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# A Mini Review on the Development of Graphene and Polyaniline-Based Nano-Sensor for Pollutant Detection

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Along with industrial development, the demand for robust and portable sensors has been increasing over the past decade. Notably, current research has paid great attention on the design of miniature sensor based on nanoparticles. Graphene and polyaniline (PANI) are the two nanoparticles receiving intense research interest in this study field owing to their unique electrically conductive property. Fundamentally, the detection of pollutant using either graphene or PANI is following two simple steps, namely the exposure of the nano-sensor to the pollutant-containing environment, and monitoring of the change in electrical conductance of the nano-sensor. In this review, current application of graphene, PANI, and their nanocomposites on the detection of different types of pollutants was revisited. The latest developments regarding the nanoparticles, substrate, pollutant type, fabrication method, and performances were summarized and compared. Based on the summarized information, future directions in further advancing the application of these nano-sensors in the industry were proposed.

## 1. Introduction

Air pollution and water pollution have been persistent environmental issues happening over the whole world. Owing to this, the needs to monitor the concentration of various pollutants in the environment has been increasing along with industrialization. The common hazardous pollutants requiring monitoring include $NH_3$ (Yang et al., 2021), $NO_2$ (Yuan et al., 2022), $CO_2$ (Kanaparthi and Singh, 2019), $CH_4$ (Shaalan et al., 2019), acetone (Xu et al., 2020), $H_2S$ (Park et al., 2020), $H_2$ (Drmosh et al., 2019), humic acid (Yeap et al., 2020), methylene blue (Zhao et al., 2019), microalgae (Oloketuyi et al., 2020). Such pollutants not only affect the air and water qualities, but also cause negative impacts on human health when being inhaled or consumed. In specific, excessive $H_2S$ in the air can cause negative health effects, such as eye irritation, loss of smell, pulmonary edema, and loss of respiration (Aguilar-Dodier et al., 2020). On the other hand, consuming water contaminated with humic acid might lead to peripheral vasculopathy of blackfoot disease (Hseu et al., 2014). Thus, the detection and monitoring of various air and water pollutants are of great importance in protecting the environment as well as human health.

Various methods have been employed for detection of the aforementioned pollutants, such as gas chromatography (GC) (Sullivan et al., 2020), high-performance liquid chromatography (HPLC) (Hameedat et al., 2022), capillary electrophoresis (CE) (Roychoudhury et al., 2020), UV-vis spectrophotometry (Drašnar et al., 2019). However, those methods require costly and bulky equipment with complicated procedures which are not suitable for in-situ or online detection. Hence, it is imperative to develop simple, practical, and economic methods to ease the pollutant detection process. One of the possible strategies is to use conductive nanoparticles to detect the pollutant concentration based on the change of nanoparticle resistance. The tiny size of the nanoparticles enables further miniaturization of the sensor besides offering the advantage of being light-weight. Among electrically conductive nanoparticles, polyaniline (PANI) has been widely studied due to its unique properties, such as easy preparation, good stability, and excellent electrical conductivity which have been proven in various electrical devices and sensor applications (Zhang et al. 2017). On the other hand, reduced graphene oxide (rGO) is a novel two-dimensional nanoparticle. It contains more adsorption sites because of the oxygen functional groups attached on the graphene nanosheets (Zhang et al., 2019).

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This mini review aims to revisit the current development on the application of PANI, rGO, and their nanocomposites to detect various pollutants. The state of art of the pollutant-detecting nano-sensor is discussed from the aspects of nanoparticles, substrate, pollutant type, fabrication method, and performances (including the response, selectivity, response time, and recovery time). In the end, this mini review provides suggestions on future research directions.

## 2. Application of nano-sensor for pollutant detection

The idea of using electrically conductive nanoparticles for pollutants detection involves a straightforward concept, whereby the attachment of pollutant molecules onto the nanoparticles will change their conductance. Accordingly, the amount of pollutant in the targeted medium can be determined via the extent of change of the conductance value. The commonly used electrically conductive nanoparticles and their nanocomposites include pure PANI (Kroutil et al., 2018), PANI/$SrGe_4O_9$ (Zhang et al., 2020), graphene oxide (Chen et al., 2019), metal/graphene (Zhao et al., 2016), graphene (Song et al., 2017), fluorinated graphene oxide (Park et al., 2016), PANI/graphene (Hakimi et al., 2018), graphene oxide/PANI (Moshayedi et al., 2020), and rGO/PANI (Bai et al., 2015). Table 1 provides the summary of recent works on the application of nano-sensor based on PANI and its nanocomposites for detection of various pollutants. Meanwhile, Table 2 provides the summary of recent works on the application of nano-sensor based on graphene and its nanocomposites. Based on Table 1 and Table 2, the common substrates can be categorized into rigid type (e.g. glass, copper, silicon) and flexible type (e.g. cotton cloth, polyethylene terephthalate, polyimide). The pollutant being mostly studied is gas type (e.g. $NH_3$) instead of liquid type. It was also found that the performance of the sensor varies by the pollutant type as well as the structure of the nano-sensor.

As shown in Figure 1, Stanford et al. (2019) fabricated a laser-induced graphene (LIG)-based flexible gas sensor which can be embedded into cement to form a refractory composite material; this sensor is responsive to various types of gases including $CO_2$, Ar, He, and air. Based on Figure 1(c), LIG-based gas sensor exhibited a highest $\Delta R/R_o$ (%) towards He, following with air, $CO_2$, and Ar.

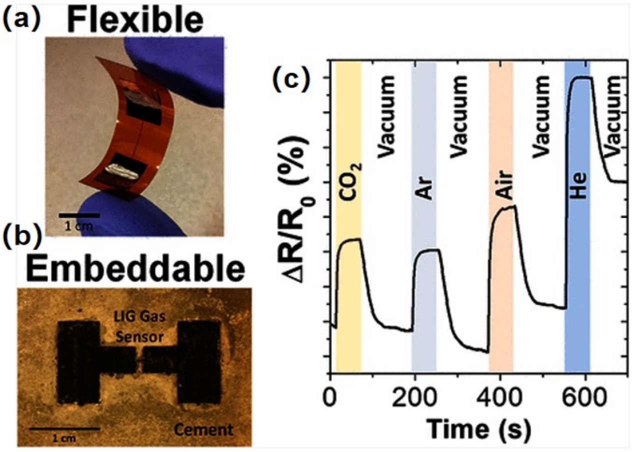

*Figure 1: Image of (a) LIG-based gas sensor on polyimide substrate, (b) LIG sensor embedded in cement, and (c) $\Delta R/R_o$ (%) of LIG-based gas sensor towards various gases (Reprinted with permission from Stanford et al. (2019). Copyright (2019). American Chemical Society)*

Bai et al. (2015) have developed a rGO-PANI nanocomposite for $NH_3$ detection. The nanocomposite was loaded onto flexible PET films. Comparison was done between PANI-PET films and rGO-PANI-PET films by exposing both types of sensor to $NH_3$ (10–100 ppm) at room temperature. Results showed that at 100 ppm of $NH_3$, the sensing response of PANI-PET film was 6.7 while the highest sensing response was up to 344.2 for rGO-PANI (1.0 wt% of rGO)-PET film. Such sensing response of rGO-PANI (1.0 wt% of rGO)-PET film was 51 times better than that of the PANI-PET film. Apparently, the hybrid of PANI and rGO has offered a synergistic improvement on the sensing properties. One possible reason is the electron transfer between PANI and rGO via $\pi$-$\pi$ interaction during the sensing process which enhances the response of the hybrid sensor. Based on their study, the optimum amount of rGO in rGO-PANI hybrid was 1.0 wt%.

In addition, Hakimi et al. (2018) studied an $NH_3$ nano-sensor fabricated with a hybridization of PANI and nitrogen-doped graphene quantum dots. They also utilized two types of metals which were Ag and Al to serve as electrodes of the sensing films. Furthermore, they studied the sensing response of 50 wt% nitrogen-doped graphene quantum dots/PANI sensors with Ag and Al electrodes under various $NH_3$ concentration. The results showed that the sensing response increased with the increasing $NH_3$ concentration from 10 ppm to 1500 ppm. This is because the amount of the molecules attaching onto the sensing site of the film increased with the increasing concentration of the gas (Sengupta et al., 2006). On the other hand, by comparing the Al electrode and the Ag electrode, it shows that the nano-sensor with Ag electrode exhibited a better sensing response to $NH_3$. This is due to the ohmic junction between the sensing film and the Ag electrode which promotes the sensing effect.

*Table 1: Summary of the recent works on the application of nano-sensor based on PANI and its nanocomposites for the detection of various types of pollutant*

| Nanoparticles | Substrate | Pollutant | Methods | Performance | Reference |
|---|---|---|---|---|---|
| Pure PANI | 100 % cotton cloth | $NH_3$ | Dip coat | • An increase in electrical resistance of the PANI-modified cotton was detected when the $NH_3$ concentration was increased from 25 to 100 ppm. | (Swe et al., 2018) |
| PANI/N-GQDs (nitrogen-doped graphene quantum dots) | Polyethylene terephthalate (PET) | $NH_3$ | Drop-cast PANI and N-GQDs were hybridized and served as the sensing film. | • The sensor of (50 wt%) PANI/N-GQDs with Ag electrode exhibited the highest sensing response of 110.92 to 1500 ppm $NH_3$ under room temperature. | (Hakimi et al., 2018) |
| PANI/MWCNT (multi-walled carbon nanotubes) | Polypropylene fabric | $NH_3$ | Spray coat | • The response and the recovery time of the nano-sensor were 9 s and 30 s.<br>• The sensing response increased slowly from 24 to 44 °C, then gradually decreased with further increasing temperature. | (Maity and Kumar, 2018) |
| PANI/DBSA (Dodecyl benzene sulphonic acid) | Prefabricated interdigitated Pt patterned glass | $NH_3$ | Spin coating | • The response time and recovery time of PANI/DBSA sensor towards 300 ppm of $NH_3$ are 6 s and 37 s . | (Yadav et al., 2019) |
| PANI/Cu-BTC (copper (II)-benzene-1,3,5-tricarboxylate) | Quartz crystal microbalance (QCM) | $H_2$ | Intense pulsed light (IPL) | • The response of PANI/Cu-BTC sensor is 5.2 times higher than the one of Cu-BTC sensor towards 40 to 160 ppm of $H_2$. | (Abuzalat et al., 2019) |
| PANI/$SnO_2$, PANI/$TiO_2$, PANI/CNT (carbon nanotubes) | Flexible PCB substrate Kapton | $NH_3$, $CO_2$, $O_2$, $NO_2$ | Direct deposition using micropipette | • PANI/$SnO_2$ and PANI/$TiO_2$ indicate a lower sensitivity to $NH_3$, but with complete reversibility. On the other hand, PANI/CNT has the lowest sensitivity to $NH_3$. | (Kroutil et al., 2018) |
| PANI/$SrGe_4O_9$ | Polyimide | $NH_3$ | In situ chemical oxidation polymerization process | • Long-term stability of the flexible PANI/$SrGe_4O_9$ nanocomposite sensor towards 0.2 ppm and 2 ppm of $NH_3$ was recorded over a period of 28 d. | (Zhang et al., 2020) |

*Table 2: Summary of the recent works on the application of nano-sensor based on graphene and its nanocomposites for the detection of various types of pollutant*

| Nanoparticles | Substrate | Pollutant | Methods | Performance | Reference |
|---|---|---|---|---|---|
| Graphene | Copper | $NH_3$ | Direct growth<br>Low pressure chemical vapour deposition (CVD) | • $NH_3$ concentration was analysed from 200 to 12,500 ppm.<br>• The sensitivity of monolayer graphene was higher than the one of the stacking one. | (Song et al., 2017) |
| Ti/Graphene | p-type silicon substrate | $NH_3$ | Direct growth<br>Chemical vapour deposition (CVD) | • $NH_3$ concentration was analysed from 20 to 400 ppm.<br>• Visible light illumination resulted in significant increase in sensitivity but shortened their corresponding recovery time. | (Zhao et al., 2017) |
| Au/graphene, Ag/graphene, Pt/graphene, Pd/graphene, Ti/graphene, Al/graphene, graphene | p-type silicon substrate | $NO_2$ | Direct growth<br>Chemical vapour deposition (CVD) | • Pt/graphene device was outstanding among all devices.<br>• It was found that all of the fabricated sensors (except Ti/graphene) experienced saturation in sensitivity at $NO_2$ concentration > 2 ppm. | (Zhao et al., 2016) |
| Fluorinated graphene oxide (GO) | $SiO_2$/Si wafer | $NH_3$ | Drop cast | • Fluorination improved the sensitivity of GO-based gas sensors. This is because the fluorine on GO surface enhanced the interaction with $NH_3$.<br>• $NH_3$ concentration was analysed from 100 to 1,000 ppm. | (Park et al., 2016) |
| Reduced graphene oxide (rGO) | Polyethylene terephthalate (PET) | Isoprene and hydrothion | Electrochemical-assisted deposition (ECAD) | • It was found that the graphene film's thickness can affect the sensor's sensitivity. | (Chen et al., 2019) |

## 3. Conclusions and future outlooks

In this review, recent progress in the development of PANI-based and graphene-based nano-sensors for various pollutant detection has been introduced along with the nanoparticles, substrate, pollutant type, fabrication method, and performances. Compared to the abundant research on gaseous pollutants, study on water-based pollutants (such as humic acid, heavy metal ions, microalgae, and dyes) is limited (Table 3) and deserves more attention from the researchers. The main challenge associated with the detection of water-based pollutant using nano-sensors could be the potential disruption of the electrical conductance by the water molecules. In particular, to what extent is the sensitivity and consistency of the sensor under liquid condition is still open for investigation. On the other hand, current research direction has shifted from rigid substrate-based sensor to flexible substrate-based sensor (such as polyimide, polyethylene terephthalate, and polyethylene naphthalate) for the potential application in wearable devices. In this regard, the type of flexible substrate as well as the binding strength of the nanoparticles on the substrate are worthy of exploration. Besides graphene and PANI, other emerging 2-dimensional nanoparticles with unique conductive properties (such as MXene and borophene) are also promising sensing materials which deserve further study.

*Table 3: The total numbers of research articles documented as of Nov 18, 2022*

| Keyword | Total research articles |
|---|---|
| (graphene OR PANI) AND (gas) AND (sensor) | 203 |
| (graphene OR PANI) AND (humic acid) AND (sensor) | 0 |
| (graphene OR PANI) AND (heavy metal ions) AND (sensor) | 3 |
| (graphene OR PANI) AND (microalgae) AND (sensor) | 0 |
| (graphene OR PANI) AND (dye) AND (sensor) | 8 |

Data sources: https://www.sciencedirect.com/

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