

# Functionalized Graphene Surfaces for Selective Gas Sensing

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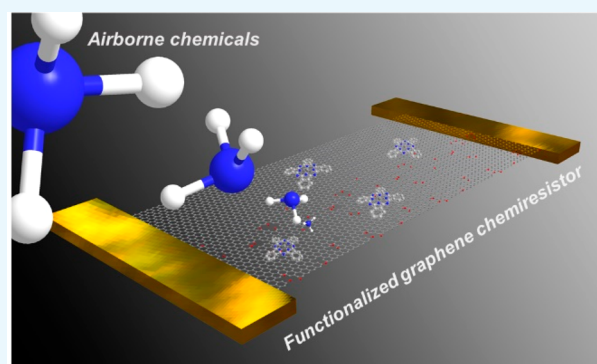
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**ABSTRACT:** Environmental monitoring through gas sensors is paramount for the safety and security of industrial workers and for ecological protection. Graphene is among the most promising materials considered for next-generation gas sensing due to its properties such as mechanical strength and flexibility, high surface-to-volume ratio, large conductivity, and low electrical noise. While gas sensors based on graphene devices have already demonstrated high sensitivity, one of the most important figures of merit, selectivity, remains a challenge. In the past few years, however, surface functionalization emerged as a potential route to achieve selectivity. This review surveys the recent advances in the fabrication and characterization of graphene and reduced graphene oxide gas sensors chemically functionalized with aromatic molecules and polymers with the goal of improving selectivity toward specific gases as well as overall sensor performance.



## INTRODUCTION

Graphene, an extended honeycomb network of  $sp^2$ -hybridized carbon atoms,<sup>1</sup> is among the strongest candidates for the development of new gas sensing technologies due to its high surface-to-volume ratio, mechanical strength and flexibility, large conductivity, and low electrical noise.<sup>2–8</sup> Methods of graphene synthesis include both top-down approaches (mechanical exfoliation from graphite) and bottom-up large-area approaches such as epitaxial growth or chemical vapor deposition (CVD). An alternative route toward large-scale production of graphene-like materials is the reduction of graphene oxide (GO) to reduced graphene oxide (rGO). rGO, as schematically presented in Figure 1a, has a graphene-like basal plane that is decorated with structural defects during its synthesis and occupied with areas containing oxidizing chemical groups.<sup>9</sup>

While gas sensors based on graphene devices have already demonstrated high sensitivity, one of the most important figures of merit, selectivity, remains a challenge.

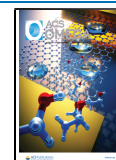
Selectivity is the ability of a gas sensor to have higher sensitivity to a specific target analyte when exposed to multiple interfering gases. This implies that the sensor's response to the target gas should be higher than the response to interfering gases. In the case of graphene chemiresistors, the sensing mechanism relies on changes in graphene's conductivity upon exposure to gaseous species. Generally, different gases with electron-withdrawing or electron-donating molecules could be adsorbed on graphene's surface and change its conductivity. Such a sensing platform has intrinsically high sensitivity, as graphene's conical band structure ensures significant con-

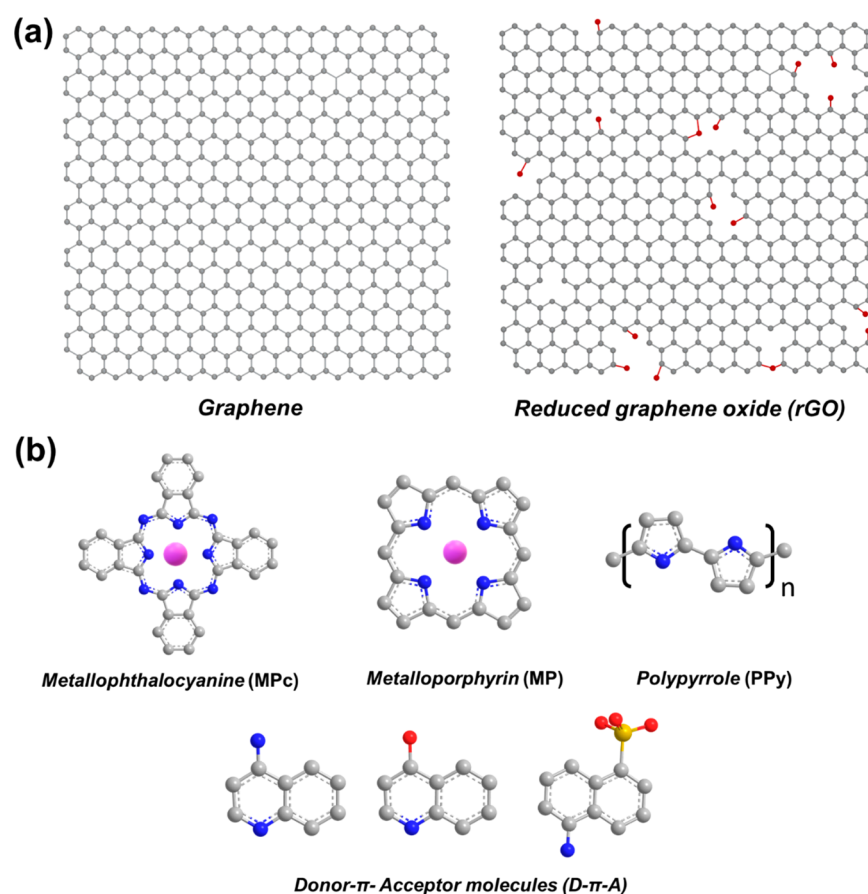
ductivity changes. At the same time, selectivity can be a challenge for a sensitive chemiresistor, as many gases can lead to large sensing responses. Functionalization of the graphene surface has been proposed as an approach to overcome this issue. In this case, a selective detection relies on the different interaction strengths between analytes and the functional species, that can preferentially anchor a desired target gas.

In the past few years, experimental advances demonstrated that surface functionalization<sup>10</sup> is indeed a promising route to achieve selectivity. Adsorbates ranging from metal oxides, metal nanoparticles, polymers, and organometallic molecules have been successfully used to improve figures of merit such as sensitivity, recovery time, and especially selectivity. In this Mini-Review, we focus on recent research exploring graphene molecular functionalization for improved sensor selectivity.

Graphene molecular functionalization can be accomplished both covalently and noncovalently. To form covalent bonds between graphene and a target molecule, several chemical transformations such as nucleophilic, cycloaddition, condensation, and electrophilic reactions are used. In this case, graphene's  $\pi$ -orbitals are involved in the bond, transforming  $sp^2$  into  $sp^3$  bonds. This change in the hybridization of graphene alters its electronic transport properties. On the other hand, noncovalent

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**Figure 1.** (a) Lattice structure of graphene and reduced graphene oxide. (b) Molecules used to functionalize graphene and rGO for sensing applications.

functionalization offers the opportunity of attaching functional groups to the graphene surface based on electrostatic interactions as van der Waals forces or  $\pi$ - $\pi$  interactions. Aromatic molecules with planar structures are ideal candidates for this purpose, since they can be easily anchored to graphene surface through  $\pi$ - $\pi$  interactions. Such noncovalent interactions do not alter the conjugated network of graphene, thus preserving its intrinsic transport properties.

Both covalent and noncovalent functional modification of graphene with electron-donating or electron-withdrawing molecules can lead to charge transfer, resulting in p-doping or n-doping of the graphene film. The charge transfer mechanisms among analytes, functional molecules and graphene play a key role in determining the gas-sensing performance of devices.

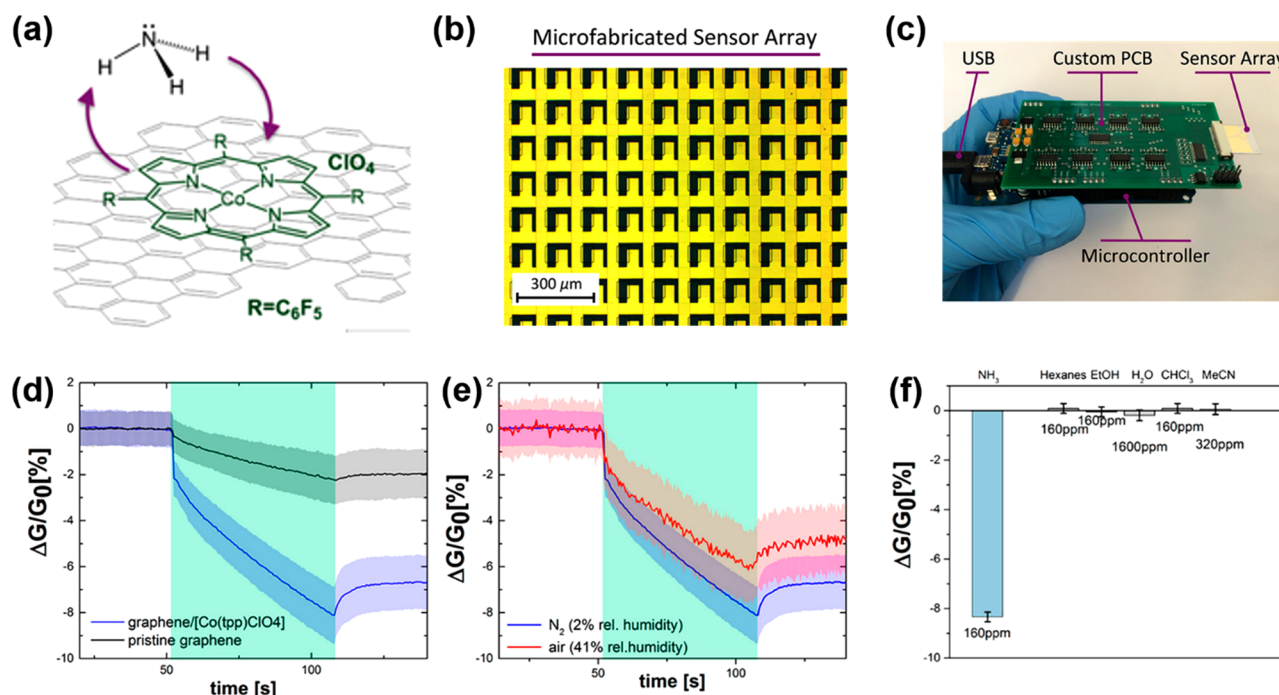
A variety of graphene hybrids have been studied as sensing material alternatives with the goal of improving the performance of bare graphene gas sensors. Organic molecules such as porphyrins and phthalocyanines (Pcs) have been used to improve the selectivity of graphene-based sensors. Porphyrins are macrocycles with 18  $\pi$ -electron conjugated ring system and can be transformed into metalloporphyrins (MPs) by substituting two hydrogen atoms with a transition metal atom at the central core (Figure 1b). The strong catalytic activity of MPs makes it an attractive functional material that can enhance the chemical response of graphene. Phthalocyanines are two-dimensional 18  $\pi$ -electron materials with high electronic delocalization. Metallophthalocyanines (MPcs) can be formed by the substitution of hydrogen atoms with a transition metal as seen in Figure 1b. Their thermal and chemical stability, together

with the highly tunable structure facilitating the design of a wide range of compounds, make MPcs promising candidates for gas sensing. Conductive polymers have also been used as a sensitive layer in graphene hybrids. Among them, polypyrrole (PPy) (Figure 1b) is a conjugated polymer that has emerged as a promising material for sensing applications due to its low cost, easy synthesis, and moderately high conductivity and wide detection of variety of volatile compounds. Moreover, its most promising feature is the ability to operate at room temperature. Donor- $\pi$ -acceptor (D- $\pi$ -A) systems are a class of molecules with delocalized  $\pi$  orbitals, in which the electron migration is facilitated from the donor to the acceptor group. These molecules usually have high chemical stability and good electronic and optical properties. D- $\pi$ -A molecules have been incorporated in graphene-based hybrids for sensing, as their structural architecture can enhance the charge transfer between graphene and a target gas analyte.

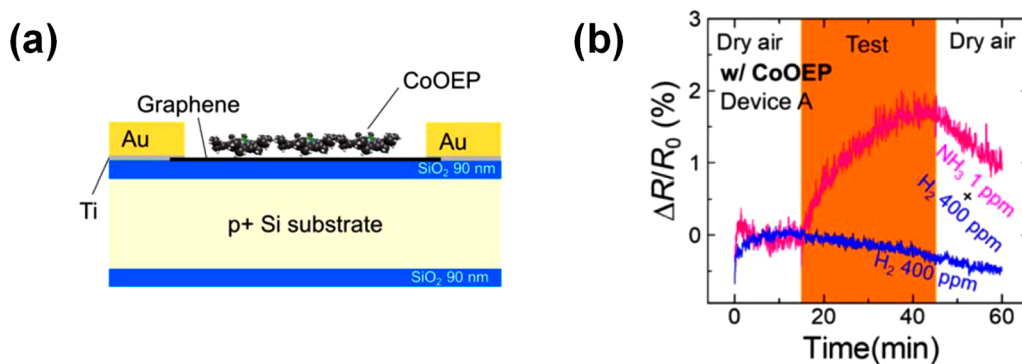
This Mini-Review is focused on the latest efforts to improve graphene sensor selectivity with the introduction of organic molecules and polymers that tailor the graphene response toward specific gases. We focus both on the surface functionalization methods and characterization and on the sensing performance, as the two aspects are interconnected.

## I. HYBRIDS BASED ON GRAPHENE/METALLOPORPHYRINS (MPs)

Porphyrins with different coordinated metals have been used for functionalizing graphene, as their aromatic backbone promotes noncovalent bonding with the graphene plane. MPs have strong



**Figure 2.** (a) Chemical structure of the Co porphyrin molecule on top of graphene. (b) Microscope image of graphene sensor array. (c) Complete measurement system and sensor array insert. (d) Mean change in conductance upon exposure to 160 ppm of NH<sub>3</sub> in nitrogen of the pristine graphene sensor and the Co porphyrin functionalized graphene with shaded regions representing plus or minus one standard deviation from the mean. (e) Mean change in conductance of the Co porphyrin functionalized graphene sheet upon exposure to 160 ppm of NH<sub>3</sub> in dry nitrogen and air. (f) Selectivity comparison of the functionalized graphene. Adapted with permission from ref 11. Copyright 2018, American Chemical Society. Photograph in part c adapted with permission from ref 11.



**Figure 3.** (a) Schematic of a CoOEP/graphene sensor.<sup>12</sup> (b) Selectivity of CoOEP/graphene sensor for ammonia against hydrogen. Adapted with permission from ref 12. Copyright 2018, American Chemical Society.

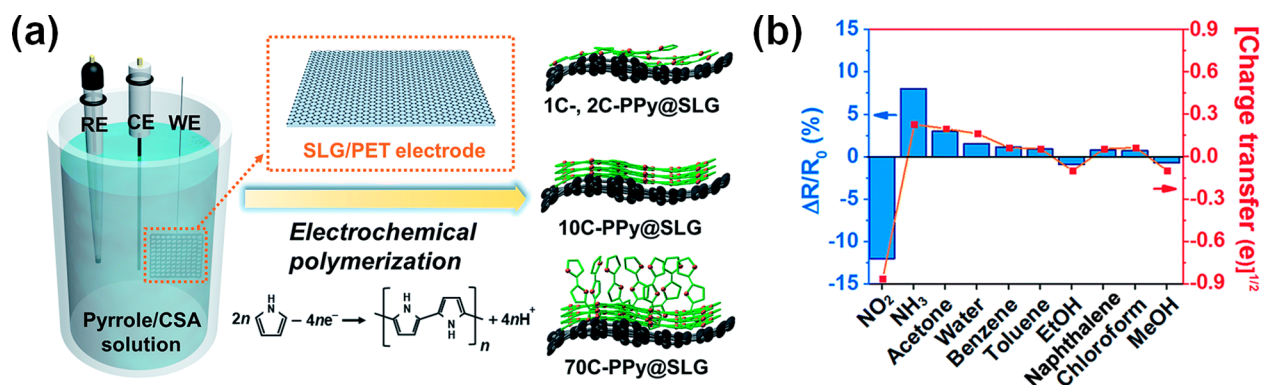
dipoles when interacting with specific gas analytes, making them good candidates for improving the selectivity of graphene gas sensors.

Mackin and co-workers<sup>11</sup> reported a highly sensitive ammonia gas chemiresistor based on CVD graphene functionalized with Co porphyrin Co(tpfp)ClO<sub>4</sub>-5,10,15,20-tetrakis-(pentafluorophenyl) porphyrinato cobalt(III) perchlorate as shown in Figure 2a. The porphyrin solution was dropcasted onto a CVD-graphene sensor array. These were tested using a system especially designed to efficiently evaluate a large number of sensors (Figure 2b,c). As shown in Figure 2d, graphene functionalization increased the sensitivity of the sensors to ammonia in comparison with pristine graphene. High sensitivity to ammonia was found for the functionalized sensors when tested in the presence of interfering compounds such as dry nitrogen or air (Figure 2e). This study finds that when

functionalized with Co porphyrin, the sensor response to ammonia increased four times. In terms of selectivity, as presented in Figure 2f, the sensors showed negligible response to water and four organic solvents in comparison to ammonia. Sensor-to-sensor variation was evaluated when testing the response of 160 sensors, and it was found that there are differences in their baseline currents. In order to overcome this problem, they note the need for future development of more uniform graphene growth, transfer, and microfabrication techniques that will reduce the variation in the sensing material properties.

Recently, hybrid Co porphyrin (CoOEP-2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine cobalt(II))/CVD graphene were evaluated as gas sensing materials.<sup>12</sup> To functionalize the CVD graphene film, a saturated chloroform Co porphyrin solution was spin-coated onto a graphene sensor array





**Figure 4.** (a) Schematic illustration of the synthesis of polypyrrole (PPy) on a single layer graphene/polyethylene terephthalate (SLG/PET) film: a three-electrode system (RE, reference electrode; WE, working electrode; CE, counter electrode), an electrochemical polymerization scheme, and  $n$ Cycles-PPy on single layer graphene. (b) Evaluation of the sensor selectivity for various target analytes (1 ppm). Adapted with permission from ref 16. Copyright 2018, Royal Society of Chemistry.

(Figure 3a). Successful graphene functionalization was evidenced by the XPS measurements of the hybrids indicating characteristic features of pyrrole rings in Co porphyrin and C=C bonds in the graphene network. The performance of the hybrid Co porphyrin/CVD graphene sensors was tested under low concentrations of  $\text{NH}_3$  (2 ppm). The functionalized sensors showed a six-times greater response to ammonia when compared to non-functionalized graphene. Since  $\text{H}_2$  can prevent accurate detection of ammonia in breathalyzers, the selectivity of the sensors was evaluated for mixtures of  $\text{H}_2$  and ammonia. The functionalized sensors did not show response to high concentrations of  $\text{H}_2$  (400 ppm), but recognized low concentrations of  $\text{NH}_3$  (1 ppm), confirming that the sensor response to ammonia is not affected by the presence of  $\text{H}_2$  (Figure 3b). Moreover, it was found that the sensitivity of the sensors to ammonia was not disrupted by the presence of high humidity concentrations. The improved sensing performance of the functionalized graphene is explained as an increase in  $\text{NH}_3$  adsorption sites in comparison with non-functionalized graphene. CVD graphene functionalized with Co porphyrins was reported also as a sensing material for detecting volatile organic compounds (VOC).<sup>13</sup> After the fabrication of the graphene channel, the Co porphyrin-5,10,15,20-tetraphenyl-21H, 23H-porphyrin cobalt(II) was deposited on the graphene by thermal evaporation. Raman spectroscopy and AFM measurements confirmed that the graphene film was a single layer. The hybrid sensors were electrically characterized in a field effect transistor (GFET) configuration. The electrical measurements revealed that sensors were n-doped, and their resistance decreased upon exposure to toluene. Moreover, functionalized graphene sensors had a higher response (>2 times) than graphene sensors, which was attributed to the formation of donor-acceptor complexes at the interface between graphene and the Co porphyrin.

Quasi-freestanding epitaxial graphene (QFeG) functionalized with Co porphyrin was reported as a hybrid material for ammonia sensing by Iezhokin and co-workers.<sup>14</sup> Functionalization was achieved by drop-casting Co porphyrin heptane dispersions on top of graphene. The Co porphyrin used in this work was CoMP-5,10,15,20-*meso*-tetrakis-nonadecylporphyrin cobalt(II). AFM measurements, Hall Effect experiments, and Density functional theory (DFT) calculations revealed that the graphene surface is covered by a single porphyrin layer. It is reported that, while QFeG has a negligible response to ammonia, the functionalized graphene hybrid can detect  $\text{NH}_3$

below 100 ppb. After functionalization, the CoMP/QFeG sensor is p-doped. Upon  $\text{NH}_3$  adsorption on the metallic Co centers, charge transfers to the underlying QFeG. Both electrical measurements and theoretical band structure calculations support the proposed electron doping mechanism that shifts the Fermi level.

In a different study, CVD graphene was functionalized with Zn porphyrins (ZnTTPOH-5-(4-hydroxyphenyl)-10,15,20-tri(*p*-tolyl) zinc porphyrin) for the detection chemical explosive molecules (TNT) in the vapor phase.<sup>15</sup> It is proposed that the ZnTTPOH molecules act as a selective spot for absorbing the TNT molecules and the electron transfer from the graphene to TNT is mediated by ZnTTPOH. The charge transfer is detected as a shift in the Dirac point by the hybrid GFETs. The selectivity of such sensors was explored against different nitroaromatic explosives (nitrobenzene, *m*-dinitrobenzene, nitromethane) and VOCs like isopropanol and acetone.

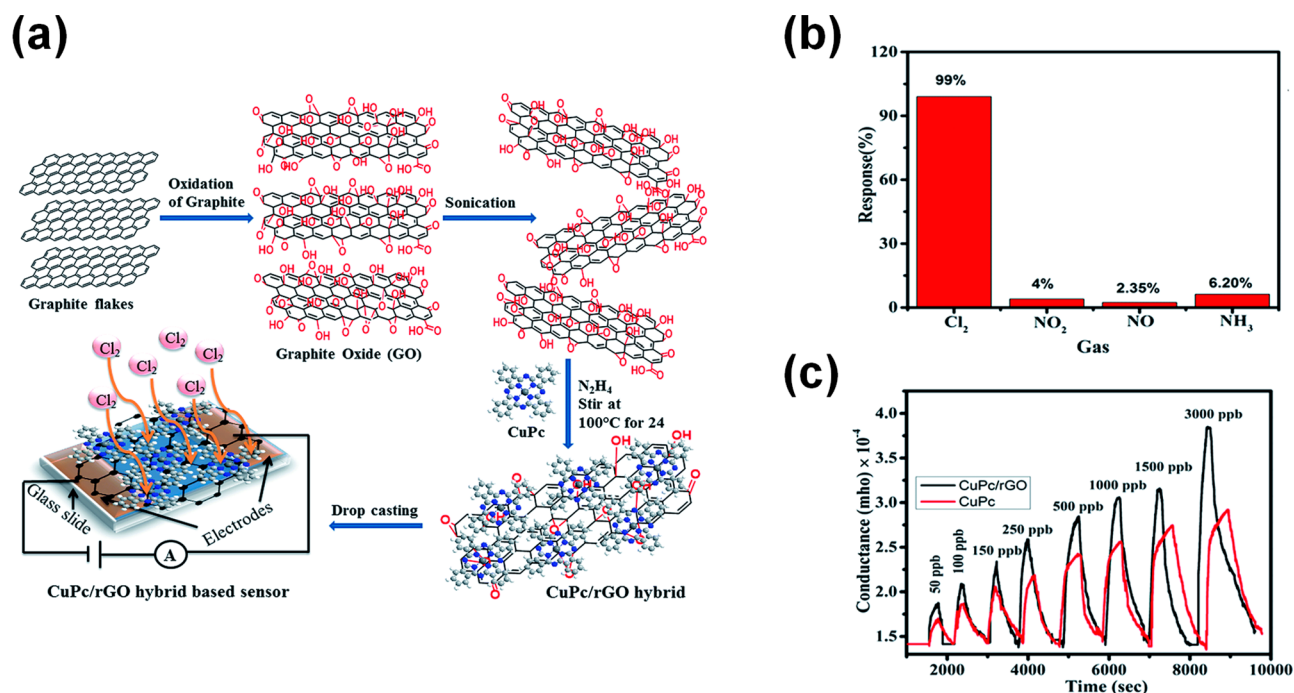
## II. HYBRIDS BASED ON GRAPHENE/POLYPYRROLE MOLECULES

Graphene functionalized with polymers usually presents porous structures that enhance the diffusion of the molecules to the sensing layers. Moreover, polymers can form strong bonds with target gases through hydrogen bonds or  $\pi$ - $\pi$  stacking, improving the selectivity of the sensors.

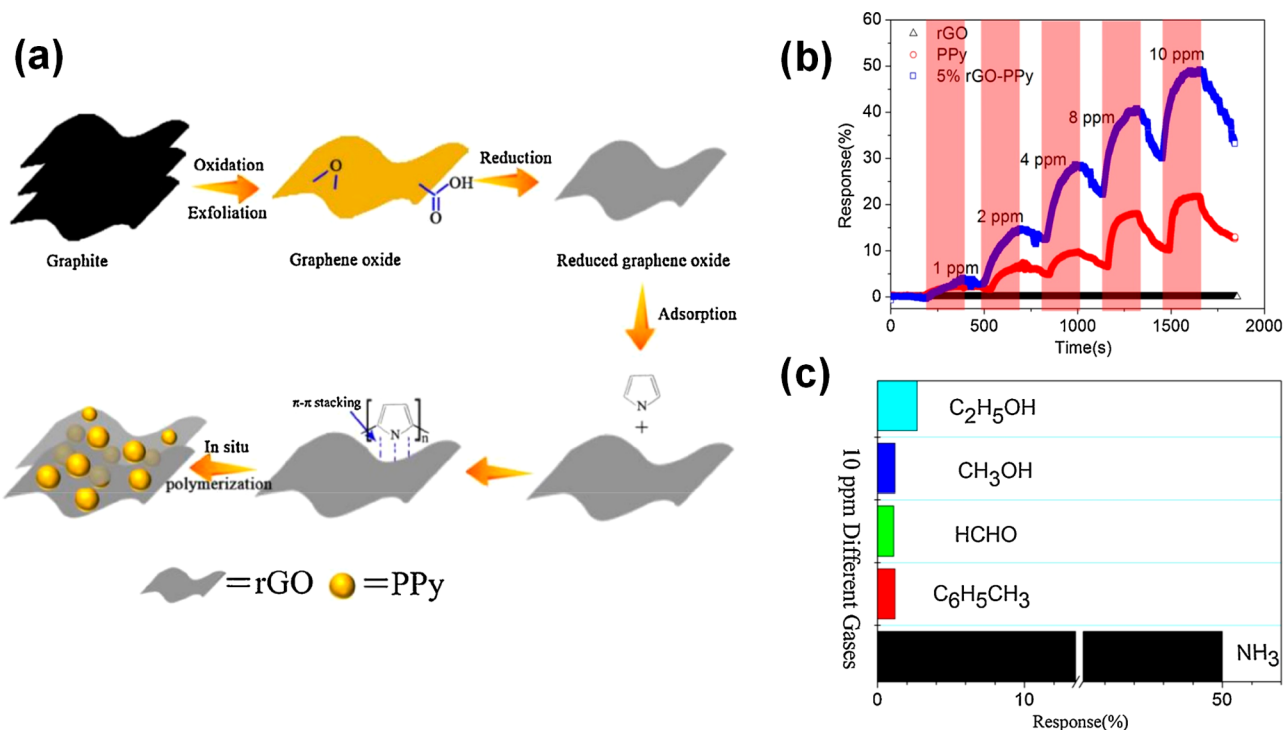
Flexible and transparent sensors based on CVD graphene functionalized with polypyrrole (PPy) were recently reported.<sup>16</sup> Graphene functionalization was achieved by electrochemical polymerization of pyrrole monomers as described in Figure 4a. The fabricated sensors were tested for different gases, showing the best detection limits of 0.03 ppb for  $\text{NO}_2$  and 0.04 ppb for  $\text{NH}_3$  (Figure 4b). It is noted that upon exposure to  $\text{NO}_2$ , the electrical resistance of the sensors decreased, while it increased when exposed to  $\text{NH}_3$ . The good sensing performance of the hybrid system was attributed to the well-ordered structure of PPy/graphene, which enhances the charge mobility.

In a similar approach, ammonia sensors were fabricated by PPy electropolymerization synthesis on CVD-grown graphene.<sup>17</sup> In general, higher response to ammonia was shown for the PPy/graphene compared to the graphene sensor without PPy layer. The sensors were exposed to 5 ppm of  $\text{NH}_3$  at room temperature, showing good selectivity for  $\text{NH}_3$  in the presence of interfering gases  $\text{CH}_2\text{O}$  and  $\text{NO}_2$ . Electron transfer from  $\text{NH}_3$





**Figure 6.** (a) Schematic representation of synthesized rGO sheets decorated with CuPc nanoflowers. (b) Response histogram of CuPc/rGO hybrid sensor to 500 ppb. (c) Conductance–time plots for different doses of  $Cl_2$ . Adapted with permission from ref 23. Copyright 2017, Royal Society of Chemistry.



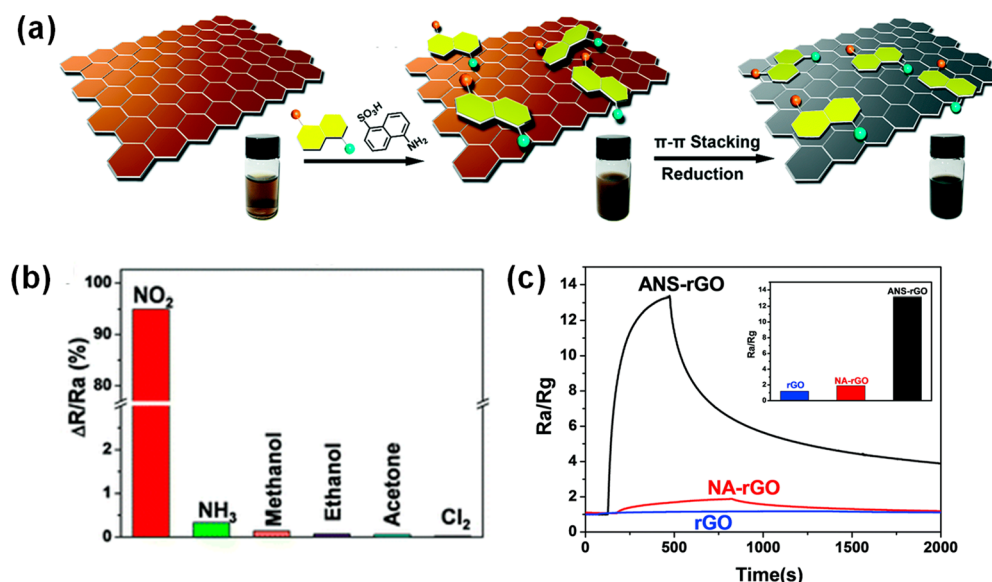
**Figure 7.** (a) Mechanism of in situ chemical oxidation polymerization mechanism of PPy on rGO. (b) Response rGO, PPy, and rGO/PPy hybrids to 1–10 ppm of  $NH_3$ . (c) Selectivity of rGO/PPy to 10 ppm different gases. Adapted with permission from ref 24. Copyright 2017, Elsevier.

DMF dispersions of MPc and rGO, followed by hydrazine reduction. XPS confirmed the noncovalent functionalization of rGO. Gas sensing performance was tested in the presence of  $NH_3$  (0.3–3200 ppm) at room temperature. The resistance typically increased with increasing concentration of  $NH_3$ . The TBPOMPc/rGO sensors recovered to its original resistance, in contrast to rGO sensors. It was found that TBPOMPc/rGO

hybrid sensors were selective toward ammonia when compared to CO,  $NO_2$ , and  $H_2$ .

A selective room temperature chemiresistor with a ppb limit of detection for  $Cl_2$  was fabricated through the functionalization of rGO with CuPc nanoflowers (Figure 6a).<sup>23</sup> Functionalization of rGO was carried out by mixing CuPc powder and GO in DMF, followed by hydrazine reduction. Structural and





**Figure 8.** (a) Schematic representation of the ANS/rGO hybrid preparation for  $\text{NO}_2$  gas-sensing applications. (b) Response of ANS/rGO sensing material to 10 ppm of  $\text{NO}_2$ ,  $\text{NH}_3$ , methanol, ethanol, acetone, and  $\text{Cl}_2$ . (c) Gas-sensing responses of rGO (1.2), naphthalene-1-sulfonic acid sodium (NA)/rGO (1.9), and ANS-rGO (13.2) upon exposure to 10 ppm of  $\text{NO}_2$  gas at room temperature. Adapted with permission from ref 27. Copyright 2017, Royal Society of Chemistry.

spectroscopic studies revealed that CuPc islands grow uniformly in a network of nanoflowers lying parallel to the rGO surface. FTIR measurements indicated the delocalization of electrons to form noncovalent interactions between CuPc and the rGO surface by  $\pi$ - $\pi$  interactions. As illustrated in Figure 6b, the hybrid material presented high selectivity toward  $\text{Cl}_2$  in comparison to other gases like  $\text{NO}_2$ , NO, and  $\text{NH}_3$ . At low concentrations of 3000 ppb of  $\text{Cl}_2$ , they report a large response characterized by response/recovery time of 190 s/545 s. The sensing mechanism was studied with Raman and electrochemical impedance spectroscopy (EIS), concluding that molecules of  $\text{Cl}_2$  are physio-adsorbed on the central metal of CuPc. It was noted that the high surface area of the CuPc nanoflowers provides many active sites for  $\text{Cl}_2$  adsorption, while the rGO provides a conductive network that enhances the sensing performance.

#### IV. HYBRIDS BASED ON REDUCED GRAPHENE OXIDE/POLYPYRROLE MOLECULES

PPy/rGO hybrids were used to develop gas sensors,<sup>24</sup> where PPy was attached to rGO through chemical oxidative polymerization (Figure 7a). FTIR and Raman spectroscopy confirmed the  $\pi$ - $\pi$  interactions of PPy and rGO sheets. Devices based on this hybrid material were evaluated as sensors for ammonia at room temperature, in different concentrations (1 to 10 ppm), showing linear dependence of the response to  $\text{NH}_3$  concentration (Figure 7b). The sensor selectivity was tested in the presence of VOCs such as toluene, formaldehyde, ethanol, and methanol. The hybrid-based graphene sensor demonstrated relatively low responses to the interfering gases and high response toward ammonia. The proposed sensing mechanism relies on the electron transfer from ammonia to PPy. In addition, due to the H-bonding and  $\pi$ - $\pi$  stacking interactions in the PPy/rGO hybrid, electron transfer processes can occur between them, leading to increased sensor resistance.

In a different approach, rGO/PPy hybrids were prepared by in situ oxidative polymerization.<sup>25</sup> Characterization with FTIR and XRD suggested the noncovalent interaction between PPy and

rGO by  $\pi$ - $\pi$  stacking. The gas sensing performance of the hybrid was evaluated at different ammonia concentrations (5–300 ppm) and a general improvement of sensitivity was observed for the PPy/rGO sensors. The high response for ammonia was due to large surface area and porous structure of the composite, which enhances the adsorption of the analyte. PPy and graphene are p-type materials, while  $\text{NH}_3$  acts as an n-type dopant causing the change in sensor resistance.

Recently, PPy/rGO ammonia sensors were obtained through electrochemical polymerization with a controllable thickness.<sup>26</sup> GO was deposited on interdigitated electrodes, followed by thermal reduction; subsequently, a thin layer of PPy was electropolymerized on the rGO surface. The sensing response was evaluated in  $\text{NH}_3$  concentrations ranging from 1 to 4 ppm and presented a linear response. It was found that the rGO sensors showed noticeably lower response at room temperature in comparison with functionalized hybrid sensors. The recovery time was improved through thermal annealing at 100 °C. The selectivity was also evaluated by exposing the sensor to different analytes such as formaldehyde and  $\text{H}_2$ . The low response to the interferential gases indicated good selectivity toward  $\text{NH}_3$ . The sensing mechanism was attributed to electron transfer between the  $\text{NH}_3$  molecules and the PPy/rGO hybrid material. Thus, synergistic effects between PPy and rGO were shown to result in significantly higher sensitivity and selectivity than the bare rGO sensor.

#### V. HYBRIDS BASED ON REDUCED GRAPHENE OXIDE/DONOR- $\pi$ -ACCEPTOR (D- $\pi$ -A) MOLECULES

Hybrids based on rGO and a D- $\pi$ -A molecule ANS–5-aminonaphthalene-1-sulfonic acid were recently reported as a promising sensor for detecting low concentration of  $\text{NO}_2$ .<sup>27</sup> The functionalization was carried out by aqueous dispersions of GO and ANS, followed by hydrazine reduction, schematically shown in Figure 8a; the ANS/rGO dispersions were then deposited on electrodes. Raman, FTIR, and XPS confirmed the graphene functionalization by  $\pi$ - $\pi$  stacking interactions. The sensing performance was evaluated at different  $\text{NO}_2$  concentrations (1

Table 1. Summary of Graphene-Based Hybrids for Gas Sensors and Their Performance Characteristics

| type of graphene | molecules | analyte gas     | concentration (ppm) | response (sensitivity) (%) | recovery time (s) | ref |
|------------------|-----------|-----------------|---------------------|----------------------------|-------------------|-----|
| rGO              | 3-CuPc    | NH <sub>3</sub> | 3200                | 15.4                       | -                 | 18  |
| rGO              | cpoPcCo   | NH <sub>3</sub> | 100                 | 42.4                       | 450               | 19  |
| rGO              | cmpoPcCo  | NH <sub>3</sub> | 100                 | 31.4                       | 540               | 19  |
| rGO              | poPcCo    | NH <sub>3</sub> | 100                 | 27.3                       | 420               | 19  |
| rGO              | mpoPcCo   | NH <sub>3</sub> | 100                 | 22.1                       | 480               | 19  |
| rGO              | ABOPcCo   | NH <sub>3</sub> | 50                  | 23.3                       | 250               | 20  |
| rGO              | APcCo     | NH <sub>3</sub> | 50                  | 6.4                        | 80                | 20  |
| rGO              | CuPc      | NH <sub>3</sub> | 50                  | 7.8                        | 480               | 21  |
| rGO              | NiPc      | NH <sub>3</sub> | 50                  | 5.5                        | 300               | 21  |
| rGO              | PbPc      | NH <sub>3</sub> | 50                  | 7.8                        | 650               | 21  |
| rGO              | TBPOCuPc  | NH <sub>3</sub> | 50                  | 8.9                        | -                 | 22  |
| rGO              | TBPONiPc  | NH <sub>3</sub> | 50                  | 8.9                        | -                 | 22  |
| CVD              | PPy       | NH <sub>3</sub> | 0.1 ppb             | 0.9                        | 10                | 16  |
| CVD              | PPy       | NH <sub>3</sub> | 1                   | 1.7                        | 300               | 17  |
| rGO              | ANS       | NO <sub>2</sub> | 10                  | 95.0                       | -                 | 27  |
| rGO              | 4AQ       | NO <sub>2</sub> | 10                  | 74.3                       | -                 | 28  |
| rGO              | CuPc      | Cl <sub>2</sub> | 500 ppb             | 99                         | -                 | 23  |
| CVD              | CoPP      | Toluene         | 10                  | 8.3                        | -                 | 13  |

Table 2. Summary of Graphene-Based Hybrids and Their Selectivity

| type of graphene | molecules                     | tested gases  | observed selectivity              | ref |
|------------------|-------------------------------|---|-----------------------------------|-----|
| rGO              | 3-CuPc                        | CO <sub>2</sub> , H <sub>2</sub> , CH <sub>4</sub> , CO   | NH <sub>3</sub>                   | 18  |
| rGO              | cpoPcCo                       | CO <sub>2</sub> , H <sub>2</sub> , CH <sub>4</sub> , CO, N <sub>2</sub> , VOCs  | NH <sub>3</sub>                   | 19  |
| rGO              | cmpoPcCo                      | CO <sub>2</sub> , H <sub>2</sub> , CH <sub>4</sub> , CO, N <sub>2</sub> , VOCs  | NH <sub>3</sub>                   | 19  |
| rGO              | poPcCo                        | CO <sub>2</sub> , H <sub>2</sub> , CH <sub>4</sub> , CO, N <sub>2</sub> , VOCs  | NH <sub>3</sub>                   | 19  |
| rGO              | mpoPcCo                       | CO <sub>2</sub> , H <sub>2</sub> , CH <sub>4</sub> , CO, N <sub>2</sub> , VOCs  | NH <sub>3</sub>                   | 19  |
| rGO              | ABOPcCo                       | Methanol, ethanol, acetone; dichloromethane; trichloromethane; carbon tetrachloride; toluene; tetrahydrofuran; propionic acid; diethyl ether, ethyl acetate | NH <sub>3</sub>                   | 20  |
| rGO              | APcCo                         | Methanol, ethanol, acetone; dichloromethane; trichloromethane; carbon tetrachloride; toluene; tetrahydrofuran; propionic acid; diethyl ether, ethyl acetate | NH <sub>3</sub>                   | 20  |
| rGO              | CuPc                          | CO <sub>2</sub> , H <sub>2</sub> , CH <sub>4</sub> , CO   | NH <sub>3</sub>                   | 21  |
| rGO              | NiPc                          | CO <sub>2</sub> , H <sub>2</sub> , CH <sub>4</sub> , CO   | NH <sub>3</sub>                   | 21  |
| rGO              | PbPc                          | CO <sub>2</sub> , H <sub>2</sub> , CH <sub>4</sub> , CO   | NH <sub>3</sub>                   | 21  |
| rGO              | TBPOCuPc                      | NO <sub>2</sub> , H <sub>2</sub> , CO   | NH <sub>3</sub>                   | 22  |
| rGO              | TBPONiPc                      | NO <sub>2</sub> , H <sub>2</sub> , CO   | NH <sub>3</sub>                   | 22  |
| CVD              | Co(tpfpp)<br>ClO <sub>4</sub> | Hexane, ethanol, H <sub>2</sub> O, chloroform, acetonitrile   | NH <sub>3</sub>                   | 11  |
| CVD              | CoOEP                         | H <sub>2</sub>  | NH <sub>3</sub>                   |     |
| CVD              | PPy                           | Acetone, water, benzene, toluene, ethanol, naphthalene, chloroform, methanol  | NH <sub>3</sub> , NO <sub>2</sub> | 16  |
| CVD              | PPy                           | Formaldehyde, NO <sub>2</sub>   | NH <sub>3</sub>                   | 17  |
| rGO              | PPy                           | Toluene, formaldehyde, methanol, ethanol  | NH <sub>3</sub>                   | 24  |
| rGO              | PPy                           | Formaldehyde, H <sub>2</sub>  | NH <sub>3</sub> , NO <sub>2</sub> | 26  |
| rGO              | ANS                           | NH <sub>3</sub> , methanol, ethanol, acetone, Cl <sub>2</sub>   | NO <sub>2</sub>                   | 27  |
| rGO              | 4AQ                           | Acetone, NH <sub>3</sub> , Cl <sub>2</sub>  | NO <sub>2</sub>                   | 28  |
| rGO              | CuPc                          | NO, NH <sub>3</sub>   | NO <sub>2</sub>                   | 23  |

ppm to 20 ppm), showing linear correlation between the response and NO<sub>2</sub> concentration. In addition, the sensor demonstrated selectivity toward NO<sub>2</sub>, while showing low response for other gases such as nitrogen dioxide, ammonia, methanol, ethanol, acetone, and chlorine as presented in Figure 8b. DFT calculations found that the donor- $\pi$ -acceptor nature of the ANS molecule facilitates the electron migration, controlling the electrical conductivity of graphene. The extra electrons present on the NH<sub>3</sub> group cause the activation of  $\pi$ -electrons on the graphene surface and enhance the charge transfer from graphene to the ANS molecule in the presence of NO<sub>2</sub>. Thus, the synergetic effect of the ANS/rGO hybrid leads to a high response to NO<sub>2</sub>. In a similar study, gas sensors based on rGO functionalized with D- $\pi$ -A molecules: 4HQ-4-hydroxyquino-

line and 4AQ-4-aminoquinoline were assessed.<sup>28</sup> The material preparation started by mixing GO water dispersions with D- $\pi$ -A molecules; then, hydrazine was added for obtaining the rGO hybrids. XPS characterization of the hybrids confirmed the presence of the N 1s peaks of the D- $\pi$ -A molecules suggesting that the molecules were assembled on top of graphene. The sensor response was evaluated for 10 ppm of NO<sub>2</sub>, and the functionalized rGO sensors were found to have a greater response in comparison with the bare rGO sensor. The selectivity in the presence of interferential gases (NH<sub>3</sub>, acetone, and Cl<sub>2</sub>) established that a higher selectivity is achieved for NO<sub>2</sub> when using the 4AQ/rGO sensor. DFT calculations assisted in determining the sensing mechanism, which was ascribed to the enhancement of charge transfer due to the high dipole moment



of 4AQ-rGO hybrids. NO<sub>2</sub> adsorption facilitates the transfer of graphene's  $\pi$  electrons to the dipolar molecules, enhancing the conductivity of the sensing material.

In Table 1, we summarize the gas sensing performance of the graphene-based hybrids. We focus specifically on the selectivity results from the literature for functionalized gas sensors, and we present a summary in Table 2.

## CONCLUSIONS AND OUTLOOK

In this mini-review, we surveyed the current progress in the development of selective graphene-based gas sensors by surface functionalization with aromatic molecules and polymers. The functionalized graphene sensors exhibit improved performance compared with those without functionalization in terms of selectivity, sensitivity, and limit of detection. Promising advances in increased selectivity have been achieved for some gases including NH<sub>3</sub>, NO<sub>2</sub>, and a variety of VOCs. Functionalization also leads to increased sensitivity, lowering the limit of detection and furthering the efforts for developing commercial technologies. Ammonia is so far the most studied analyte. From the surveyed literature, the cpoCoPc/rGO hybrid presented the lowest detection limit, down to 3.7 ppb of ammonia. On the other hand, at 50 ppm of ammonia, the hybrid ABOPcCo/rGO exhibited the higher response of 23.3%. While progress has been made in the field of functionalized graphene sensors, there remain open questions and challenges.

On the material preparation side, sensor to sensor variation remains a challenge. Standardized methods of graphene transfer and surface cleaning before functionalization are still lacking. Most studies do not present characterization studies of the graphene surface prior to the functionalization, which could be an important determining factor for the device performance. Once materials are prepared, typically spectroscopic techniques are used to infer the molecule–graphene interactions. More effort is needed to fully understand to what extent the surface functionalization is heterogeneous and what are the effects of the heterogeneity. Exploring different methods and parameters for molecular deposition, assisted by scanning probes, could provide such insights. More efforts are also needed for understanding the sensing mechanisms. Theoretical modeling will be invaluable in deciphering the complex charge transfer processes between analyte, functional molecules, and the graphene film. The ability to engineer selective hybrids by judiciously choosing grafted chemical species that target specific analytes will require a deeper understanding of the sensing mechanisms and the specific details of the interaction between the graphene hybrid and the gas analyte. The rapidly evolving field of selective graphene gas sensors will likely focus in the future on detecting other gases beyond the ones explored so far.

In that direction, the difficulty will be to develop methods for increasing the sensitivity toward less interacting analytes. Moreover, the response time of graphene hybrid sensors is less studied than sensitivity or selectivity, yet it can be a critical figure of merit in many applications. More work in understanding the fundamental limits of the response time as well as accurately measuring the response time in graphene sensors will be needed in the future.

One of the main challenges in validating the selectivity of graphene sensors is testing them in realistic conditions under the presence of gas mixtures. For example, environmental sensors should be able to detect a specific target gas in the presence of gases commonly found in air (CO<sub>2</sub>, H<sub>2</sub>, or humidity). In applications like breath analysis, biosensors should discern the

target analyte from gases like CO<sub>2</sub> and VOCs usually present in human breath. In future experiments, it will be important to design sensor testing schemes that provide informative data for selectivity under realistic conditions.

As the field of selective functionalized graphene sensors will evolve, we also anticipate that more efforts will be extended toward the design and implementation of device arrays patterned to detect several molecules at the same time. Combined with features that are already demonstrated such as mechanical flexibility, selectivity, and sensitivity, these chemical noses have the potential to become next-generation environmental monitors.

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### Notes

The authors declare no competing financial interest.

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## LIST OF ABBREVIATIONS

3-CuPc, 1,8,15,22-tetra-iso-pentyloxyphthalocyanine copper  
Co(tpfpp)ClO<sub>4</sub>, 5,10,15,20-tetrakis(pentafluorophenyl) porphyrinato cobalt(III) perchlorate  
cmpoPcCo, tetra- $\beta$ -(4-carboxy-3-methoxyphenoxy) phthalocyanine cobalt  
cpoPcCo, tetra- $\beta$ -carboxylphenoxyphthalocyanine cobalt  
poPcCo, tetra- $\beta$ -phenoxyphthalocyanine cobalt  
mpoPcCo, tetra- $\beta$ -(3-methoxyphenoxy) phthalocyanine cobalt

ABOPcCo, tetra- $\alpha$ -(*p*-aminobenzyloxy) phthalocyanine cobalt  
APcCo, tetra- $\alpha$ -aminophthalocyanine cobalt  
TBPOMPc, 1,8,15,22-tetra-(4-*tert*-butylphenoxy)-metallophtalocyanine  
CoOEP, 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphine cobalt(II)  
CoMP, 5,10,15,20-*meso*-tetrakis-nonadecylporphyrin cobalt(II)  
ZnTTPOH, 5-(4-hydroxyphenyl)-10,15,20-tri(*p*-tolyl) zinc porphyrin  
ANS, 5-aminonaphthalene-1-sulfonic acid  
4AQ, 4-aminoquinoline  
4HQ, 4-hydroxyquinoline

## REFERENCES

- (1) Hideo, A.; Mildred, S. D. *Physics of Graphene*, 1 ed.; Springer International Publishing: 2014.
- (2) Gupta Chatterjee, S.; Chatterjee, S.; Ray, A. K.; Chakraborty, A. K. Graphene-metal oxide nanohybrids for toxic gas sensor: A review. *Sens. Actuators, B* **2015**, *221*, 1170–1181.
- (3) Meng, F.-L.; Guo, Z.; Huang, X.-J. Graphene-based hybrids for chemiresistive gas sensors. *TrAC, Trends Anal. Chem.* **2015**, *68*, 37–47.
- (4) Wang, T.; Huang, D.; Yang, Z.; Xu, S.; He, G.; Li, X.; Hu, N.; Yin, G.; He, D.; Zhang, L. A Review on Graphene-Based Gas/Vapor Sensors with Unique Properties and Potential Applications. *Nano-Micro Lett.* **2016**, *8* (2), 95–119.
- (5) Shivananju, B. N.; Yu, W.; Liu, Y.; Zhang, Y.; Lin, B.; Li, S.; Bao, Q. The Roadmap of Graphene-Based Optical Biochemical Sensors. *Adv. Funct. Mater.* **2017**, *27* (19), 1603918.
- (6) Tian, W.; Liu, X.; Yu, W. Research Progress of Gas Sensor Based on Graphene and Its Derivatives: A Review. *Appl. Sci.* **2018**, *8* (7), 1118.
- (7) Nag, A.; Mitra, A.; Mukhopadhyay, S. C. Graphene and its sensor-based applications: A review. *Sens. Actuators, A* **2018**, *270*, 177–194.
- (8) Mackin, C.; Fasoli, A.; Xue, M.; Lin, Y.; Adebisi, A.; Bozano, L.; Palacios, T. Chemical sensor systems based on 2D and thin film materials. *2D Mater.* **2020**, *7* (2), 022002.
- (9) Tarcan, R.; Todor-Boer, O.; Petrovai, I.; Leordean, C.; Astilean, S.; Botiz, I. Reduced graphene oxide today. *J. Mater. Chem. C* **2020**, *8* (4), 1198–1224.
- (10) Georgakilas, V.; Otyepka, M.; Bourlinos, A. B.; Chandra, V.; Kim, N.; Kemp, K. C.; Hobza, P.; Zboril, R.; Kim, K. S. Functionalization of Graphene: Covalent and Non-Covalent Approaches, Derivatives and Applications. *Chem. Rev.* **2012**, *112* (11), 6156–6214.
- (11) Mackin, C.; Schroeder, V.; Zurutuza, A.; Su, C.; Kong, J.; Swager, T. M.; Palacios, T. Chemiresistive Graphene Sensors for Ammonia Detection. *ACS Appl. Mater. Interfaces* **2018**, *10* (18), 16169–16176.
- (12) Sawada, K.; Tanaka, T.; Yokoyama, T.; Yamachi, R.; Oka, Y.; Chiba, Y.; Masai, H.; Terao, J.; Uchida, K. Co-porphyrin functionalized CVD graphene ammonia sensor with high selectivity to disturbing gases: hydrogen and humidity. *Jpn. J. Appl. Phys.* **2020**, *59* (SG), SGGG09.
- (13) Pyo, S.; Choi, J.; Kim, J. Improved photo- and chemical-responses of graphene via porphyrin-functionalization for flexible, transparent, and sensitive sensors. *Nanotechnology* **2019**, *30* (21), 215501.
- (14) Iezhokin, I.; den Boer, D.; Offermans, P.; Ridene, M.; Elemans, J. A. A. W.; Adriaans, G. P.; Flipse, C. F. J. Porphyrin molecules boost the sensitivity of epitaxial graphene for NH<sub>3</sub> detection. *J. Phys.: Condens. Matter* **2017**, *29* (6), 065001.
- (15) Gajrush, A. S.; Surya, S. G.; Walawalkar, M. G.; Ravikanth, M.; Rao, V. R.; Subramaniam, C. Ultra-sensitive gas phase detection of 2,4,6-trinitrotoluene by non-covalently functionalized graphene field effect transistors. *Analyst* **2020**, *145* (3), 917–928.
- (16) Yoon, T.; Jun, J.; Kim, D. Y.; Pourasad, S.; Shin, T. J.; Yu, S. U.; Na, W.; Jang, J.; Kim, K. S. An ultra-sensitive, flexible and transparent gas detection film based on well-ordered flat polypyrrole on single-layered graphene. *J. Mater. Chem. A* **2018**, *6* (5), 2257–2263.
- (17) Tang, X.; Lahem, D.; Raskin, J.; Gérard, P.; Geng, X.; André, N.; Debliquy, M. A Fast and Room-Temperature Operation Ammonia Sensor Based on Compound of Graphene With Polypyrrole. *IEEE Sens. J.* **2018**, *18* (22), 9088–9096.
- (18) Zhou, X.; Wang, X.; Wang, B.; Chen, Z.; He, C.; Wu, Y. Preparation, characterization and NH<sub>3</sub>-sensing properties of reduced graphene oxide/copper phthalocyanine hybrid material. *Sens. Actuators, B* **2014**, *193*, 340–348.
- (19) Guo, Z.; Wang, B.; Wang, X.; Li, Y.; Gai, S.; Wu, Y.; Cheng, X. A high-sensitive room temperature gas sensor based on cobalt phthalocyanines and reduced graphene oxide nanohybrids for the ppb-levels of ammonia detection. *RSC Adv.* **2019**, *9* (64), 37518–37525.
- (20) Wang, B.; Wang, X.; Li, X.; Guo, Z.; Zhou, X.; Wu, Y. The effects of amino substituents on the enhanced ammonia sensing performance of PcCo/rGO hybrids. *RSC Adv.* **2018**, *8* (72), 41280–41287.
- (21) Li, X.; Wang, B.; Wang, X.; Zhou, X.; Chen, Z.; He, C.; Yu, Z.; Wu, Y. Enhanced NH<sub>3</sub>-Sensitivity of Reduced Graphene Oxide Modified by Tetra- $\alpha$ -Iso-Pentyloxymetallophthalocyanine Derivatives. *Nanoscale Res. Lett.* **2015**, *10* (1), 373.
- (22) Yu, Z.; Wang, B.; Li, Y.; Kang, D.; Chen, Z.; Wu, Y. The effect of rigid phenoxy substituent on the NH<sub>3</sub>-sensing properties of tetra- $\alpha$ -(4-*tert*-butylphenoxy)-metallophtalocyanine/reduced graphene oxide hybrids. *RSC Adv.* **2017**, *7* (36), 22599–22609.
- (23) Kumar, S.; Kaur, N.; Sharma, A. K.; Mahajan, A.; Bedi, R. K. Improved Cl<sub>2</sub> sensing characteristics of reduced graphene oxide when decorated with copper phthalocyanine nanoflowers. *RSC Adv.* **2017**, *7* (41), 25229–25236.
- (24) Sun, J.; Shu, X.; Tian, Y.; Tong, Z.; Bai, S.; Luo, R.; Li, D.; Liu, C. Facile preparation of polypyrrole-reduced graphene oxide hybrid for enhancing NH<sub>3</sub> sensing at room temperature. *Sens. Actuators, B* **2017**, *241*, 658–664.
- (25) Tiwari, D. C.; Atri, P.; Sharma, R. Sensitive detection of ammonia by reduced graphene oxide/polypyrrole nanocomposites. *Synth. Met.* **2015**, *203*, 228–234.
- (26) Tang, X.; Raskin, J.-P.; Kryvutsa, N.; Hermans, S.; Slobodian, O.; Nazarov, A. N.; Debliquy, M. An ammonia sensor composed of polypyrrole synthesized on reduced graphene oxide by electropolymerization. *Sens. Actuators, B* **2020**, *305*, 127423.
- (27) Pei, W.; Zhang, T.; Wang, Y.; Chen, Z.; Umar, A.; Li, H.; Guo, W. Enhancement of charge transfer between graphene and donor- $\pi$ -acceptor molecule for ultrahigh sensing performance. *Nanoscale* **2017**, *9* (42), 16273–16280.
- (28) Jia, R.; Xie, P.; Feng, Y.; Chen, Z.; Umar, A.; Wang, Y. Dipole-modified graphene with ultrahigh gas sensibility. *Appl. Surf. Sci.* **2018**, *440*, 409–414.