A HYBRID GAS SENSOR BASED ON COMPOUND OF GRAPHENE WITH POLYPYRROLE

Xiaohui Tang[a,*], Driss Lahem[b], Jean-Pierre Raskin[a], Marc Debliquy[c]

[a]*ICTEAM, Université catholique de Louvain (UCL), Place du Levant, 3, 1348 Louvain-la-Neuve, Belgium*
[b]*Department of Materials Science, Materia Nova ASBL, 7000 Mons, Belgium*
[c]*Materials Science Department, University of Mons, 7000 Mons, Belgium*

Abstract

In this work, we design a new hybrid sensor in which graphene (G) combined with an ultrathin polypyrrole (PPy) layer is employed for the sensing layer. The sensor consists in a CVD grown graphene transferred on top of an insulator substrate and an ultrathin PPy layer deposited on graphene by electropolymerization. Here, the thin PPy layer with porous nature plays important roles for the sensor sensitivity, selectivity and response/recovery times. Graphene serves as a support material for the PPy electropolymerization and also provides the efficient pathway for electron transfer. The present sensor is used to detect ammonia (NH$_3$) and shows high response (in the ppm range) at room temperature. The sensor also exhibits a good selectivity for NH$_3$ compared with other interference gases and rather good immunity to humidity. The results indicate that the combination of PPy and G is a very promising as a chemical sensor material. Our research is beneficial forward the commercial design and fabrication of sensors fulfilling the specifications of praticalreal applications.

Keywords: **graphene; polypyrrole; hybrid sensor; ammonia**

1. Introduction

Ammonia (NH$_3$) is one of the most harmful pollutant gases. It injures the human skin, eyes, respiratory tract, liver and kidneys beyond 25 ppm concentration [1,2]. Moreover, NH$_3$ plays a decisive role in particulate matter (PM) formation. Most of NH$_3$ in our life environment is emitted directly or indirectly by chemical industries and human activities. Agriculture is responsible for 94% of the total NH$_3$ emissions in the EU in 2010 [3]. It was reported that the patients with renal disorders or ulcers exhale NH$_3$ concentration in the range from 0.8 to 14 ppm, while in normal subjects it is in the range of 0.15−1.8 ppm [4].

Although plenty of NH$_3$ sensors have been studied and investigated in the literature [5,6,7], it is still a great challenge to develop ultrasensitive sensing devices. Metal oxides, catalytic metals and conducting polymers were used as sensing materials in sensor preparations. Some of them may be expensive, high power consumption and operate at high temperature, or show low performance (such as short life time, low selectivity). Therefore, it is urgent need to develop NH$_3$ sensors which are sensitive, specific, reliable, cheap, and operating at room-temperature.

Graphene (G) has attracted much attention for the sensor applications. Single layer graphene with largest surface-to-volume ratio possesses the potential ability to detect a single molecule. Moreover, the high carrier mobility of graphene inherently ensures low electrical noise and power consumption. Graphene-based sensors have been exploited for detecting various types of gases, for example NH$_3$, NO$_2$, H$_2$, O$_2$, CO$_2$, CO, CH$_4$, SO$_2$, H$_2$S, and VOCs [8,9,10,11,12]. For the NH$_3$ sensors, the research works mainly focus on reduced graphene oxide (rGO). In this kind of sensors, the contact resistance between the metal electrodes and rGO makes the sensing

response complex and not well understood. The literature presents contradictory reports. Fowler *et al.* (2009) [13] claimed that the contact resistance does not play a significant role in their sensor response. While Lu *et al.* (2009) [14] believed that the contact resistance is likely to contribute to the overall sensing response since the Schottky barrier variation is induced by the adsorbates.

The conductivity of polymers, such as polypyrrole (PPy) can be easily controlled by redox reactions. Apart from that, PPy has shown high performance including high sensitivity for gases, environmental stability, and biocompatibility [15]. The most interesting feature of the PPy sensor is its ability to properly operate at room temperature. The first NH_3 sensor with PPy as sensing material goes back to 1983 by Nylander *et al.* [16]. They used the filter paper impregnated by PPy to measure the response to NH_3 vapor.

The compounds of rGO with PPy have been extensively exploited as electrode materials for electrochemical supercapacitors [17,18]. On the other hand, these materials can be used in gas sensors because of their high sensitivity, easy synthesis, and cost effectiveness [19]. Jang *et al.* (2013) [20] indicated that the improved sensitivity of the PPy/rGO sensor is mainly attributed to the effective electron transfer between NH_3 and PPy, as well as the efficient electron pathway in rGO. Tiwari *et al.* (2015) [21] found that incorporation of rGO into PPy improves not only the sensitivity but also the response time. Although the PPy/rGO sensor reported by Hu *et al.* (2014) [22] exhibits a good sensitivity and selectivity to NH_3, the sensor recovery is relatively slow (longer than 5h) in ambient condition. Recently, Xiang *et al.* (2015) [23] prepared a sensor with the compound of PPy and graphene nanoplatelets, which shows a resistance variation of 22.6% for 50 ppm NH_3.

We summarize in Table 1 the recently published NH_3 sensors based on PPy film, rGO, compounds of PPy and rGO, and related materials, operating at room temperature. The research of the hybrid sensors based on PPy and graphene focuses on rGO. According to our literature survey, we did not find the NH_3 sensors made by the compounds of the CVD grown graphene with PPy. In this work, we design a new NH_3 sensor, in which a very thin layer of PPy is deposited on the CVD grown graphene by electropolymerization. Hereafter, our sensor refers to the PPy/G sensor. The sensor sensitivity, selectivity, reproducibility, and stability are examined. The influence of humidity on the sensor resistance is also tested. The key parameters of our sensor are also listed in the table for comparison purpose.

Table 1. Summary of recent research results for NH_3 sensors based on PPy film, rGO, compounds of PPy and rGO, and related materials at room temperature.

Sensor Type	Sensing Material	Synthesis Method	Reponse Value	Detection Limit	Response Time	Recovery Time	Reference
IDA	Ppy film	Electropolymerization	55%/500ppm	8 ppm	>100 min	>120 min	[24]
IDA	Ppy+rGO	Chemical Reduction	2,4%/1ppb	1 ppb	1,4 s	76 s+IR	[22]
IDA	PPy film	Electropolymerization	16%/40ppm	3 ppm			[25]
IDA	PPy nanofibers	Chemicalpolymerization		10 ppm	10 s	25 s	[26]
IDA	PPyNTs+Ag	Chemicalpolymerization	54%/40ppm	10 ppm		500 s	[27]
IDA	G-PEDOT:PSS	Chemicalpolymerization	9,6%/500ppm	5 ppm	3 min	5 min	[28]
IDA	PPy+rGO	Chemical Reduction	22%/100ppm			310 s	[29]
IDA	PANi+rGO	Chemical Reduction	37,1%/50ppm	20 ppm	18 min	2 min	[30]
Chemiresistor	PPy+rGO	Chemical Oxidation	34,7%/500ppm	3 ppm	400 s		[21]
Chemiresistor	PPy NTs/NWs	Electropolymerization	10%/1,25ppm	1 ppm		> 40 min	[7]
Chemiresistor	Ppy+rGO	Chemicalpolymerization	102%/50ppm	1 ppm	36s	16s	[23]
Chemiresistor	PPy+MWCN	Chemical Oxidation	3,07%/200ppm		34 s	3 min	[31]
Chemiresistor	PPy NTs/NRs	Chemical Oxidation	44%/100ppm	20 ppm	5 min	5 min	[2]
Chemiresistor	PPy NW	Chemicalpolymerization	0,06%/1ppm	40 ppm	15 min		[32]
Chemiresistor	**PPy+G(CVD)**	**Electropolymerization**	**3.3%/1ppm**	**1 ppm**	**5 min**	**10 min**	**This work**

IDE: interdigitated electrodes, PANi: polyaniline, PPy: polypyrrole, rGO: reduced graphene oxide, NWs: nanowires, NRs: nanorods, NTs: nanotubes, MWCN: multi-walled carbon nanotubes. The rest of the abbreviations can be found in the related references.

2. Sensor fabrication and measurement setups

The PPy/G sensor fabrication consists of electrode building, graphene transfer, and PPy synthesis. A pair of Au electrodes is first defined on a SiO_2/Si substrate by lithography and lift-off process. Then the CVD grown graphene is transferred on top of the electrodes (see the insert of Fig. 1a). The PPy synthesis is carried out by electropolymerization at room temperature. The detail of the electropolymerization process can be found in our previous work [33]. Figure 1b illustrates the electropolymerization setup, in which the transferred graphene is used as the working electrode. The counter and reference electrodes are made of Pt and AgCl/Ag, respectively. When a voltage pulse is applied to the working electrode, a thin PPy layer (20 nm) is synthesized on the graphene surface. For comparison, a thicker PPy film (0.5 µm) is also synthesized by increasing the number of the voltage pulses under the same conditions. After gluing and wire bonding in a 24 pin dual-in-line package (Fig 1a), the sensor is ready for measurements. Figure 1c displays the setup of the sensing measurements. The sensor resistance is recorded with NH_3 diluted in humid air (50% relative humidity) at different concentrations from 1 to 5 ppm at room temperature. The relative change in resistance between the two electrodes is measured to investigate the sensor response, which is defined as $\Delta R/R_0 = (R - R_0)/R_0$, where R_0 and R are the sensor resistance before and after exposure to the target gas, respectively. The response time is defined as the time to reach 90% of the total measured resistance change, while the recovery time refers to the time required for recovering the measured resistance to 90% of its original value. The resistance measurements are performed at a DC bias of 0.6 V.
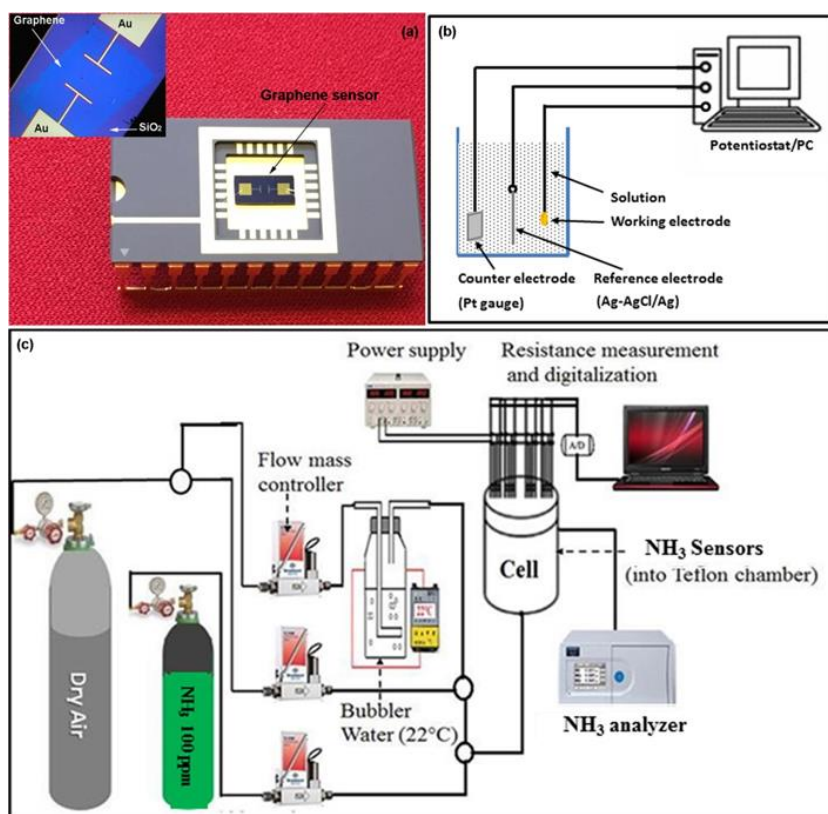

Figure 1: (a) A PPy/G sensor wire-bonded to 24 pin dual-in-line package; (b) an electropolymerization setup; and (c) a sensing measurement setup.

3. Results

3.1 Physical characterization

The morphology of the graphene surface and PPy/G compound is characterized by optical microscopy and scanning electron microscopy (SEM). Figure 2a shows the top-view optical microscopy image of graphene before the PPy synthesis. It can be seen that graphene is composed of isolated and contiguous hexagonal flakes [34]. Most part of graphene is single layer. Bilayer and triple layer graphene are found in certain regions. Figure

2b exhibits the top-view SEM image of the PPy/G compound. The thin PPy layer has a thickness of about 20 nm. Some small cavities can be observed in the PPy surface.
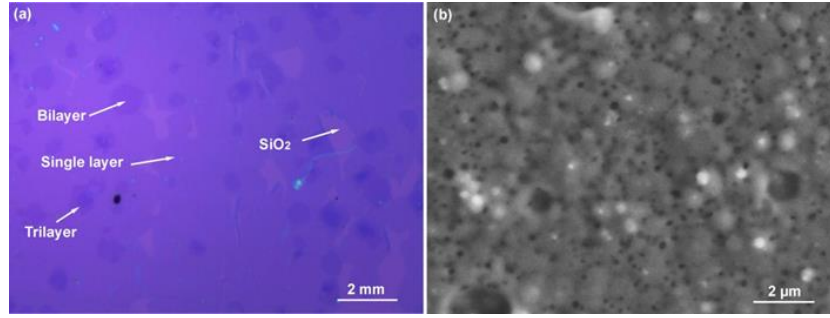

Figure 2: (a) A top-view optical microscopy image for graphene before the PPy synthesis; and (b) a top-view SEM image of the PPy/G compound, showing a porous nature.

3.2 Resistance response

Figure 3a shows the resistance response after the PPy/G sensor is exposed to three cycles of 5 ppm NH_3. The NH_3 exposure time is 10 min, followed by 10 min of purge with humid air. The sensor has a repeatable response of about 10%, suggesting a good repeatability. The response and recovery times of the sensor are estimated to be about 5 and 10 min, respectively. Moreover, the resistance response maintains unchanged after two months, indicating a good stability. Figure 3b presents the resistance responses to different concentrations of NH_3. A resistance response of 3.3% is obtained for 1 ppm NH_3. Figure 2c plots the resistance response as a function of NH_3 concentration. The resistance response is linearly dependent on the NH_3 concentration from 1 to 5 ppm. Figure 3d gives the resistance response for the PPy/G sensor with a PPy thickness of 20 nm and the pure 0.5-μm-thick PPy sensor. The resistance response of the latter is shifted for comparison purpose in the figure. Although the resistance response of the PPy/G sensor is weaker than that of the pure PPy sensor, the former has faster response/recovery times than the latter. The reason will be discussed in section 4. To completely and rapidly recover the pure PPy sensor to its initial state, ultraviolet, or infrared illumination, or elevated temperature is needed for accelerating the desorption of NH_3 molecules.
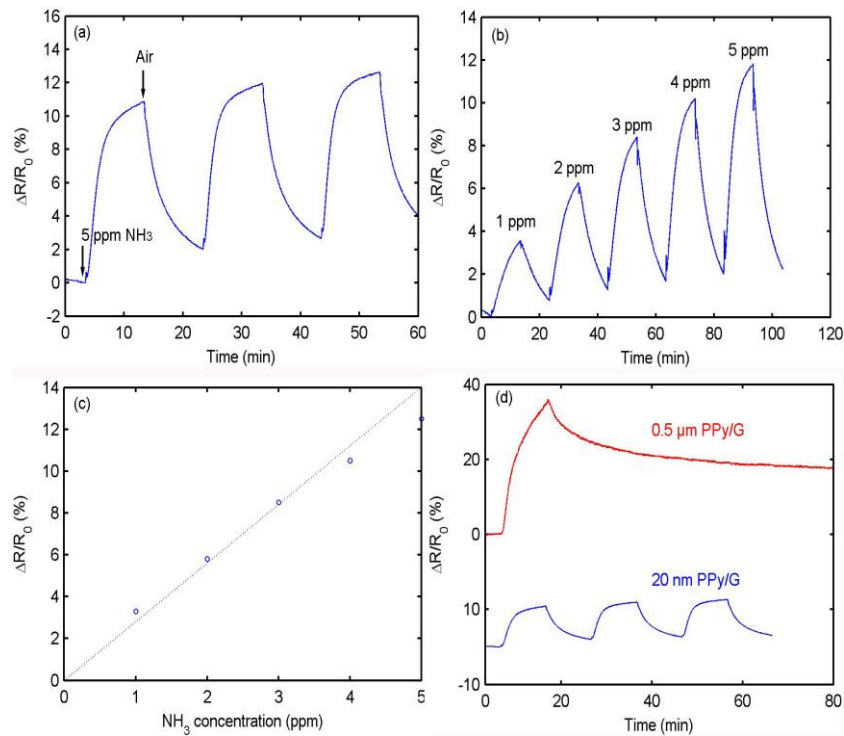

Figure 3: Resistance response of a typical PPy/G sensor at 20°C and at relative humidity of 50%: (a) for 5 ppm NH_3; (b) for NH_3 concentration in a range from 1 to 5 ppm; (c) the resistance response as a founction of NH_3 concentration; and (d) for the PPy/G sensor with a PPy thickness of 20 nm and the pure 0.5-μm-thick PPy sensor to detect 5 ppm NH_3.

3.3 Selectivity

To investigate the PPy/G sensor selectivity, formaldehyde (CH_2O) and nitrogen dioxide (NO_2) are chosen as the interference gases. Figure 4 presents the resistance response of the sensor exposed to 5 ppm CH_2O and NO_2. For comparison, the resistance response of the sensor exposed to 5 ppm NH_3 is also given in the figure. For the cases of CH_2O and NO_2, a visible resistance response is not observed except for some abnormal resistance changes. This confirms that the PPy/G sensor has a good selectivity to NH_3 compared with CH_2O and NO_2. In addition, the PPy/G sensor also shows much higher resistance response compared to the pure graphene sensor. Fu *et al.* (2017) [35] indicated that the weak response of the pure graphene sensor for NH_3 is due to its chemically inert and free of dangling bonds. Particularly, the initial state of the pure graphene sensor can only be recovered by heating in vacuum.
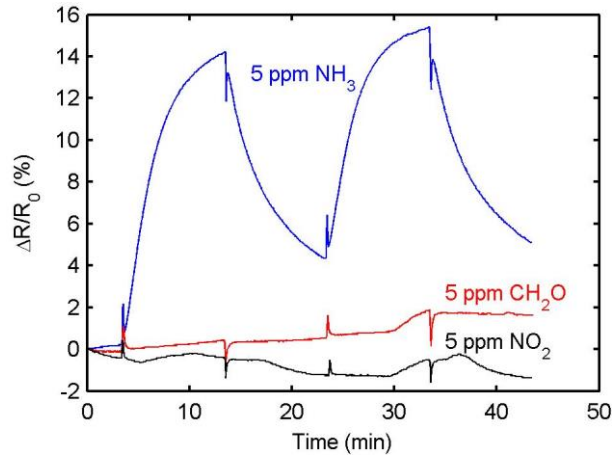

Fig. 4: Resistance response of the PPy/G sensor for 5 ppm NH_3, CH_2O and NO_2, at 20°C and at relative humidity of 50%.

3.4 Humidity influence

We test the influence of relative humidity (RH) variations on the PPy/G sensor. As shown in Figure 5a, the resistance variation is about 2% for relative humidity change in the range from 20 to 80%. Specifically, a relative humidity change of 10% brings a resistance response variation of 0.3% in average (in Figure 5b). This value is much smaller than the resistance response of 3.3% obtained for 1 ppm. When relative humidity is higher than 80%, the sensor resistance increases significantly (about 20%). However, the relative humidity of real-life condition is between 20 to 80%, we can conclude that the present sensor has a good immunity to humidity.
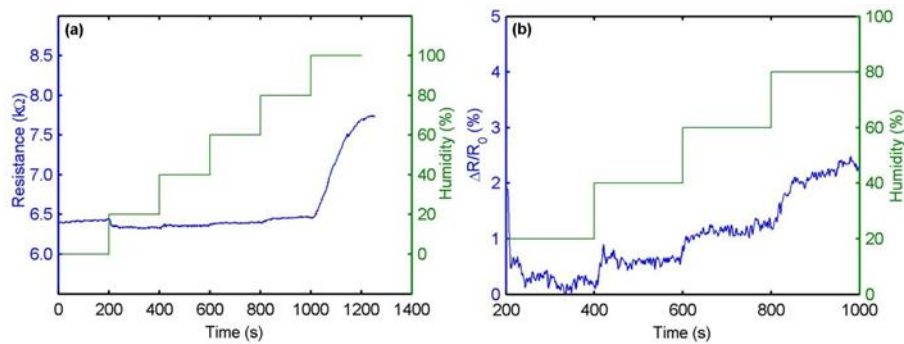

Figure 5: Influence of humidity on the PPy/G sensor: (a) resistance behavior in the range from 0 to 100% RH; and (b) resistance variation in the range from 20 to 80% RH at room temperature.

4. Discussion

When the PPy/G sensor is exposed to NH_3 gas, its resistance is increased. This is attributed to the charge transfer between NH_3 molecules and the PPy/G sensor surface [36]. According to our previews work, the PPy layer and as-transferred graphene act as p-type semiconductors. Based on the Hall measurements, Schedin $et\ al.$ (2007) [37] reported that NH_3 is an electronic donating gas. The adsorption of NH_3 on the PPy/G sensor surface induces the interaction between the NH_3 molecules and the PPy/G compound. The electron transfer from NH_3 molecules to the compound reduces or depletes the number of holes in the PPy/G compound, thereby the resistance enhancement.

The PPy/G sensor performance, such as the sensitivity and response/recovery times, is related to the PPy thickness and its morphology. The ultrathin PPy layer on top of graphene is deposited by electropolymerization which provides a homogenous and porous nature. The cavities existing in the ultrathin PPy layer allow the NH_3 molecules to quickly come into the PPy/G compound and react with it. This interaction is reversible. The thick PPy film provides more reactive sites for the adsorption of NH_3 molecules, leading to a better resistance response. However, the NH_3 molecules desorption from the thick PPy film is slower due to the non-hollow structure and longer diffusion pathways. This translates to longer response/recovery times. The idea feature of the PPy layer should be a single layer with uniform porosities, which expose all of its chemical bonds to the environment or the target molecules.

Additional hole donors NO_2 should enhance hole density in the existing p-type PPy/graphene compound and generate a significant decrease in resistance, while additional electron donors CH_2O should cause depletion of holes and hence raise in the resistance [38]. However, a significant change in resistance is not observed in Figure 4. This is contruduted to the fact that both NO_2 and CH_2O molecules have no the related interaction with PPy. In addition, Schedin $et\ al.$ (2007) indicated that graphene can make the interaction with various molecules, including NO_2 and CH_2O. The presence of the thin PPy layer hinders the interaction between interference gases and graphene. These suggests that the thin PPy serves as a filter, greatly improving the selectivity of the present sensor.

It was reported that the resistance of graphene functionalized by carboxylic increases with humidity due to its hydrophilic nature [39]. However, almost all the PPy/G sensor surface is uniformly covered by PPy, which is generally stable at low humidity and low temperature. This may explain that the PPy/G sensor is less influence by relative humidity in the range 20 to 80%. However, higher relative humidity influences the PPy performance [40], thus the PPy/G sensor is heavily affected at high humid environment (RH > 80%).

It is emphasizing that graphene under the PPy layer eases the transport of charge carriers due to its high mobility. Apart from that, fewer PPy molecules on the graphene surface allow the NH_3 molecules pass through the cavities to react with sp^2-bonded carbon of graphene. The synergistic effect may multiply the reaction between NH_3 and the PPy/G compound, thereby increasing the sensor sensitivity. The incorporation of graphene accelerates the reaction of PPy to NH_3 [28], shortening the response/recovery times. Moreover, the low contact resistance between graphene and Au results in signal/noise ratio, further improving the sensor performance.

Conclusion

In this work, we develop a new sensor, in which a very thin layer of PPy is synthesized on top of the CVD grown graphene by electropolymerization. The sensor shows a resistance response of 3.3% for 1 ppm NH_3. The response time and recovery time are 5 and 10 min, respectively. The ultrathin PPy layer with porous nature plays important roles for the sensitivity, selectivity and response/recovery times of the PPy/G sensor. Graphene serves as a support material for the PPy electropolymerization, provides the efficient pathway for electron transfer, and improves the sensor performance. Our results indicate that the PPy/G compound is interesting as a chemical sensor material. Further work is required to optimize electropolymerization conditions for targeting the practical sensing applications and commercial fabrication.

Acknowledgments

References

[1] Risby, T.H., Solga, S.F., 2006. Current status of clinical breath analysis. Applied Physics B 85, 421–426.

[2] Ishpal, Kaur, A., 2013. Spectroscopic investigations of ammonia gas sensing mechanism in polypyrrole nanotubes/nanorods. Journal of Applied Physics 113, 094504.

[3] European Environment Agency, http://www.eea.europa.eu/

[4] Chartuprayoon, N., Hangarter, C.M., Rheem, Y., Jung, H., Myung, N.V., 2010. Wafer-Scale Fabrication of Single Polypyrrole Nanoribbon-Based Ammonia Sensor. The Journal of Physical Chemistry C 114, 11103–11108.

[5] Timmer, B., Olthuis, W., Berg, A. van den, 2005. Ammonia sensors and their applications—a review. Sensors and Actuators B: Chemical 107, 666–677.

[6] Šetka, M., Drbohlavová, J., Hubálek, J., 2017. Nanostructured Polypyrrole-Based Ammonia and Volatile Organic Compound Sensors. Sensors 17, 562.

[7] Piraux, L., Antohe, V.-A., Ferain, E., Lahem, D., 2016. Self-supported three-dimensionally interconnected polypyrrole nanotubes and nanowires for highly sensitive chemiresistive gas sensing. RSC Adv. 6, 21808–21813.

[8] Chen, C.W., Hung, S.C., Yang, M.D., Yeh, C.W., Wu, C.H., Chi, G.C., Ren, F., Pearton, S.J., 2011. Oxygen sensors made by monolayer graphene under room temperature. Applied Physics Letters 99, 243502.

[9] Hong, J., Lee, S., Seo, J., Pyo, S., Kim, J., Lee, T., 2015. A Highly Sensitive Hydrogen Sensor with Gas Selectivity Using a PMMA Membrane-Coated Pd Nanoparticle/Single-Layer Graphene Hybrid. ACS Applied Materials & Interfaces 150209062057005.

[10] Pandey, P.A., Wilson, N.R., Covington, J.A., 2013. Pd-doped reduced graphene oxide sensing films for H_2 detection. Sensors and Actuators B: Chemical 183, 478–487.

[11] Huang, L., Zhang, Z., Li, Z., Chen, B., Ma, X., Dong, L., Peng, L.-M., 2015. Multifunctional Graphene Sensors for Magnetic and Hydrogen Detection. ACS Applied Materials & Interfaces 7, 9581–9588.

[12] Tang, X., Mager, N., Vanhorenbeke, B., Hermans, S., Raskin, J.-P., 2017. Defect-free functionalized graphene sensor for formaldehyde detection. Nanotechnology 28, 055501.

[13] Fowler, J.D., Allen, M.J., Tung, V.C., Yang, Y., Kaner, R.B., Weiller, B.H., 2009. Practical Chemical Sensors from Chemically Derived Graphene. ACS Nano 3, 301–306.

[14] Lu, G., Ocola, L.E., Chen, J., 2009. Reduced graphene oxide for room-temperature gas sensors. Nanotechnology 20, 445502.

[15] Zaidi, S.A., Shin, J.H., others, 2014. Molecularly imprinted polymer electrochemical sensors based on synergistic effect of composites synthesized from graphene and other nanosystems. International Journal of Electrochemical Science 9, 4598–4616.

[16] Nylander, C., Armgarth, M., Lundstrôm, I., 1983. An ammonia detector based on a conducting polymer. Anal. Chem. Symp. Ser 17, 203-207.

[17] Sahoo, S., Dhibar, S., Hatui, G., Bhattacharya, P., Das, C.K., 2013. Graphene/polypyrrole nanofiber nanocomposite as electrode material for electrochemical supercapacitor. Polymer 54, 1033–1042.

[18] de Oliveira, H.P., Sydlik, S.A., Swager, T.M., 2013. Supercapacitors from Free-Standing Polypyrrole/Graphene Nanocomposites. The Journal of Physical Chemistry C 117, 10270–10276.

[19] Whitby, R.L.D., Korobeinyk, A., Mikhalovsky, S.V., Fukuda, T., Maekawa, T., 2011. Morphological effects of single-layer graphene oxide in the formation of covalently bonded polypyrrole composites using intermediate diisocyanate chemistry. Journal of Nanoparticle Research 13, 4829–4837.

[20] Jang, W.-K., Yun, J., Kim, H.-I., Lee, Y.-S., 2013. Improvement of ammonia sensing properties of polypyrrole by nanocomposite with graphitic materials. Colloid and Polymer Science 291, 1095–1103.

[21] Tiwari, D.C., Atri, P., Sharma, R., 2015. Sensitive detection of ammonia by reduced graphene oxide/polypyrrole nanocomposites. Synthetic Metals 203, 228–234.

[22] Hu, N., Yang, Z., Wang, Y., Zhang, L., Wang, Y., Huang, X., Wei, H., Wei, L., Zhang, Y., 2014. Ultrafast and sensitive room temperature NH_3 gas sensors based on chemically reduced graphene oxide. Nanotechnology 25, 025502.

[23] Xiang, C., Jiang, D., Zou, Y., Chu, H., Qiu, S., Zhang, H., Xu, F., Sun, L., Zheng, L., 2015. Ammonia sensor based on polypyrrole–graphene nanocomposite decorated with titania nanoparticles. Ceramics International 41, 6432–6438.

[24] Carquigny, S., Sanchez, J., Berger, F., Lakard, B., Lallemand, F., 2009. Ammonia gas sensor based on electrosynthesized polypyrrole films. Talanta 78, 199–206.

[25] Patois, T., Sanchez, J.-B., Berger, F., Rauch, J.-Y., Fievet, P., Lakard, B., 2012. Ammonia gas sensors based on polypyrrole films: Influence of electrodeposition parameters. Sensors and Actuators B: Chemical 171–172, 431–439.

[26] Wang, W., Li, Z., Jiang, T., Zhao, Z., Li, Y., Wang, Z., Wang, C., 2012. Sulfonated Poly(ether ether ketone)/Polypyrrole Core–Shell Nanofibers: A Novel Polymeric Adsorbent/Conducting Polymer Nanostructures for Ultrasensitive Gas Sensors. ACS Applied Materials & Interfaces 4, 6080–6084.

[27] Yang, X., Li, L., Yan, F., 2010. Polypyrrole/silver composite nanotubes for gas sensors. Sensors and Actuators B: Chemical 145, 495–500.

[28] Seekaew, Y., Lokavee, S., Phokharatkul, D., Wisitsoraat, A., Kerdcharoen, T., Wongchoosuk, C., 2014. Low-cost and flexible printed graphene–PEDOT:PSS gas sensor for ammonia detection. Organic Electronics 15, 2971–2981.

[29] Wang, Y., Zhang, L., Hu, N., Wang, Y., Zhang, Y., Zhou, Z., Liu, Y., Shen, S., Peng, C., 2014. Ammonia gas sensors based on chemically reduced graphene oxide sheets self-assembled on Au electrodes. Nanoscale research letters 9, 1–12.

[30] Huang, X., Hu, N., Zhang, L., Wei, L., Wei, H., Zhang, Y., 2013. The NH_3 sensing properties of gas sensors based on aniline reduced graphene oxide. Synthetic Metals 185–186, 25–30.

[31] Bachhav, S.G., Patil, D.R., 2015. Study of Polypyrrole-Coated MWCNT Nanocomposites for Ammonia Sensing at Room Temperature. Journal of Materials Science and Chemical Engineering 03, 30–44.

[32] Hernandez, S.C., Chaudhuri, D., Chen, W., Myung, N.V., Mulchandani, A., 2007. Single Polypyrrole Nanowire Ammonia Gas Sensor. Electroanalysis 19, 2125–2130.

[33] André, D., Krumpmann, A., Debliquy, M., Lahem, D., 2016. Nanostructured TiO_2 Layers for Photovoltaic and Gas Sensing Applications, in "Green Nanotechnology - Overview and Further Prospects". In: Marcelo L. Larramendy and Sonia S. (ED.). InTech, http://www.intechopen.com/books/green-nanotechnology-overview-and-further-prospects/nanostructured-tio2-layers-for-photovoltaic-and-gas-sensing-applications.

[34] Tang, X., Reckinger, N., Poncelet, O., Louette, P., Ureña, F., Idrissi, H., Turner, S., Cabosart, D., Colomer, J.-F., Raskin, J.-P., Hackens, B., Francis, L.A., 2015. Damage evaluation in graphene underlying atomic layer deposition dielectrics. Scientific Reports 5, 13523.

[35] Fu, W., Jiang, L., van Geest, E.P., Lima, L.M.C., Schneider, G.F., 2017. Sensing at the Surface of Graphene Field-Effect Transistors. Advanced Materials 29, 1603610.

[36] Latif, U., Dickert, F., 2015. Graphene Hybrid Materials in Gas Sensing Applications. Sensors 15, 30504–30524.

[37] Schedin, F., Geim, A.K., Morozov, S.V., Jiang, D., Hill, E.H., Blake, P., Novoselov, K.S., 2007. Detection of Individual Gas Molecules Absorbed on Graphene. Nature Materials 6, 652–655.

[38] Tang, X., Raskin, J.-P., Lahem, D., Krumpmann, A., Decroly, A., Debliquy, M., 2017. A Formaldehyde Sensor Based on Molecularly-Imprinted Polymer on a TiO_2 Nanotube Array. Sensors 17, 675.

[39] Jung, D., Han, M., Lee, G.S., 2014. Humidity-sensing characteristics of multi-walled carbon nanotube sheet. Materials Letters 122, 281–284.

[40] Cho, J.-H., Yu, J.-B., Kim, J.-S., Sohn, S.-O., Lee, D.-D., Huh, J.-S., 2005. Sensing behaviors of polypyrrole sensor under humidity condition. Sensors and Actuators B: Chemical 108, 389–392.