspired by nature) where the size, the shape and the charge allow the selective detection of biological target species like as proteins, bacteria, viruses and DNA. Additionally, this new generation of sensors mainly operates in aqueous media where the energy cost for the molecular recognition is reduced due to the water molecules that temporally "occupy" the bioreceptor prior the recognition. For gaseous species, the recognition is different and non-specific interactions dominate their affinity with the medium. Scientific groups have further exploited the possibility to synthesize molecular receptors that could eventually mimic the specificity of biological receptors reproducing the concept of binding site complementarity and shape recognition. Macrocyclic compounds such as cyclodextrins (CDs), calixarenes and cavitands have been widely employed due to their common presence of cavities with molecular dimensions, which can act as molecular receptors.

In the last years many research groups have reported the development of sensors employing carbon nanomaterials such as carbon black, carbon nanofibers, carbon nanotubes and graphene[12]. These materials are very attractive because they allow for developing simple, chemoresistive devices operating at low temperatures, even at room temperature. Even though carbon nanomaterials are particularly sensitive to their local chemical environment of the gas phase, their functionalization seems essential if the aim is to selectively detect a few target gases or vapours. Indeed, different approaches have been reported for functionalizing carbon nanomaterials in view of tailoring their gas sensing properties. Most of these functionalization strategies consist of creating controlled defects, decorating the outer sidewalls of nanofibers, nanotubes or the surface of graphene with metal or metal oxide nanoparticles, grafting functional groups such as carbonyl, carboxyl or amine groups or more complex molecules such as macrocyclic compounds[13]. Here we will review the approach of employing macrocyclic compounds grafted to carbon nanomaterials for developing gas sensors and sensor systems, with special emphasis in the results achieved for selectively detecting BTEX compounds. In such an approach carbon nanomaterials play the role of transducing element (able to collect and transport efficiently electronic charge) and the grafted macrocyclic compounds are the selective molecular receptors, i.e. implement a receptor function in the gas sensor.

2. Cyclodextrins

Cyclodextrins are macrocyclic oligosaccharides which contain a hydrophobic cavity presenting hydroxyl groups at both rims that make them water soluble. The most common CDs consist of six, seven or eight α-D-glucopyranose units conjoined through α-(1→4)-glycosidic bonds and are respectively named *α*-, *β*-, *γ*-CDs. They are, therefore, suitable to capture hydrophobic guests in aqueous media, where numerous host-guest complexes have been reported. Nevertheless, in the solid-gas interface, the selectivity is mainly driven by London dispersion interactions, size and shape fit. Selectivity can be increased by modifying the chemical groups on both rims. Table 2 summarizes some applications of modified CDs in gas sensing.

Table 2. Examples of modified cyclodextrins with their gas sensing properties

Modified CD	Transducer	Selective to	Interferent(s)	Limit of detection	Ref.
2,6-Per-O-(*t*-Butyl-dimethylsilyl)-*a*-CD	QCM (quartz crystal microbalance)	Benzene	Methane, propane, butane, pentane, ethyne, ammonia, nitrobenzene, toluene	0.088 mg·dm^{-3} in air	[14]
Polyaniline-*β*-CD Composite	Resistive	Toluene	Benzene	N/C	[15]
Potassium iodide and *α*-CD	Optical	Ozone	Humidity	Several ppb in air	[16]
γ-CD and potassium ions	Gas sorption analyser	Formaldehyde	N/C	N/C	[17]

Only few examples of carbon nanomaterials functionalized with CDs have been reported so far. Duarte and co-workers[18] developed a conductive polymer nanocomposite (CPC) chemoresistor based on linear and branched polyamides synthesized from bifunctional and heptafunctional *β*-CD monomers and (Z) octadec-9-enedioic-*N*-hydroxysuccinimide ester bearing a multiwalled carbon nanotube (MWCNT) conducting architecture. The latter sensor was formed through a spray deposition of the CNTs and the CD polymers (dispersed separately in an organic solvent) layer by layer on interdigitated ceramic substrate. The same group has demonstrated the ability of CPC based gas sensor to reversibly detect polar and non-polar VOCs with an expected limit of detection to lay in the low ppb range. Furthermore, polyamide synthesized from *β*-CD$(NH_2)_2(OH)_{19}$ is shown to be selective towards propanol in nitrogen gas carrier. This happens due to the strong hydrophilic character that the 19 hydroxyl moieties offer to the compound making it able to generate many hydrogen bonds with polar protic solvents.

Employing the same principle, Nag and co-workers[19] developed a quantum resistive chemical vapour sensor based on an array of *β*-CD functionalized reduced graphene oxide (RGO). Pyrene adamantane (PYAD) was used to non-covalently tether the CDs to the RGO by self-assembly. This innovative connection allows the π-π stacking of pyrene with graphene in one end and the inclusion of adamantane in CD cavity in the other end, preserving the accessibility of the analytes to functional sites (route a). They also compared a parallel route (route b) by simply non-covalently binding perbenzylated CD with RGO (RGO@PBCD).

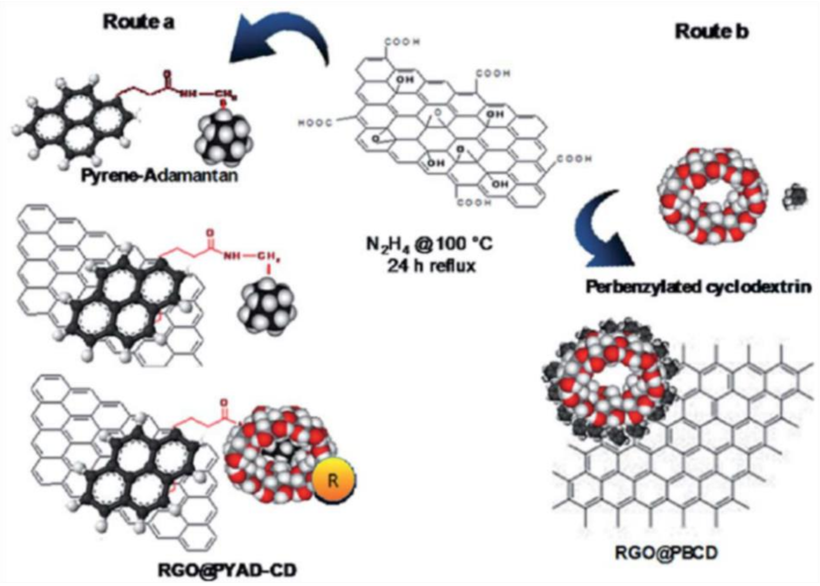

Figure 1. Two routes synthesis of functionalized CD to reduced graphene. Reproduced from [17], © Royal Society of Chemistry, 2014, with permission.

The CD modified graphene was sprayed layer by layer onto interdigitated electrodes controlling the resistance of the device. The authors demonstrated the selective detection of benzene as low as 400 ppb with a signal-to-noise ratio of 88 with the RGO@PBCD without sensitivity to humidity in nitrogen carrier gas.

Following the strategy of employing a sensor array rather than a single sensor, Pi-Guey Su and co-workers[20] designed an array of quartz crystal microbalance (QCM) sensors allowing the differentiation of NH_3 (1000-5000 ppm), CO (1500-7500 ppm) and NO_2 (10-50 ppm) from their tertiary mixture. This discrimination was possible by treating the data of the sensors by principal component analysis (PCA). Graphene oxide (GO), *β*-CD functionalised GO and *N*-substituted pyrrole derivative-based films were used as sensitive layers for gas sensing. The *β*-CD was non-covalently attached to the GO through π-π stacking by simply mixing them. Each material was deposited on the QCM by spin coating.

3. Calixarenes and derivatives

Calixarenes are similar to the cyclodextrins' cyclic structure and have generated interest over the last century because of their easy and tuneable synthesis as macrocyclic molecular receptors. They are composed of phenolic units joined at *meta* position through methylene bridges. Calix[*n*]arenes are preferably synthesized with *n*= 4, 6, 8 (building blocks) units. Hence, they possess variable cavity dimension with the possibility to functionalize their upper and/or lower rim to tailor their affinity with a target guest molecule through different non-covalent interactions such as π-π stacking, cation-π and CH-π interaction and hydrogen bonding.

A review on calixarene based materials for gas sensing application written by Chilin Zou and co-workers highlights the new development in the field of monitoring and detection of hazardous gases[21]. Table 3 shows some examples of gas sensing applications employing modified calixarenes.

Table 3. Modified calixarenes with their gas sensing properties

Modified calixarene	**Transducer**	**Selective to**	**Interferent(s)**	**Limit of detection**	**Ref.**
5,11,17,23-Tetrakis(*tert*-butyl)-25-carboxymethoxy-26,27,28-tris(ethoxycarbonylmethoxy)calix[4]arene polymer	Optical (colorimetric)	NO_2/N_2O_4	N/C	N/C	[22]
calix[4]arenes derivatives	QCM	N/C	Chloroform, benzene, toluene, and ethanol	N/C	[23]
25,27-(Dipropylmorpholinoacetamido)-26,28-dihydroxycalix[4]arene	QCM, surface plasmon resonance (SPR)	N/C	Dichloromethane, chloroform, benzene, and toluene	1.48 ppm for dichloromethane in air	[24]
calix[4]azacrown	Luminescence	Tetrahydrofuran	Acetone, methanol, dichloromethane, ethyl acetate, cyclohexane, *n*-hexane, benzene,	N/C	[25]

			toluene, trifluoroacetic acide and petroleum ether		
calix[4]arenes derivatives	QCM	Methylene chloride	Acetone, acetonitrile, carbon tetrachloride, chloroform, N,N-dimethylformamide, 1,4 dioxane, ethanol, ethyl acetate, dioxane, xylene, toluene, methanol, *n*-hexane, water	54.1 ppm in air	[26]

Despite the numerous examples that can be found in the literature about the ability of calixarenes for trapping gas molecules with high affinity, only one work on calixarene functionalized carbon nanomaterials for gas sensing has been reported recently. Baysak and co-workers[27] report the use of SWCNTs, the side-walls of which were non-covalently functionalized with pyrene bearing calix[4]pyrrole. Sensors were implemented as chemoresistors by coating a filter paper with calixarene functionalized SWCNTs contacted with two planar electrodes. Fast response and higher affinity for acetone (20 to 500 ppm) compared to other VOCs were reported. Nevertheless, recent reports, where the calixarene is attached to the carbon nanomaterial via π-π stacking[28-30] (including pyrene modification of the calixarene) or covalent bonding[31,32] or incorporated in a composite[33], have demonstrated selective recognition of target analytes, but in aqueous media only.

4. Deep cavitands

Derived from resorcinarene scaffolds, deep cavitands have been widely studied for their synthetic versatility and selective complexation with target molecules. Notably, deep cavitands can be designed by respectively tuning their bridging group connected to the phenolic moieties of the resorcinarene. As a result, it is possible to control the dimensions, the shape and the binding groups of the formed cavity.

Cram and co-workers were the pioneers to study cavitands as potential molecular receptors via the host-guest strategy[34]. Dalcanale and co-workers did a subsequent work by modifying the bridging group of the resorcinarene in order to monitor VOCs in air. They have recently published a review highlighting their progress[35]. Briefly, in their last study they found out that rigidifying the cavity of the quinoxaline cavitand (QxCav) introducing four ethylenedioxy bridges at the upper rim (EtQxBox) improves the interaction with aromatic guests compared to the conformational mechanism of the QxCav[36].

This subtle modification allows additional interaction with toluene, ethylbenzene and xylene guest than with benzene due to the upper rim that is too far to interact with benzene. They further implemented the EtQxBox as preconcentrator coupled to miniaturized photoionization detector and by using a smart temperature programme, benzene is selectively desorbed and its LOD reaching the ppb level. This approach is illustrated in Figure 2.

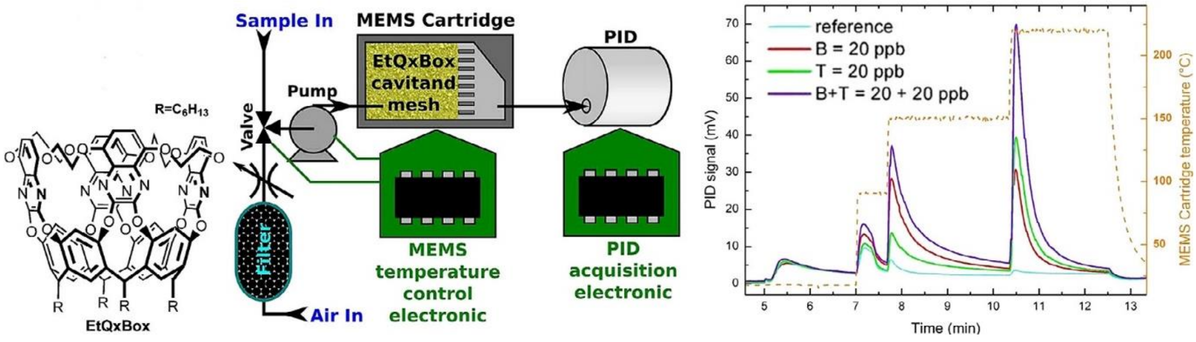

Figure 2. Representation of EtQxBox cavitand structure (on the left) with a scheme of the benzene monitoring device (center) and typical responses of the PID detector to a temperature ramp. Reproduced from [33], © American Chemical Society, 2013, with permission.

Recently, Llobet and co-workers studied the possibility to couple the promising gas sensing properties of cavitands with MWCNTs as resistive gas sensors[37]. They first grafted gold nanoparticles on oxygen plasma treated MWCNTs where the thioether-legged-QxCav is further tethered on gold by a self-assembled monolayer approach (QxCav-Au-MWCNTs). This functionalization process is illustrated in the upper part of Figure 3.

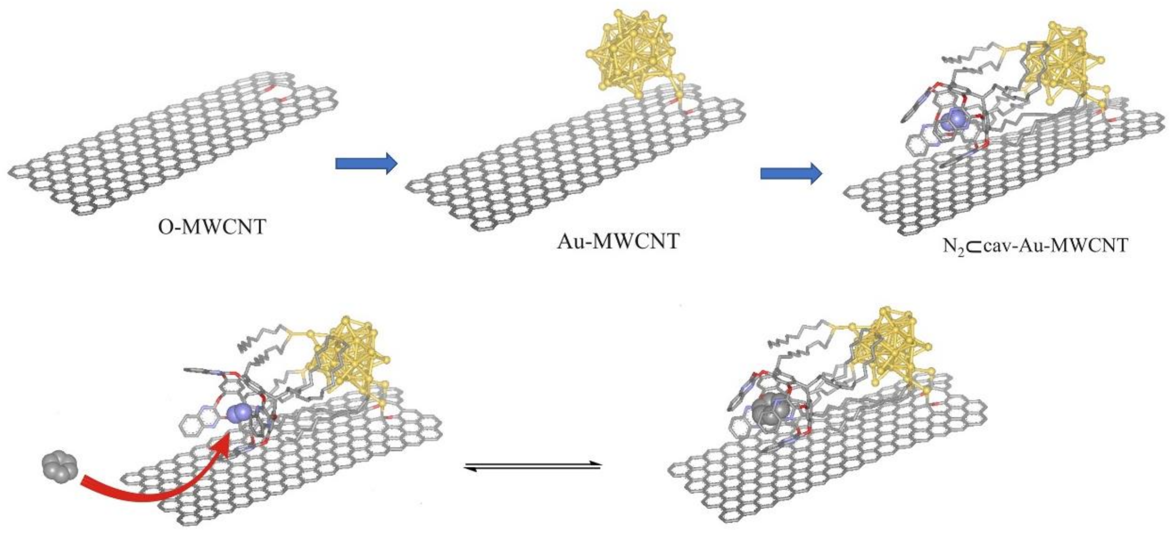

Figure 3. (top) Fabrication scheme of the QxCav-Au-MWCNTs hybrid nanomaterial where Au-RF-sputtering is followed by the self-assembly of thioether legged QxCav monolayer on the Au-NP surface. (bottom) Schematic representation of the sensing event of a benzene molecule. Adapted from [37], © John Wiley and Sons, 2015, with permission.

Upon a sensing event, a charge transfer is observed between the cavitand and the Au-MWCNTs changing the general conductivity of the system. Figure 4 illustrates several response and recovery cycles for the sensors to increasing benzene concentrations in the ppb range. The sensor showed clearly higher sensitivity for benzene than for other aromatic and non-aromatic VOCs, with a limit of detection of 600 ppt in dry air. Nevertheless, a non-negligible cross sensitivity with NO_2 and ambient humidity was observed. However, this can be overcome, at least partially, by adding a sensor employing bare Au-MWCNTs, which are extremely sensitive to NO_2 and poorly responsive to benzene. The use of a filter at the inlet of the detector would help removing ambient moisture and thus the undesired cross-sensitivity effect of humidity.

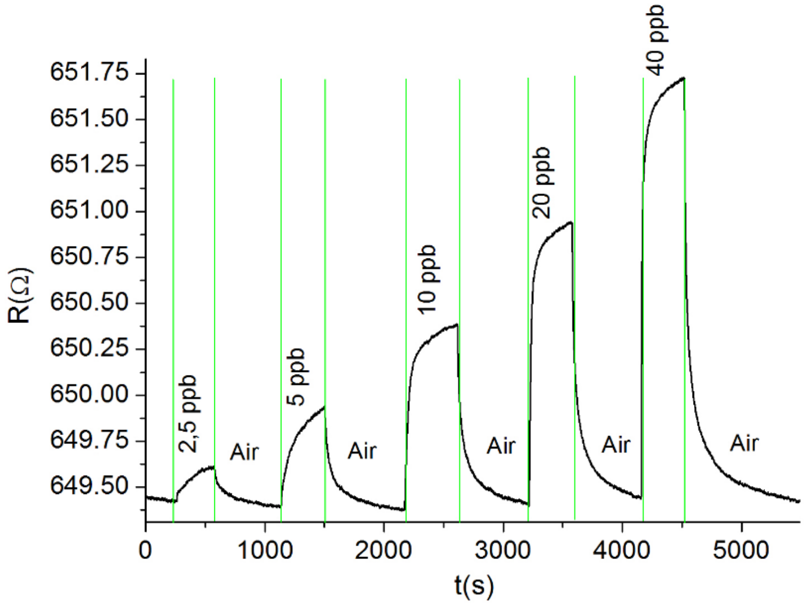

Figure 4. Response and recovery cycles to successively increasing concentrations of benzene for a chemoresistive sensor employing a QxCav-Au-MWCNTs hybrid nanomaterial. Adapted from [37], © John Wiley and Sons, 2015, with permission.

5. Conclusions

The covalent or non-covalent functionalization of carbon nanomaterials with macrocycles opens fascinating opportunities for advancing towards molecular recognition in the gas phase. Cyclodextrins, calixarenes and deep cavitands have been employed because they present cavities with molecular dimensions, which can act as molecular receptors. Nowadays, it is possible to finely control the dimensions, the shape and the binding groups of the formed cavity. In other words, macrocycles are becoming engineered scaffolds that point towards mimicking the specificity of biological receptors, reproducing the concept of binding site complementarity and shape recognition.

In the development of gas sensors employing macrocycles, two main approaches can be identified. On the one hand, macrocycle compounds are employed to functionalize carbon nanomaterials in view of obtaining new functional adsorbent materials, i.e. more efficient and with improved selectivity. These adsorbents are then employed as coatings in gravimetric transducers or in the miniaturized pre-concentration units of gas detectors. On the other hand, macrocycle-functionalized carbon nanomaterials are also used in simple, chemiresistive gas sensors in which the carbon nanomaterial is merely an efficient means of conducting free charge carriers and the receptor function is played by the macrocycles attached.

The techniques employed in the synthesis of macrocycles and in the functionalization of carbon nanomaterials are well-known and allow for implementing solution processing of gas sensitive devices. This implies that such techniques are suitable for the mass production of both hybrid nanomaterials and sensors at low production costs, allowing cost-effective commercialization.

Some of the reported hybrid nanomaterials show remarkable sensitivity and selectivity to aromatic VOCs and, in particular, quinoxaline-bridged cavitand-functionalized MWCNT sensors show very high sensitivity toward low levels of benzene in dry air (i.e., experimentally tested down to 2.5 ppb), with a theoretical lower detection limit of 600 ppt. In addition, both detection and baseline recovery are run at room temperature, which implies that sensors operate at low power consumption.

However, sensors still suffer from cross-sensitivity issues, namely to ambient moisture and to oxidizing species such as ozone or nitrogen dioxide. Some solutions exist already to tackle such problems, like using filters for trapping water at the inlet of the detector system or using an array of sensors with partial selectivity and chemometrics. However, these solutions are sub-optimal because filters are cumbersome, may alter the profile of VOCs or become saturated and, using sensor arrays and pattern recognition adds complexity, makes calibration and re-calibration more difficult and increases overall cost. Should these cross-sensitivity issues be ameliorated by further increasing the performance of functional materials, macrocyclic compound functionalised carbon nanomaterials may soon be integrated in a new generation of inexpensive, hand-held analysers or wearable detectors for BTEX compounds with potential applications in workplace safety or environment monitoring.

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