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Hybrid and 2D nanomaterials

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Abstract: In order to still improve the performances of chemical sensors, numerous hybrid materials were synthesized that combined at least two types of materials reported in the three previous chapters. We will distinguish materials combining macrocyclic molecules with polymers, those in which these molecules are associated to carbonaceous materials, mainly carbon nanotubes (CNTs) and graphene, and organic-inorganic hybrid materials. In this chapter, we will also include 2D materials introduced recently as sensing materials after the huge development of graphene and graphene oxide-based materials.

Key Words

Macrocycles, polymers, carbon nanotubes, graphene, graphene oxide, hybrid materials, 2D materials, synthesis

5.1 Macrocycle - polymer hybrid materials

In conductometric and optical sensors, all the molecules used in organic electronics can be potentially used as sensing materials. They are conjugated molecules, among them macrocyclic molecules, such as porphyrins and phthalocyanines, pentacene, perylene derivatives, oligomers and conjugated polymers. Additionally, with other transducers, as acoustic and optical transducers, very different types of molecules can be used. Among

macrocyclic molecules, the most important families used in chemosensing are phthalocyanines and porphyrins. They exist as monomacrocyclic molecules, with a weak conductivity, but also as double or triple decker complexes, mainly with rare earth metal ions as coordination centers. The latter are highly more conductive. From the first report on phthalocyanines as sensing materials by Bott and Jones [1], lots of sensor studies dealt with phthalocyanine or porphyrin-containing sensing materials. They were used with different transduction modes, but mainly conductometric transducers, namely resistors, field-effect transistors (FET) and heterojunctions [2]. They allowed detecting strong oxidizing agents as ozone and nitrogen dioxide in the ppb range and less redox active gases as ammonia in the ppm range as well.

A useful approach to overcome some of the physical limitations of phthalocyanines, including their poor processability and their too high crystallinity, involves combining these materials with non-conducting polymers, such as poly(vinylalcohol) (PVA), polystyrene (PS), poly(methyl methacrylate) (PMMA) [3]. Phthalocyanines were incorporated in the polymer by dissolution in a common solvent and deposited by solution processing, namely solvent-cast or spin-coating technics. Even though they seem very basic technics, if the deposition conditions are well controlled, such as the concentration of the solution, the acceleration, the speed and the rotation time, spin-coating can lead to highly reproducible films, in thickness and homogeneity, as exemplified by $\text{Cu}(\text{tBu})_4\text{Pc}$ /polystyrene films [4].

Due to their optical properties, porphyrins have been used in optical sensors to detect ammonia and VOCs. Incorporated in polymers, in particular silicone elastomers and thermoplastics, like ethyl cellulose, polyvinyl chloride (PVC) and nitrocellulose, films were obtained and revealed to be able to detect NH_3 down to about 1 ppm in 10 s, with a good reversibility, by measurement of the absorbance in the visible region [5]. The stability of the films was very short in silicone elastomers, due to photochemical oxidation of the ring and to their reaction with traces of ozone, currently present at 10-30 ppb indoors. The highest stability was observed for PVC modified by a plasticiser, but the devices remain sensitive to relative humidity variations.

A particular case in the porphyrins series is this of indium octaethylporphyrin complex (HOInOEP), which exhibits a dimer-monomer equilibrium in the presence of a donating VOC capable to coordinate the indium(III) cation (eq. 1).

A red shift of the maximum wavelength of the Soret band, from 390 nm in the dimer, by more than 15 nm, was observed in the monomer [6]. Thus butylamine, the more lipophilic tested amine was detected at sub ppm concentrations whereas the less lipophilic amine, namely NH_3 , was detected down to 10 ppm.

The hydrophilicity of sensing materials can be adjusted by the composition of the polymer. Thus the acrylic acid-acrylamide (70/30 in mol/mol) co-polymer exhibits an electrical resistance highly stable, up to 80% of relative humidity (RH), whereas this of pure polyacrylic acid decreases rapidly at RH higher than 50% [7]. When a monophthalocyanine is mixed with an insulating polymer, the resulting hybrid material is too resistive for conductometric measurements, but can be used with other transduction modes. Thus the hydroxy gallium phthalocyanine, HOGaPc, was incorporated in cellulose, via its soluble trimethylsilylated form, leading to an amorphous material (Fig. 5.1) [8]. This hybrid material showed a higher sensitivity to ozone (at 100 ppb) than the pure crystalline HOGaPc films, with a better reversibility, as measured by the Kelvin-Zisman vibrating capacitor probe.

Fig. 5.1 AFM images of HOGaPc and Cellulose-HOGaPc mixture as deposited on ITO substrates, and view of the two components.

A particular case is that of lutetium bisphthalocyanine, LuPc_2 . Because of its high conductivity, it can be incorporated in an insulating polymer while remaining suitable for

conductometric measurements. Thus resistors made from LuPc₂-polymethylmethacrylate (PMMA) blends deposited by spin-coating were used to detect ozone in the ppb range (Fig. 5.2) [9]. The best results were obtained with 80/20 % (w/w) LuPc₂/PMMA blends.

Fig. 5.2 Schematic view of the radical anion Pc^{•-}, LuPc₂ and PMMA.

It allows keeping homogeneous conducting films, with a high sensitivity to redox active species due to the radical nature of LuPc₂, but with smaller crystallinity than with pure LuPc₂ films. This makes easier the diffusion of gaseous molecules inside the sensing material.

On the contrary, the association of poor conducting molecules like monophthalocyanines with polymers must be carried out with conducting polymers, if we want to keep sensing materials suitable for conductometric or electrochemical measurements. In addition, it is known that the response of conducting polymers to gases can be modulated by the initial conductivity of the sensing polymer and by the nature of counter anions, as shown with polypyrrole for the detection of NH₃ [10]. All phthalocyanine-polymer hybrid materials showed enhanced sensitivity to gases relative to pure conducting polymers, as mentioned by Hatchett and Josowicz in their review devoted to composites of conducting polymers as sensing materials [3]. Thus hybrid materials combining polypyrrole (PPy) with an ionic phthalocyanine, namely a sulfonated cobalt phthalocyanine (s-CoPc), as counteranion, were electrosynthesized at the surface of Pt electrodes [11]. The small interelectrode distance, typically 5 μm, allowed the polymer growing from one electrode to the other one during the electrodeposition, leading to a resistor suitable for conductometric sensing. It was shown that ionic macrocycles modify the morphology of films, with smaller

crystallites and lower roughness compared to the materials obtained with rather small anions, like perchlorate or naphthalene sulfonate, as shown by optical topomicroscopy images (Fig. 5.3) [12].

Fig. 5.3 Schematic view of the coulombic interactions between the sulfonated CoPc and polypyrrole and an optical topomicroscopy image of an electrodeposited film of the hybrid material.

s-CoPc provided hydrophilic properties to the blend, and it induces conductivity variation upon humidity, but only at very low relative humidity (RH) levels, between 0 and 20% RH. At higher RH, the conductivity of PPy/s-CoPc varied only slightly (Fig. 5.4 left). Then, the response to ammonia (NH_3), in the range 20-100 ppm remained almost constant in a broad range of RH (20-80%), whereas the response of PPy synthesized with ClO_4^- as counterions exhibited a stronger variation at high RH values. The interference between NH_3 and H_2O on the response of conjugated polymers can also be modified by their association in blends with non conducting polymers, like PMMS and PS [13].

Fig. 5.4 Response to ammonia of a PPy/s-CoPc hybrid material – based resistor (left) and of a LuPc₂/Cu(F₁₆Pc) Molecular Semiconductor – Doped Insulator (MSDI) heterojunction (right), with exposure/recovery cycles (1 min / 4 min), under various relative humidity levels.

When chemical sensors are used in real environment, the effect of humidity has to be considered. Water was believed to act as donor species on molecular materials, even in the presence of rather strong donor adsorbates, such as ammonia [14]. As a result, water is expected to induce a decrease of conductivity of LuPc₂. Thus the effects of NH₃ and H₂O should be qualitatively the same. It seems the case in LuPc₂ resistors, even though the water content changes the sensing feature versus NH₃ [15]. A competition phenomenon in the adsorption-desorption process occurs, besides the contribution coming from the electron-donating nature of both the molecular material and gases, which makes the sensor response dependent on the applied experimental protocol, in particular the gas flow and the duration of exposure periods. However, NH₃ and H₂O molecules can induce opposite effects.

Thus n-type Molecular Semiconductor – Doped Insulator heterojunctions (MSDIs), which combine a low conducting sub-layer, e.g. Cu(F₁₆Pc), with a high conducting top layer, such as LuPc₂, exhibit a conductivity decrease under water vapors but an increase under ammonia (Fig. 5.4 right) [2]. This means that, in n-MSDIs, NH₃ and H₂O do not act in the same way. Water molecules act as traps for positive charge carriers in the highly conductive p-type top layer, leading to a conductivity decrease of this material, due to a mobility decrease, but keeping constant the energy barrier at the interface between the two materials [16]. In the contrary, NH₃ molecules neutralize positive charge carriers by

electron transfer leading to a decrease of both the conductivity of the top layer and the energy barrier at the interface between the two materials. This second effect being the most important, it results in a current increase in the device, contrarily to what is observed for a resistor made from LuPc_2 , in which both NH_3 and H_2O molecules induce a current decrease. Organic semiconductor--based Schottky diodes were widely reported as gas sensors [17], but heterojunctions combining two molecular materials and used as gas sensors are very rare. Additionally to MSDIs, we can cite phthalocyanine--based p-n heterojunctions by Inta Muzikante et al [18], which behaves electrically as classical p-n diodes with an important rectification ratio between the forward and reverse currents. The highest relative response was observed in the inverse polarization regime.

Recently, a new device combining two materials, namely a double lateral heterojunction made from the electrodeposited poly(tetrafluoroaniline) covered by LuPc_2 , showed a high sensitivity to NH_3 , with a sub ppm LOD [19]. Another topic recently opens is that of ambipolar materials that can exhibit a positive or a negative response to a given gas depending on a targeting parameter [20,21].

5.2 Macrocycle - carbonaceous compound hybrid materials

Even though this part has to be considered as a complement of chapter 4, we can cite the reviews M. Prato et al. on covalent functionalization of single wall CNTs (SWCNTs) [22,23]. It includes amidation and esterification of oxidized SWCNTs in which oxygenated functions (carbonyl, carboxyl, hydroxyl, and so on ...) appear on opened tubes. However, more elaborate methods have been developed, including cycloadditions, electrophilic and nucleophilic or radical additions. Examples of chemical groups introduced in SWCNTs are given in Fig. 5.5. Electrochemical methods developed for electrodes modification, such as the diazonium salt route, has been applied on CNTs to generate a series of aromatic ring substituted materials.

Fig. 5.5 Schematic view of SWCNTs functionalized by (from left to right and top to bottom) alkyl, fluorine, pyrrolidine ring, carboxylic acid, ester, amine, amide and aromatic ring.

Because of their poor intrinsic solubility, often CNTs need to be associated with a surfactant or functionalized, if we want to prepare thin films by a solution processing technique [24]. The covalent grafting on CNTs is the first possibility, starting from carboxylic acid or amino modified CNTs, for examples, making them capable to react with amine or carboxylic acid groups-containing macrocycles, respectively [25,26], as illustrated on Fig. 5.6 with SWCNTs [27].

Fig. 5.6 View of ZnPc chemically linked to a SWCNT obtained by reaction of a carboxyphenoxy-substituted ZnPc with amine functionalized SWCNTs.

However, it highly modifies the electrical properties of materials. It is the reason why noncovalent functionalization is often preferred [28]. It occurs mainly via π - π interactions that preserve the structure and properties of CNTs. Thus apart from pyrene-containing molecules well-known to strongly interact with CNTs [29,30], extended aromatic π -system such as porphyrins and phthalocyanines are good candidates for such a functionalization. Another nice example of selectivity improvement of CNTs-based sensing materials is that of covalently attached quinoxaline-bridged resorcin[4]-arene cavitands to gold nanoparticles anchored on oxygen plasma treated carbon nanotubes [31]. A high selectivity towards benzene was obtained, compared to other studied VOCs, including toluene and xylene, with a response towards benzene about ten times higher than for toluene and 100 times than for *o*-xylene, at concentrations of 100 ppb for all the gases (Fig. 5.7). Keeping in mind the lower saturation vapor pressure of xylenes compared to benzene, leading to an easier adsorption at a given molar concentration in air of xylenes compared to benzene, most of BTEX sensors are more sensitive to xylenes. So, the present selectivity is a huge performance.

Fig. 5.7 Schematic view of a SWCNT decorated by a covalently attached quinoxaline-bridged resorcin[4]-arene cavitand to a gold nanoparticle anchored and the relative response of the resistor to VOCs (adapted from [31]). Credit: Permission requested from Wiley

The simplest way to incorporate phthalocyanines in carbonaceous materials-based electrodes is to mix a phthalocyanine in powder with carbon paste, resulting after

compression in a syringe in a working electrode that can be used in electrochemical sensors [32,33]. Such modified electrodes allowed to evaluate the bitterness in foods and beverages, giving rise to the so-called electronic tongues [32,34]. For AQM applications, phthalocyanines were also incorporated in carbon black and deposited as sensing films by spray cast, from suspensions containing both components. Thus a series of resistors, with non substituted MPc ($M = \text{Co, Cu, Fe, Sn, Zn}$) and substituted phthalocyanines, ZnPcR_4 ($R = \text{NO}_2, \text{tBu}$) and MPc(O-n-octyl)_8 ($M = \text{Cu, Zn}$) were exposed to ammonia and VOCs [35]. $\text{ZnPc(NO}_2)_4$ exhibited the highest response to NH_3 (30 ppm), whereas hybrid materials with phthalocyanines bearing alkoxy donating groups were unsensitive to NH_3 .

Since the non-covalent functionalization of CNTs preserves the electrical properties of nanotubes, hybrid materials were used as sensing materials associated with conductometric transducers, in particular by association with macrocyclic molecules. Thus M. Penza et al. showed that resistors made from MWCNTs films, grown by chemical vapor deposition technique onto alumina substrates previously coated with cobalt nanosized catalysts, and covered by metallotetraphenylporphyrins, MTPP ($M = \text{Mn, Zn}$), deposited by solvent cast, exhibit an increased sensitivity towards VOCs, compared to naked CNTs-based resistors [24]. The resistance of MTPP-modified CNTs were only slightly lower than this of pristine CNTs, but the response to gases was modified with a relative response higher for MnTPP towards all the tested VOCs, namely ethyl alcohol, ethylacetate, acetone and toluene, in the 30-100 ppm range, but triethylamine, for which the response order was $\text{CNTs} > \text{ZnTPP} \approx \text{MnTPP}$. The selectivity change from naked to modified CNTs was sufficient to discriminate between these VOCs, from a three sensors array, after a principal component annalysis. It was shown that the π - π interactions were strong enough to ensure the tacking of metalloporphyrins on CNTs [36].

As an example of phthalocyanine-containing hybrid materials, we can cite those prepared from a suspension of SWCNTs in DMF and a solution of a CoPc decorated with hexafluoroisopropanol substituents [37]. After sonication and stirring, the solution was filtered through a 0.22 μm teflon membrane, and the solid washed with DMF and rinsed with ethyl alcohol and dried. Thermogravimetric analyses allowed to determine that the hybrid material contained about one third of CoPc derivative in mass, equivalent to 1 CoPc molecule per 240 C atoms. These analyses show that the washing steps do not remove the

macrocycles out of the CNTs surface, indicating again strong interactions between the two components of the material. The sensor was prepared by drop-casting of a suspension of CoPc derivative-SWCNTs between gold electrodes. The resistance increased under exposition to dimethyl methylphosphonate (DMMP), a simulant of the sarin. The sensitivity was high and the detection at 0.5 ppm easy, with a good S/N ratio, indicating that the limit of detection was still better. More interesting is the selectivity to DMMP, compared to other VOCs, like methanol, dichloromethane, hexane and even water, due to specific strong hydrogen bonding between DMMP and hexafluoroisopropanol substituents beared by the phthalocyanine ring. Again, macrocyclic molecules bring processability and selectivity to CNTs while maintaining their electrical properties. SWCNTs decorated by tetratertibutyl copper phthalocyanine, octaethyl porphyrin (H₂OEP) and tetraphenylporphyrin (H₂TPP) by drop casting a dispersion of the materials were used to detect BTX [38]. It is believed that ethyl moieties of H₂OEP favors interaction with alkyl containing analytes, but the first effect of the functionalization is the increase of the specific surface area.

5.3 Polymer - carbonaceous compound hybrid materials

CNT – containing hybrid materials can be easily obtained by incorporating small percents of CNTs into a polymer, as exemplified by the incorporation of 1 % of MWCNTs in polyepichlorhydrin, increasing the sensitivity of SAW sensors towards toluene, compared to the pure polymer, but without modifying the detection of octane, because of π – π interactions [39]. Carboxylic acid functionalized MWCNTs were also used to decorate mono-dispersed PMMA microbeads (PMMAMB 2 μ m in diameter) leading to a segregated network of MWCNTs bridging PMMAMB, which showed a certain selectivity towards methanol compared to water, toluene and chloroform [40].

Even though covalent grafting on CNTs generally reduces their conductivity, it is not the case when conducting polymers are involved. Thus PPy was used as a cationic polyelectrolyte with SWCNTs functionalized with carboxylate groups [41]. This PPyⁿ⁺/SWCNT-CO₂ⁿ⁻ material was used as sensing material in QMB sensors towards 1-butanol, in the ppb range. However, the same material combined with SWCNTs bearing

tetraphenylporphyrin molecules (TPPH₂) exhibited an higher response to 1-butanol, both being highly more sensitive than porphyrin-substituted polypyrrole without CNTs (Fig. 5.8).

Fig. 5.8 Schematic view of a H₂TPPH₂-substituted polypyrrole in its partially oxidized form (left) and of the corresponding starting monomer (right).

PANI/MWCNT-based nanocomposite synthesized by in-situ chemical oxidative polymerization of aniline monomer with MWCNT-CO₂ⁿ⁻ showed a higher sensitivity to NH₃, with a sub ppm LOD. This response increased the RH value[42]. Starting from a suspension of SWCNTs and hexafluoroisopropanol substituted polythiophene, a percolative network was obtained as chemiresistive sensors for chemical warfare agents [43].

The electrodeposition of camphorsulfonic acid (CSA) doped PANI on carboxylated SWCNTs was optimized to minimize the sensitivity to humidity, down to no sensitivity at all for a particular polymer thickness, allowing the response to NH₃ to be almost unaffected by RH variations [44]. Without NH₃, it is believed that the resistance increase of carboxylated SWCNTs under H₂O is exactly compensated by the resistance decrease of CSA-doped PANI. This was explained by a proton exchange – assisted electronic conduction mechanism. However, it tends to also diminish the response to NH₃.

In the case of PANI electrodeposited on MWCNTs used to detect aromatic hydrocarbons, the increase of conductivity under the target species was attributed to dipole-dipole interactions that uncoil the polymer chain and decrease the interchain hopping distance for charge carriers [45].

5.4 Hybrid materials including inorganic materials

Inorganic materials can be associated with conducting polymers or organic semiconductors. The simplest way is the addition of metal oxides nanoparticles into a polymer matrix and their deposition by solvent casting or spin coating [46], but the morphology of the film highly depends on the solubility of both components with, in general, a high tendency to aggregation. When the polymerization is carried out in the presence of MOx particles, hybrid materials are obtained, with a more intimate interaction between both materials [47]. With such electrochemical method, the use of a cross-linked PANI, associated with CeO₂ nanoparticles, led to a better stability of the response to NH₃ [48]. Such localized n-p heterojunctions can also be obtained by covering a nanostructured inorganic material by an organic semiconductor, e.g. with n-type ZnO nanowires or ZnS nanoparticles covered by a p-type MPc [49,50]. This method can be generalized, since it allows using every method to depose a nanostructured inorganic material, generally with a high temperature process (see chapter 2), then covering by an organic material using vacuum evaporation or some solution processing technique, depending on its solubility. The top layer can also be deposited by electrodeposition on the conducting sublayer, to form a diode, as in the case of n-ZnO/PANI and n-CdS/PANI, used to detect liquefied petroleum gas [51,52]. Electrodeposited PANI was also used to decorate electrospun n-type TiO₂ fibers leading to sensors that work as electric current switches when NH₃ gas was absorbed by PANI nanoparticles, again due to the existence of localized heterojunctions, with a sub ppb LOD [53]. Pure organic core-shell PANI – based composites with a poly(butyl acrylate) or poly(vinylidene fluoride) core and a composite based on PANI nanofibers embedded in a polyurethane (PU) matrix showed also a high sensitivity to NH₃ [54].

For a recent review on PANI-based nanocomposites we can cite the review by Pandey [55]. Other common conducting polymers, such as polypyrrole (PPy) and polythiophene (PT) were also associated with nanostructured SnO₂, ZnO, MoO₃ or WO₃ to detect a series of VOCs, NH₃, NO₂, CO, CO₂ or H₂S, with generally better performances than with the pristine components. Starting from nanobuilding blocks, a large variety of organic-inorganic hybrid materials of tunable properties can be synthesized via various pathways

that involve different types of interactions, namely coordinative, ionic, hydrogen, π - π and Van der Waals interactions, as reviewed by Kaushik [56].

In the heterojunctions, the improvement of the sensing performances, including an increase selectivity towards gases, is related to the key role played by the interfaces. This is the reason why reducing the size of domains increases the effect of heterojunctions. The advantages of heterojunctions are well described in the review of Akbar devoted to nanoscale metal oxide-based heterojunctions [57]. Other conductometric devices combine organic and inorganic materials, such as an hybrid n-p-n $\text{WO}_3/\text{LuPc}_2$ heterojunction, with a configuration analog to the above mentioned MSDI, used to detect NH_3 in humid atmosphere [58]. An ambipolar hybrid organic-inorganic thin film transistor, consisting of pentacene and ZnO as semiconductors was also reported as gas sensor [59]. Interestingly, most of the hybrid organic-inorganic material-based sensors can operate at room temperature.

Beside metal oxides and sulfides, polymers were also covalently bound to metal nanoparticles as sensing materials in resistors, via a 4-aminothiophenol linker. The poly (3,4-ethylenedioxythiophene-co-thiophene-3-acetic acid), a copolymer of PEDOT, linked to Ni and Pd particles were used to detect selectively toluene and acetone, respectively [60]. It works by a change of the work function of metals that interact with a certain degree of selectivity with different VOCs.

Beside these inorganic-containing materials, we should also cite the metal organic frameworks (MOF) that allow the separation of gases, because of their porosity and the specific interactions they developed with VOCs. It is out of the scope of this chapter to show the numerous MOFs used as sensing materials, but we can cite a review that shows that MOF-based sensors are mostly designed with optical and acoustic transducers [61]. However, conductive 2D MOF have been recently obtained using 2,3,6,7,10,11-hexahydroxytriphenylene and 2,3,6,7,10,11-hexamino- triphenylene as ligands associated with Cu(II) and Ni(II) as metal centers [62]. A sensor array built with a family of structurally analogous 2D MOFs provided a clear discrimination between different categories of VOCs [63].

5.5 2D component-containing hybrid materials

Since the first detection of individual molecules by graphene reported by Novoselov [64], graphene, graphene oxide and hybrid materials based on these 2D compounds were highly used as sensing materials, firstly because of their high surface-to-volume ratio. Thus reduced graphene oxide (rGO) was associated to Co_3O_4 [65] or to polyaniline (PANI) [66] to get a high sensitivity to NH_3 . The rGO- Co_3O_4 composite nanofibers were prepared via electrospinning, starting from a GO- Co_3O_4 -polyvinyl pyrrolidone suspension, followed by thermal annealing up to 800 °C [65]. The resulting rGO- Co_3O_4 composite appeared as nanofibers embedded into amorphous carbon. The encapsulation of oxide nanocrystals avoids their aggregation. The rGO/PANI material was obtained by in situ reduction of GO by the oxidative polymerization of aniline [66,67]. A particular graphene-PANI nanocomposite including PANI nanoparticles and nanofibers deposited on a flexible substrate revealed a sub ppm LOD [68]. Such in situ reduction of GO was also achieved in the presence of SnCl_2 , leading to a SnO_2 /rGO composite [69].

Another synthetic way to obtain rGO-based nanostructures was the use of microwaves. GO was first coated with SnO_2 nanoparticles in a microwave-assisted synthesis in benzyl alcohol, in the presence of SnCl_4 as SnO_2 precursor, followed by the deposition of Pt nanoparticles by the reduction of H_2PtCl_6 in ethylene glycol, again assisted by microwave radiation [70]. The Pt- SnO_2 /rGO nanocomposite showed enhanced hydrogen sensing performance relative to that of the corresponding pure and binary systems. In another example, rGO films were detached from a quartz substrate and transferred onto AgNPs and AgNWs films obtained by spray coating, then covered by interdigitated gold electrodes [71]. The sensors prepared with AgNWs were more sensitive to NH_3 than those containing AgNPs.

The recent emergence of a new variety of 2D materials created new opportunities in the field of electronics and optics, but also in the field of chemical sensors. Transition metal chalcogenides, of general formula MX_2 ($\text{M} = \text{Mo}, \text{W}$ and $\text{X} = \text{S}, \text{Se}$ or Te), due to their semiconducting properties, are well suitable for conductometric transducers. For an overview on the synthesis, structure, spectroscopy and applications of 2D metal chalcogenides, see a review by Dubretret et al. [72] and a special issue in Acc. Chem. Res.

[73-75]. Associated with molecular materials, they can form what are called van der Waals p-n heterojunctions, e.g. with pentacene and MoS₂ [76]. As for graphene, their high surface-to-volume ratio makes these 2D materials suitable for chemical sensing applications, where perturbations to the surface resulting in charge redistribution are readily manifested in the transport characteristics, as exemplified by the detection of trimethylamine by MoS₂ [77]. Because MoS₂-based gas sensors still suffer from long response and recovery times, especially at room temperature, they have been photoactivated under UV light [78] and also combined with other materials. Thus a 2D graphene/MoS₂ heterostructure where exfoliated MoS₂ flakes bridged graphene lines exhibited a negative response to NO₂ and a positive response to NH₃ [79]. However, the fabrication of the device remained rather sophisticated.

MoS₂ was also associated with GO as a hybrid composite obtained by simply mixing MoS₂ and GO suspensions and spin coating on a substrate before thermal annealing [80]. An ultrasensitive NO₂ detection, with a LOD of 50 ppb, even at room temperature, was obtained with a MoS₂/graphene hybrid aerogel. An electrically conductive graphene aerogel with ultrahigh surface area was prepared from GO, then coated by ammonium thiomolybdate and the MoS₂ formation initiated by annealing at 450 °C under hydrogen, the final material being obtained after a second annealing in the presence of sulfur [81].

MoS₂ can also be decorated by metals, for example by vacuum deposition of Pd on drop-casted nanosheets of MoS₂, Cr/Au electrodes being deposited on the top of the hybrid material. The obtained hydrogen sensors exhibited a LOD of 50 ppm [82].

However, even though MoS₂ offers a high sensitivity towards various gases, depending on the second component associated with, it was also reported as a good sensing material for humidity. Thus a MoS₂/GO-based resistor exhibited a very high sensitivity to humidity, the current being multiplied by 55 at 35 % RH and by $1.6 \cdot 10^3$ at 85 % RH [83]. In the case of Pt – decorated MoS₂, with a ratio of Pt/MoS₂ of 1/4 (w/w), the current was even multiplied by $4 \cdot 10^3$ at 85 % RH [84]. With gold, the decoration of MoS₂ was achieved chemically, by adding a HAuCl₄ solution to an aqueous dispersion of chemically exfoliated MoS₂ at room temperature and stirring for 30 min [85]. The obtained suspension was filtered on a porous alumina membrane, then alumina was dissolved in a 3 M NaOH solution, finally the MoS₂ films floating at the solution surface was transferred on

electrodes. The resistors showed a current increase under ethanol and acetone, but a current decrease under toluene and hexane, whereas the pristine MoS₂ resistor showing a current decrease in the four cases. Clearly the incorporation of Au NPs brings some selectivity.

5.6 Challenges in hybrid materials–based gas sensing

The combinations of macrocycles, polymers, carbonaceous materials and inorganic materials are infinite, in particular if we combine more than two of them. As an example, we can cite the case of an electrochemical sensor in which hemin, an iron porphyrin complex, deposited on the surface of a Pt/ZnO/PPy structure, acts as an electrocatalyst to detect NO_x at the sub micromolar level in aqueous solution [86]. Another example is that of CNT/PPy chemiresistors in which the polymer bears calix[4]arenes that ensure the selective recognition of aromatic VOCs like BTX [87]. Elsewhere, whatever the efforts made on the characterization of materials, the response obtained with a given hybrid material still depends on the nature of electrodes and on the interface between the electrodes and the sensing material. So, sensing performances can be tuned by various electrode treatments, such as plasma treatment, temperature annealing or by chemical modification of electrodes, e.g. by self-assembly monolayers, or by electrochemical methods [88]. Finally, as soon as applications in real atmospheres are envisaged, a key attention need to be paid to the cross sensitivity with humidity, which has to guide us in the choice of the different components of the hybrid material used as sensing material. Finally, the choice of a sensing material has to be thought simultaneously with the choice of the type of transducer, as a function of the target application and the physical parameters modified by the analytes need to be considered.

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