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Indium Oxide Doped Polyaniline for Detection of Formaldehyde

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Abstract

Polyaniline (PANI) and a polyaniline derivative (poly (2,5-dimethyl aniline)) were evaluated for their sensitivity towards formaldehyde. Among the two polymer backbones evaluated, polyaniline seemed more sensitive towards formaldehyde. Therefore, to further enhance sensitivity towards formaldehyde, polyaniline was doped with different weight percentages of indium oxide and further evaluated for its sensing capabilities such as sensitivity, selectivity, and stability. It was found that PANI with 1.25 wt.% of In₂O₃ was most sensitive towards

formaldehyde, while PANI with 5 wt.% of In_2O_3 was most selective towards formaldehyde over benzene interferent. It was observed that sensitivity and selectivity trends for PANI doped with different wt.% of In_2O_3 were reverse of each other. All sensing materials were found stable.

1. Introduction and Background

Volatile organic compound (VOC) detection is important for health and environmental protection.^[1] The long VOC list also includes formaldehyde (F), benzene (B), acetone (A), ethanol (E) and acetaldehyde (Ac), which can be present indoors and outdoors. Exposure to even low concentration of VOCs can cause discomfort in the eyes, nose and throat, shortness of breath, nausea and headaches. Exposure to high concentrations can cause damage to the liver, kidneys and nervous system.

Formaldehyde (F) has been extensively used in the manufacturing of plastics and resins.^[2] It is used as a disinfecting and preservative agent on a daily basis both at the industrial and domestic levels. It is a common indoor and outdoor toxic organic pollutant.^{[3][4]} Formaldehyde is also responsible for the sick building syndrome.^{[5][6]} Exposure to formaldehyde can cause irritation in eyes, nose, throat and skin, and can lead to harmful and chronic respiratory problems in the long term. Therefore, it is important to be able to detect formaldehyde present in the surroundings.

Several techniques have been explored in the literature for developing a reliable sensor for formaldehyde detection. Some of these involve a sensor device that is capable of converting information about the interaction between analyte and sensor into a measurable signal (like

change in mass, resistance, conductance, capacitance, etc.). Most of these sensors employ inorganic or organic sensing materials for detection.^[7]

Inorganic sensing materials are metal oxide sensors (MOS) like NiO, In₂O₃, TiO₂, ZnO, WO₃, MoO₃, etc. These metal oxides display enhanced sensitivity and low lower limit of detection (LOD), operating at high temperatures (typically 300 - 400 C). Therefore, they require an integrated heating source in the sensor, which ultimately increases the size, complexity and energy requirement of the sensor. The high operating temperatures may consequently lead to more than typical sensor 'wear and tear' (baseline drift and stability issues). On the other hand, organic material-based sensors consist of (often conducting) polymeric materials (as sensing materials), like polyaniline (PANI), polypyrrole (PPy), poly (3,4-ethylene-dioxythiophene) (PEDOT), polyethyleneimine (PEI), etc. Organic conducting polymeric sensing materials are acceptably stable and capable of sensing VOCs at room temperature. Polymeric materials like PANI are very versatile and can be further altered by addition of dopants to modify the PANI morphology or modify the synthesis procedure to improve sensing properties.^[8] The sensing characteristics of these polymeric materials can be enhanced by incorporating dopants (acids or amines) to increase their conductivity,^{[6][9]} or metal oxide nanoparticles to modify their structure/surface morphology.^[10] The result is the preparation of organic/inorganic hybrid structures for increased charge transport,^[11] or molecularly imprinted polymers on nanotubes, all purportedly enhancing sensitivity.^[12]

Any sensing material can be characterized based on important sensing characteristics such as sensitivity, selectivity, stability, operating temperature, and response and recovery times. The

performance of sensing materials is influenced by their microstructure, surface morphology, porosity, interaction energy, catalytic activity, and chemical affinity.^{[8][13]}

The sensitivity of a sensor refers to the detection of the lowest concentration of the analyte in question. A sensor is considered sensitive when it can produce a greater change in signal on a small change in the concentration of the analyte. The sensor or the sensing material may display a different degree of sensitivity for different ranges of concentration of the analyte. For a sensing material, sensitivity is its ability to detect and sorb the lowest concentration of the target analyte. It can be calculated as the amount of the target analyte sorbed divided by the total concentration of the target analyte upon exposure.

The higher the concentration of the target analyte sorbed, the better the sensitivity of the sensing material. The sensing material can be considered sensitive if it displays a sensitivity greater than 0.45. Of course, all these literature estimates are rough guidelines and their validity depends on the specific case. For a sensor, sensitivity is the minimum detectable signal, which is also known as limit of detection (LOD). LOD for a sensor is usually defined as three times the level of background or baseline noise.

Next, selectivity is a measure of how much the sensing material prefers the target analyte over other possible interferent gas(es), when exposed to a mixture of gases. This can be quantified as the ratio of the concentration of the target analyte sorbed to the concentration of the interferent gas sorbed.

It is important to conduct selectivity studies since the target analyte (usually) exists with several other interferent gases. For instance, in the case of sensing formaldehyde, it is practical to study

the interaction of the sensing material in the presence of gases with the same functional groups such as acetaldehyde, or molecules with similar size such as methanol, and possibly molecules with other functional groups such as ethanol, acetone and benzene, as they might exhibit a similar sensing mechanism. A common characteristic in the literature is that almost 90% of the published papers investigate sensitivity only, and hardly ever selectivity or stability.

Selectivity studies can be conducted in two ways. Firstly, by exposing sensing materials to an individual single gas source and comparing their sorption value for different analytes. Secondly, by exposing the sensing material to a mixture of two or more gases (of known, usually equal, concentrations) and then comparing the sorption values. The latter is a more realistic approach as it gives an actual perspective on how a sensing material would interact with the analyte in the presence of other interferent gases. The approach does take into account possible synergistic and/or antagonistic interactions between analytes and substrates. It is more tedious experimentally but certainly more complete. As such, it is sorely missing in the body of sensor literature (with only a few exceptions). The latter approach was used to evaluate potential sensing materials for their selectivity/affinity towards formaldehyde in the presence of an interferent gas (benzene, B) in this study.

Stability is related to several aspects, including the mechanical integrity of the sensing material, reusability of the sensing material, and effectiveness of the sensing material with ageing.

Stability studies are important since an ideal sensor should be able to resist adverse environmental conditions and still detect the target analyte.

In this study, two conductive polymer backbones, polyaniline (PANI) and poly(2,5-dimethyl aniline (P25DMA) were evaluated for their sensitivity towards formaldehyde. Subsequently, the polymer with higher sensitivity towards formaldehyde was doped with different weight % of metal oxide (indium oxide (In_2O_3)) and evaluated for its sensitivity and selectivity towards formaldehyde, and also for overall stability.

2. Experimental

2.1 Preparation of Polymeric Materials

For the synthesis of polyaniline (PANI), monomer (aniline) and initiator (ammonium persulfate (APS)) were purchased from Sigma-Aldrich (Oakville, Ontario, Canada). Metal oxide (MO) nanoparticles (used for doping) of indium (III) oxide (In_2O_3) (nanopowder, <100 nm particle size), were also purchased from Sigma-Aldrich. Deionized (DI) water was used as the reaction medium, and for washing and rinsing. Ethanol (ACS grade) was used as received for additional washing and rinsing of the synthesized polymers.

PANI was prepared using aniline monomer, APS, and DI water in the same proportions as the recipe in Stewart et al.^[14] The starting formulation involved 1.02 g (1 ml) of aniline and 50 ml of deionized water, which were mixed in a 100 ml round bottom flask using a sonicator for 30 min. The flask containing the reaction mixture was cooled for 30 min at -1 °C in a temperature-controlled cooling bath. 2.5 g of APS was dissolved in 12 ml of DI water and added to the reaction mixture, and the reaction was initiated. The reaction mixture was left to polymerize at -1 °C for 6 hours. The flask was under mild agitation throughout the polymerization. After

completion of the 6 hours, the polymer solution was filtered using Whatman #5 filter paper and washed with DI water first and then with ethanol, at least three times. The polymer powder was then left to dry in the fumehood for 24 hrs or more. The dried polymer was then scraped, collected and stored in a vial in a cool dry place.

To obtain doped PANI, the dopant was added in the formulation above. For instance, in the case of PANI doped with 5% In_2O_3 , the starting solution involved 5% indium oxide (by weight with respect to monomer), 95% aniline (by weight), and 50 ml of deionized water (all added in a 100 ml round bottom flask). The rest of the synthesis procedure followed the same steps as above. PANI samples were prepared in its pristine (undoped) form and also doped with 0.625%, 1.25%, 2.5%, 5%, and 10% (by weight) of indium oxide.

2.2 Characterization/Gas Sorption

Analyte-containing gases used for evaluating polymeric gas sensing materials were purchased from Praxair (Mississauga, Ontario, Canada). Gases containing 10 parts-per-million (ppm) of formaldehyde (F) and 10 ppm of benzene (B) were of standard grade, in nitrogen. Pure nitrogen (also from Praxair, 5.0 grade) was used to purge samples before being tested.

The test set-up for evaluation of sorption of gases onto sensing materials has been described previously by Stewart and Penlidis^[15] and a schematic is shown in **Figure 1**. 0.1g of each polymeric sensing material was deposited into a 100 ml round bottom flask. These flasks containing sensing materials were purged with dry nitrogen for at least 1 hour before evaluating them for gas sorption. Purged sensing materials were then exposed to gas mixtures containing

known concentration of one or more analytes. All the sorption tests were conducted at room temperature ($\sim 24^{\circ}\text{C}$) (unless otherwise stated) and approximately 15 psi.

The nature of the test set-up was such that the gas streams from the gas cylinders are made to pass over the sample chamber and en-route to gas chromatograph to determine the gas concentration. The difference between the gas concentration in case of an empty flask (without sensing material) and that with the flask containing sensing material in the sample chamber was taken as the amount of the gas sorbed onto the sensing material. The gas concentration in both cases was analyzed using a gas chromatograph (GC). The GC used in this study is a highly specialized Varian 450 GC (purchased from Scion Instruments, Edmonton, Alberta, Canada), equipped with a very sensitive photon discharge helium ionization detector (PDHID) to determine the gas concentration. The PDHID detector is capable of detecting very low gas concentrations down to parts-per-billion (ppb) level.

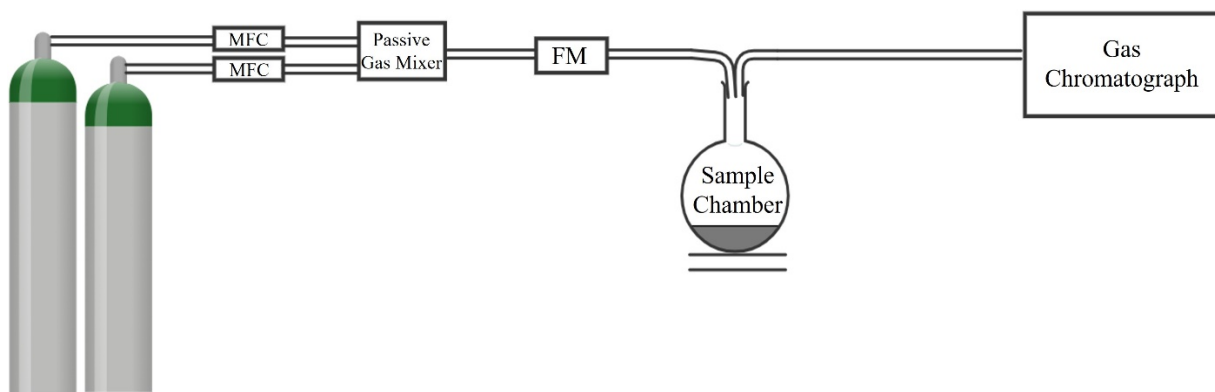


Figure 1: Schematic diagram of experimental test set-up for sorption testing (MFC- mass flow controller; FM- flowmeter)

For all gas sorption studies, potential polymeric sensing materials were evaluated based on the amount of the gas sorbed by 0.1 g of polymer. For sensitivity, the sensing materials were exposed to a single gas source, such as formaldehyde (F) 10 ppm and benzene (B) 10 ppm. For selectivity of F over another gas, sensing materials were exposed to a mixture of two gases, such as F/B (5/5 ppm each). For stability studies (effect of temperature), sensing materials were exposed to F 10 ppm (source) and the temperature was varied by heating the flask containing the sensing material from ~25°C to ~60°C. For other stability-related studies (effect of ageing), sensing materials prepared at different times in the last decade were exposed to F 10 ppm gas source. Sensing materials (used in this study and in earlier investigations) were all stored in 20 ml glass vials in a cool dry place.

2.3 Characterization/Morphology

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) analyses for all samples were performed at the facilities of the University of Waterloo Advanced Technology Laboratory (WATLAB) using a Zeiss Ultra Plus FESEM machine. The instrument was equipped with different detectors; the in-lens detector mode seemed to be appropriate for most of the sample images. A 10 kV of accelerating voltage was applied while capturing the surface morphology of the samples.

3. Results and Discussion

3.1 Sensitivity (F Sorption)

In the first step, pristine (undoped) PANI and P25DMA were evaluated for sorption of formaldehyde (F) from an F 10 ppm source. The sorption results for PANI and P25DMA are presented in **Figure 2**, where yellow bars represent % sorption of formaldehyde, and red and blue markers represent individual measurements and average sorption of formaldehyde in ppm, respectively (the same colour coding is used in other figures that follow). All sorption measurements were independently replicated at least once (independent replicates consist of the whole experimental trial genuinely replicated from scratch at different times, usually spread out over a few weeks). The validity of the sorption results was also confirmed using statistical tools (Analysis of Variance (ANOVA) and Fisher's Least Significant Difference (LSD) tests).

From the formaldehyde sorption results of pristine PANI and P25DMA shown in Figure 2, it seemed that PANI sorbed slightly more formaldehyde than P25DMA, suggesting that PANI is marginally superior. The difference between the average sorption levels of formaldehyde for PANI and P25DMA was analyzed and found to be statistically significant at the 5% significance level.

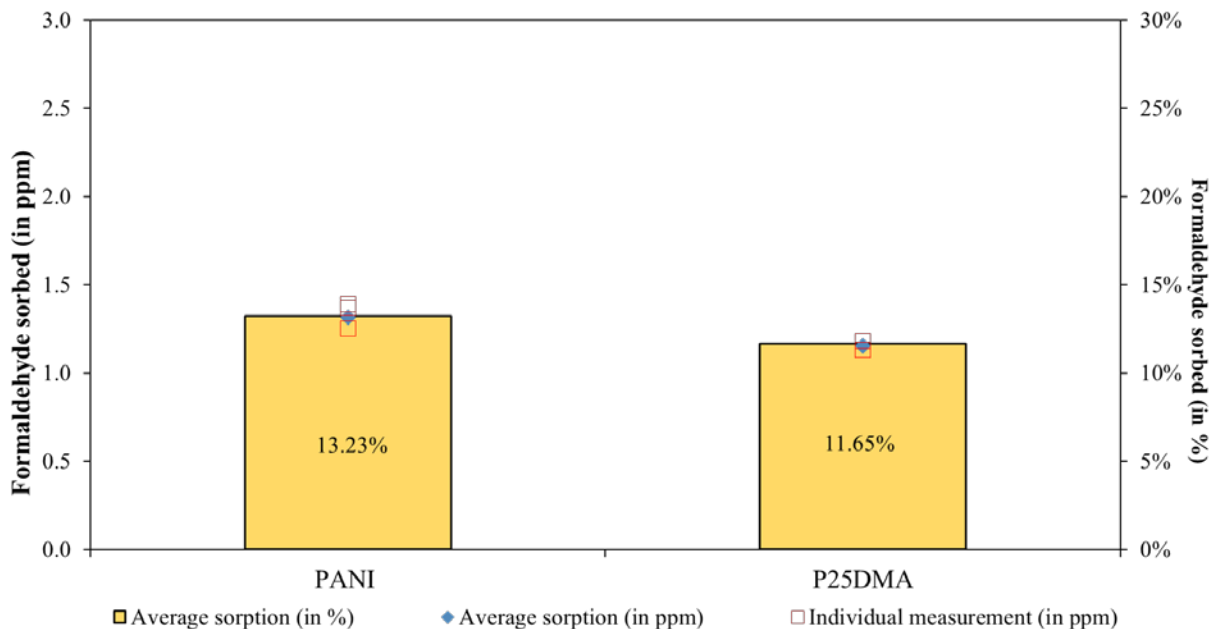


Figure 2: Formaldehyde sorption for PANI and P25DMA; (Source: 10 ppm formaldehyde in nitrogen)

PANI and P25DMA sorption of F results presented in Figure 2 are also in agreement with the sorption trends observed by Wang et al. [16] and Itoh et al. [17]. Wang et al. [17] observed a change in measured signal response of 8% on exposure to 50 ppm F in the case of $(\text{PANI})_x\text{MoO}_3$, whereas Itoh et al. [16] observed a 3.9% change on exposure to 10 ppm F source in the case of $(\text{P25DMA})_x\text{MoO}_3$. These responses are not necessarily on actual ppm of gas sorbed but rather on measured change in resistance signal response.

The (slightly) lower sorption of F with P25DMA compared to PANI can be attributed to the presence of two methyl groups in P25DMA. The methyl groups in P25DMA seem to cause more steric hindrance compared to PANI. [18][19] This suggests that the backbone microstructure and

surface morphology of the polymeric material seem to influence its sensing characteristics. To further enhance sensitivity of PANI towards formaldehyde, PANI was doped with different weight percent levels of In_2O_3 dopant, and all materials (doped and undoped) were examined for their sensitivity towards formaldehyde.

In the second step, PANIs doped with typical amounts of In_2O_3 (5% and 10% In_2O_3) were evaluated for their sorption of formaldehyde. From the results shown in **Figure 3**, one can see that PANI doped with 5% In_2O_3 seems to sorb more formaldehyde than pristine PANI and PANI doped with 10% In_2O_3 . This suggests that on doping PANI with In_2O_3 metal oxide, sensitivity towards formaldehyde seems to have improved. Moreover, it was also subsequently observed that PANI doped with a lower amount of In_2O_3 (i.e., lower than 5% In_2O_3) seemed to sorb even better. Hence, more PANI materials doped with different wt. % of In_2O_3 (lower than 5 wt. %) were examined for their sensitivity towards formaldehyde.

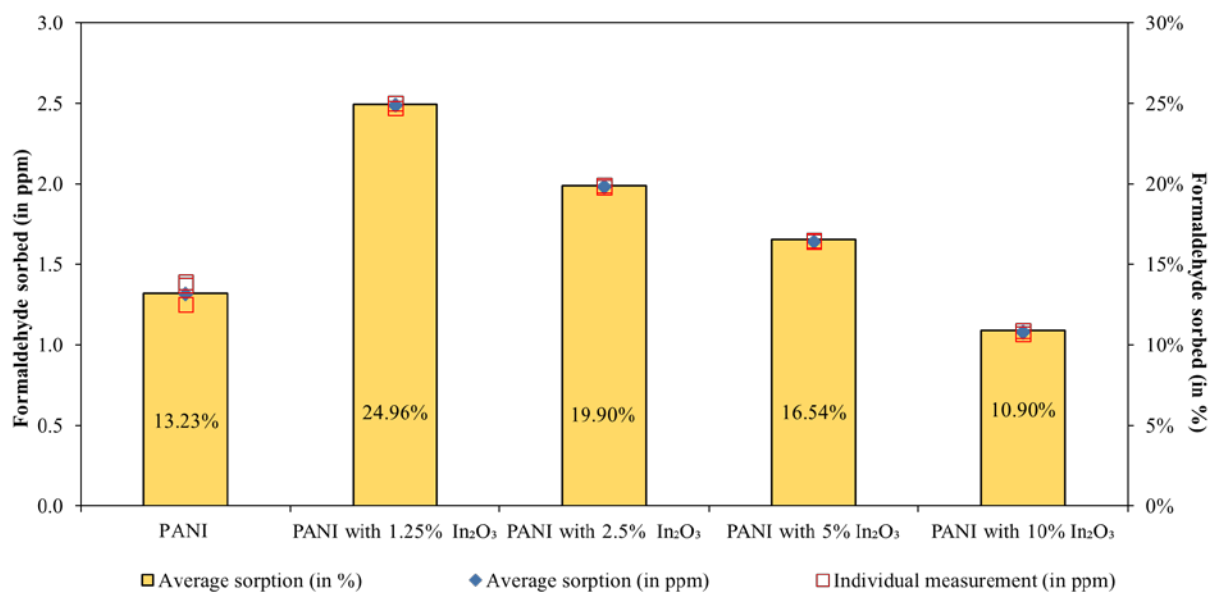


Figure 3: Formaldehyde sorption for PANI and doped PANI with In₂O₃; (Source: 10 ppm formaldehyde in nitrogen)

Again, from the sorption results shown in Figure 3, sensitivity towards formaldehyde seemed to further improve on decreasing the wt. % of In₂O₃ dopant from 5 % to 2.5%, and even further from 2.5% to 1.25 % in PANI. This clearly indicated that sorption of formaldehyde in PANI was directly related to the amount of In₂O₃ dopant incorporated in PANI, and the presence of an optimum. Hence, PANI and doped PANI with different wt.% of In₂O₃ samples were selectively scanned under SEM to check metal oxide incorporation and surface morphology.

Data obtained for selected doped PANI from EDX are shown in **Table 1**. Firstly, the metal oxide incorporation results make sense, except for the upper bound of the recipe with 2.5% indium oxide. One cannot incorporate more metal oxide than was originally present in the synthesis

recipe. Secondly, one never expects perfect incorporation and detection by EDX. Usually, even under more or less ideal conditions, the detected metal oxide weight % will be lower than what has been used in the recipe (error sources are in both dispersions of metal oxide (during synthesis) and detection during EDX (one has to live with a finite number of images and hence investigated areas of the sample). Thirdly, a higher relative error is expected at a lower weight % of metal oxide in the recipe (due to the above reasons). Hence, the incorporation results (and confirmations by EDX) of Table 1 look reasonable.

Table 1: Measured metal oxide incorporation in different polymeric materials

Polymeric Nanocomposite (synthesis conditions)	Weight percent of the metal oxide incorporation (average and % error bounds)
PANI with 2.5% In ₂ O ₃	1.93% (1.1194%, 2.74%)
PANI with 5% In ₂ O ₃	2.94% (1.97%, 3.9%)
PANI with 10% In ₂ O ₃	7.36% (6.31%, 8.41%)

More specifically, the % of metal oxide incorporation was measured over the area of a full image for roughly 96 seconds to get a good representation of the whole sample. For PANI with 2.5% In₂O₃, the incorporation estimate for the full imaged area was fairly close to what was available during synthesis, however, the localized spot estimation ranged roughly from 4.44% to 47.89% of In₂O₃ (see **Figure 4** for a representative example of two ‘spots’ scanned). This suggests that In₂O₃ seems to disperse in the polymer as clusters/aggregates of indium oxide nanoparticles in and around the polymer chains. This is evident from the white coloured clusters (indium oxide) present between the black coloured polymer (carbon) in Figure 4. Similar observations about

metal incorporation were also observed in Scott et al. [20] while evaluating polymeric materials for acetone detection. Consequently, metal oxide incorporation could also have a significant effect on surface morphology and therefore, sorption capabilities of the polymeric nanocomposites.

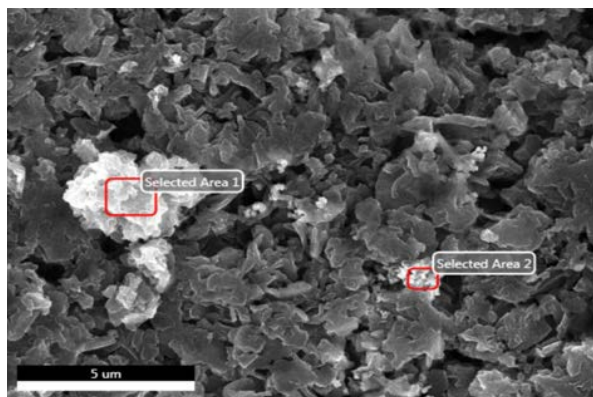
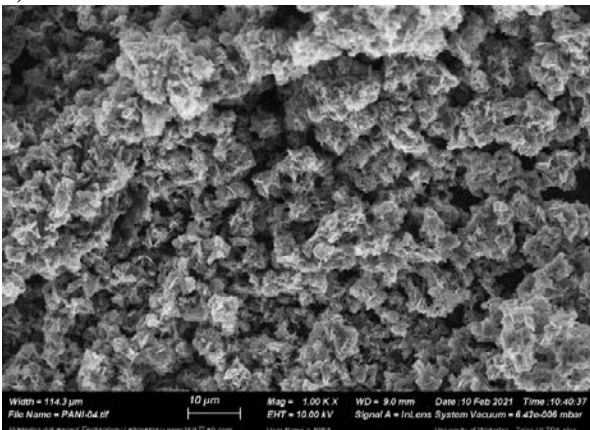


Figure 4: PANI with 2.5% In₂O₃ 'spots' selected for localized EDX scans (5000X magnification)

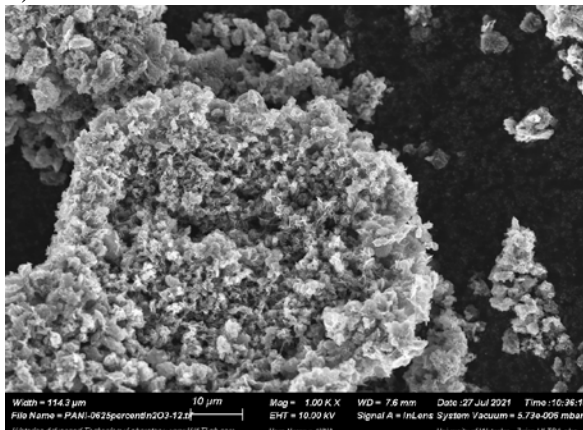
Subsequent SEM scans of pristine PANI and PANI doped with In₂O₃ in **Figure 5a-f** led to several corroborating observations. Firstly, pristine PANI (Figure 5a) exhibits a 'grainy particulate' morphology (typical of long polymeric chains that are entangled and form a fibrous structure), offering sufficient interstitial space/area among the 'grains', almost like a porous catalyst particle or a polymer particle produced by suspension polymerization. This 'porous' grainy/fibrous surface seems to behave as if having 'pores and cavities', which can 'trap' the gas analyte molecules as they pass over the polymer sample. The 'cavities' (interstitial space) bear a resemblance to the hollow catalyst spherical particle that forms a porous/fibrous structure as it fractures accommodating an exothermic polymerization (or an exothermic catalytic reaction).

Secondly, the morphology of PANI seems to change with varying amounts of indium oxide dopant in PANI. PANI with 0.625 wt.% of In_2O_3 (Figure 5b) seems to have a mixture of sheet-like (although to a lesser extent) and fibrous structures. PANI with 1.25 wt.% In_2O_3 (Figure 5c) and PANI with 2.5 wt.% In_2O_3 (Figure 5d) seem to exhibit a morphology like a (layered) stack of “sliced cactus sheets” with rounded edges; the latter (Figure 5d) also have some fibrous ends. On the other hand, PANI with 5 wt.% In_2O_3 (Figure 5e) and PANI with 10 wt.% In_2O_3 (Figure 5f) appear as a mixture of entangled fibrous structures (as in the original PANI) but with relatively minor, i.e., less, sheet-like topology similar to that observed for PANI with 0.625 wt.% In_2O_3 (Figure 5b). The modification in the PANI structure from “basic fibrous” to “layered sheet-like” seems to be related to the addition amount of In_2O_3 dopant during synthesis.

a)



b)



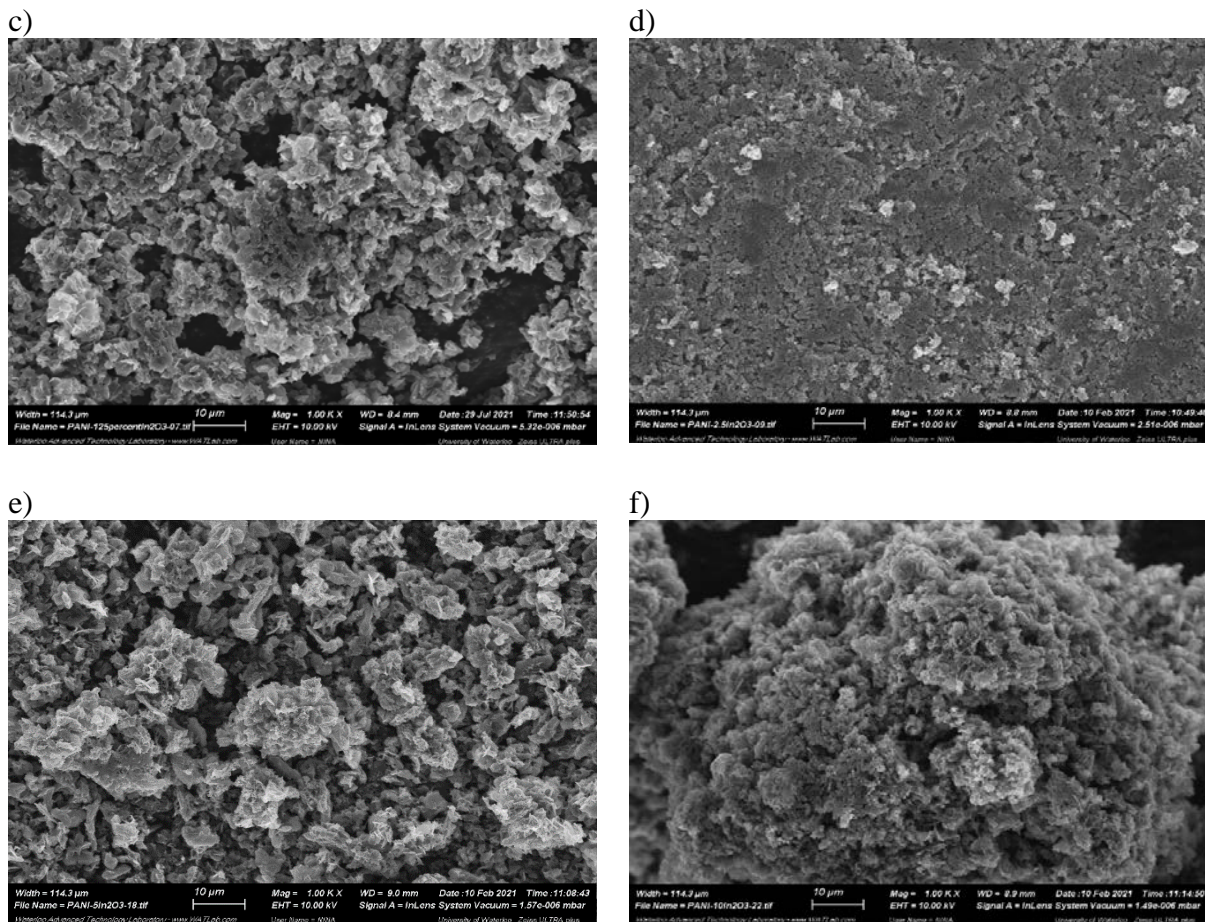
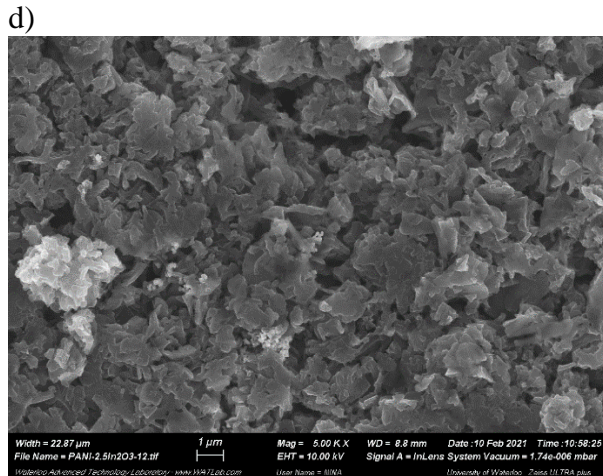
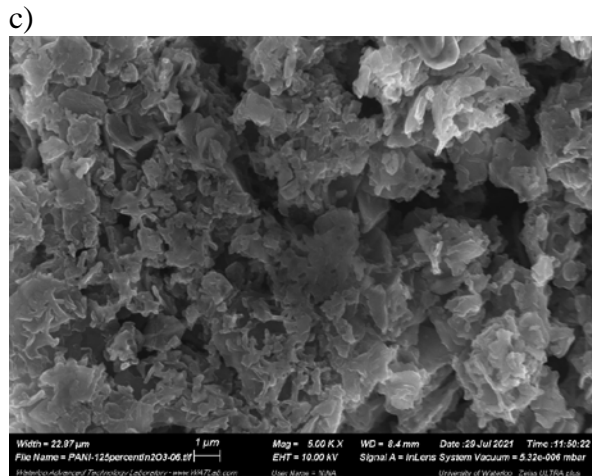
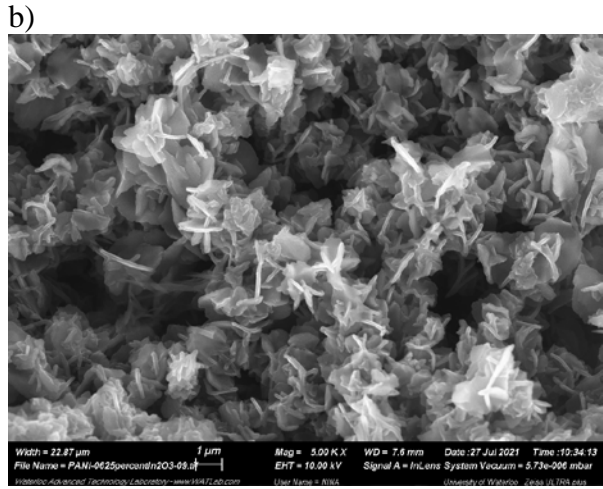
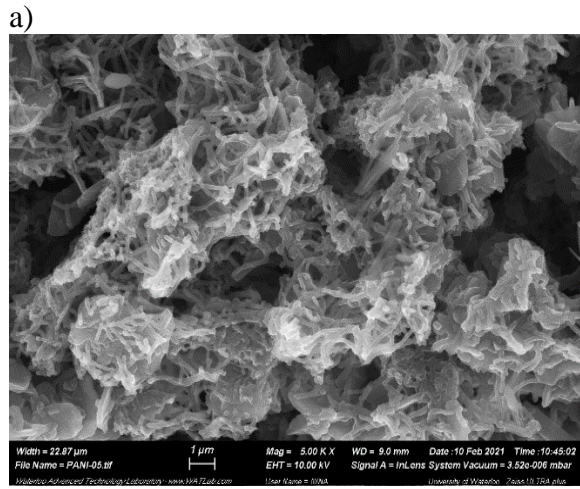


Figure 5: Surface morphology of a) PANI, b) PANI doped with 0.625% In₂O₃, c) PANI doped with 1.25% In₂O₃, d) PANI doped with 2.5% In₂O₃, e) PANI doped with 5% In₂O₃, f) PANI doped with 10% In₂O₃, all at 1000X magnification

The SEM scans of PANI and doped PANI samples shown in Figure 5a-f were further magnified at 5000X (**Figure 6a-f**) to observe more detailed variation in morphology with varying amounts of In₂O₃ dopant in PANI. More specifically, one can see from Figure 6a-f that the fibrous PANI

structure seems to evolve towards a more layered sheet-like morphology with a decrease in wt.% of In_2O_3 from 10 wt.% to 1.25 wt.%. It seems that on decreasing wt.% of In_2O_3 in PANI further than 1.25 wt.% (Figure 6c), the morphology recedes to fibrous morphology from sheet-like morphology.



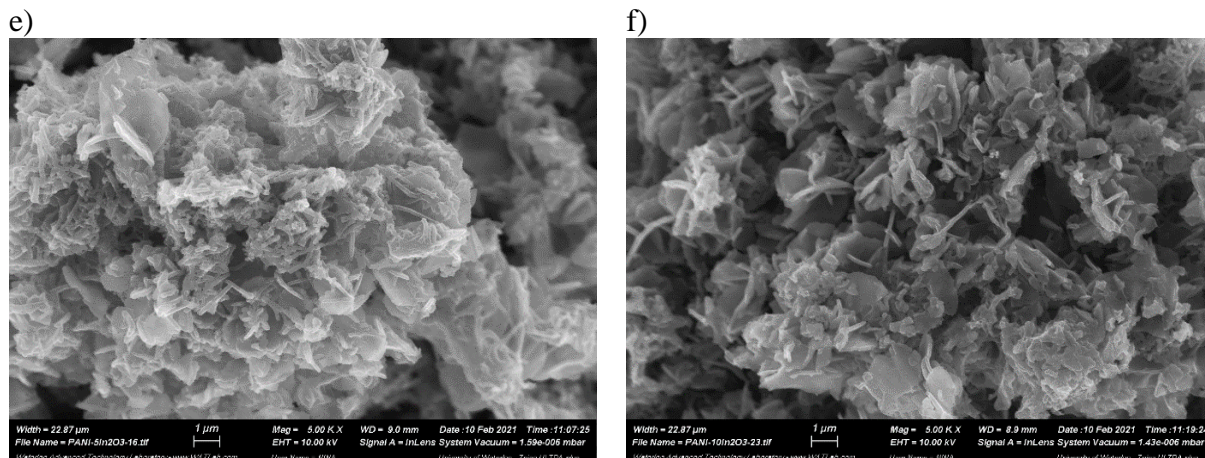


Figure 6: Surface morphology of a) PANI, b) PANI doped with 0.625% In_2O_3 , c) PANI doped with 1.25% In_2O_3 , d) PANI doped with 2.5% In_2O_3 , e) PANI doped with 5% In_2O_3 , f) PANI doped with 10% In_2O_3 , all at 5000X magnification

It is known that the surface to volume ratio increases with the flattening of the surface for the same volume. The flat sheet-like morphology of PANI with 1.25 wt.% In_2O_3 (Figure 5c/Figure 6c) and PANI with 2.5 wt.% In_2O_3 (Figure 5d/Figure 6d) seems to possess a relatively higher surface area to volume ratio compared to the fibrous morphology, thus increasing the area available to promote more sorption of the target gas analyte. The stacking of the polymeric sheets seems to create a layered 2D structure (for Figure 5c/Figure 6c and Figure 5d/Figure 6d) that not only increases surface area but also mechanical integrity of the polymer structure compared to the roughly entangled polymeric chains (in Figure 5a/Figure 6a). The morphology of PANI with 1.25% In_2O_3 (Figure 5c/Figure 6c) seems to be optimal for promoting more sorption of formaldehyde, as per the results of Figure 3. This is probably due to striking a

balance between the dispersion of the metal oxide and avoiding too much metal oxide that may cause some 'destruction'/fracturing of the polymer structure.

3.2 Selectivity (F/B Sorption)

Selectivity was evaluated for PANI and the whole series of PANI doped with In_2O_3 in the presence of benzene (B) interferent. Stewart et al. ^[4] observed an increase in selectivity of PANI towards formaldehyde over benzene and other interferent gases on doping PANI with NiO, especially PANI with 15% NiO. Doping PANI with metal oxide not only seemed to improve sensitivity towards formaldehyde but also improved selectivity of formaldehyde over other interferents. **Figure 7** shows sorption results for selectivity of PANI and doped PANI with different loadings of In_2O_3 for F/B. Several observations can be made.

The selectivity trends for the sorption of F (from F/B gas mixture) are comparable to the sensitivity trends observed when F 10 ppm was the only gas source (Figure 3) for PANI vs PANI doped with 5% and 10% In_2O_3 . The sorption of formaldehyde increases when PANI is doped with 5% In_2O_3 , but the sorption does not increase further on doping PANI with 10% In_2O_3 . The amount of F sorbed but also the selectivity ratio of F over B are higher for PANI with 5% In_2O_3 (selectivity estimate of 3.91) than PANI with 10% In_2O_3 (selectivity estimate of 0.92) (see **Table 2** for average selectivity values).

Further, on decreasing In_2O_3 loading from 5% to 2.5% and from 2.5% to 1.25% in PANI, sorption of F from F/B source decreased (see Figure 7 for sorption data) unlike sensitivity trends discussed earlier (in Figure 3). PANI with 1.25% In_2O_3 seems to sorb the least B but it does not

sorb more F compared to PANI and doped PANI with different wt.% of In_2O_3 . Therefore, improvement in sorption of F with a decrease in wt.% of In_2O_3 in PANI from 5% to 1.25% does not stand true for sorption of F from an F/B gas mixture (as per the selectivity values from the F over B studies).

The selectivity ratio of F over B decreased on decreasing In_2O_3 loadings in PANI from 5% to 1.25% unlike decreasing from 10% to 5% of In_2O_3 in PANI. This suggested that PANI with 5% In_2O_3 seems to be the optimal amount of In_2O_3 loading in PANI based on selectivity studies. It must be noted that the selectivity trends seem to be opposite of the sensitivity trends for PANI with different loadings of In_2O_3 in the 1.25% to 5% range. Sensitivity of PANI towards F (Figure 3, F 10 ppm source) seems to increase on decreasing the wt.% of In_2O_3 in PANI from 5% to 1.25%, while selectivity towards F over B (Figure 7, from a source of F/B 5/5 ppm each) seems to increase on increasing the wt.% of In_2O_3 in PANI from 1.25% to 5%.

Table 2: Average selectivity values for PANI and doped PANI with different wt. % of In_2O_3

Sensing Material	Average selectivity values of F over B
PANI	1.46
PANI with 1.25% In_2O_3	2.37
PANI with 2.5% In_2O_3	2.46
PANI with 5% In_2O_3	3.91
PANI with 10% In_2O_3	0.92

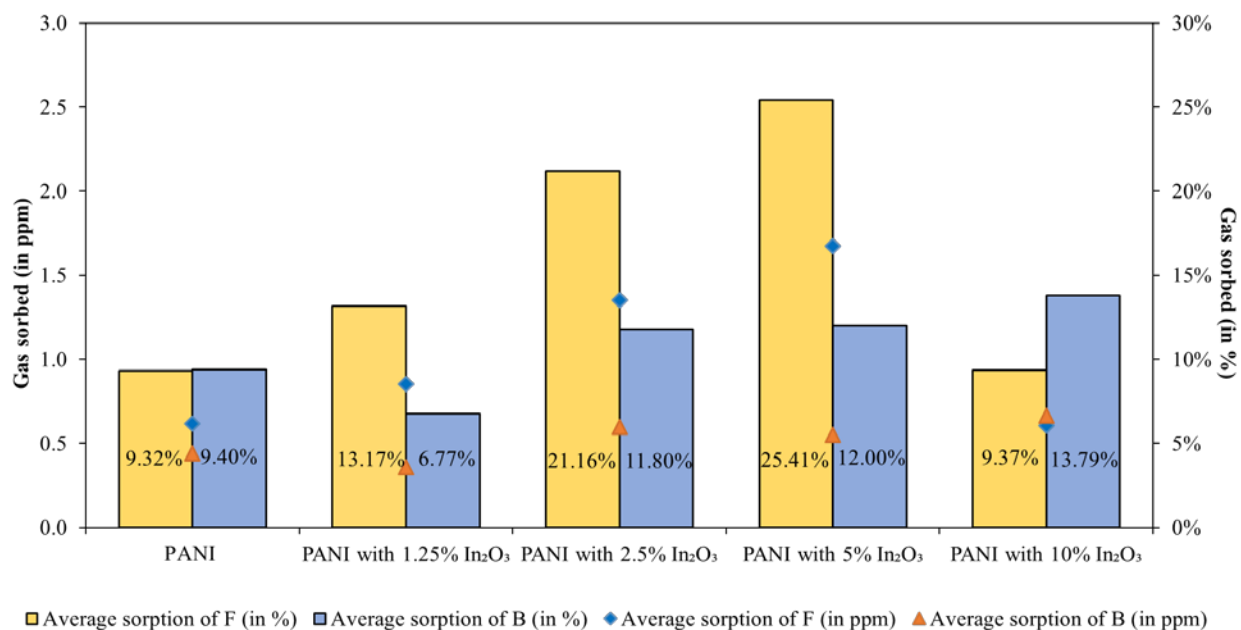


Figure 7: Formaldehyde and benzene sorption for PANI and doped PANI with In₂O₃; (Source: 5 ppm of formaldehyde in nitrogen/ 5 ppm of benzene in nitrogen)

The reverse sensitivity and selectivity trends for PANI doped with In₂O₃ can be explained further with the changing surface morphology of PANI with varying wt. % of In₂O₃ dopant through the SEM images shown in Figures 5 and 6. The evolving morphology of PANI with different loadings of In₂O₃ dopant not only affects the sensitivity trends but also the selectivity trends. From the selectivity trends discussed earlier in Section 3.2, it was observed that the selectivity of PANI doped with different wt.% of In₂O₃ decreased with decreasing the wt.% of In₂O₃ dopant from 5 wt.% to 1.25 wt.% (but not from 10% to 5 wt.% (see Figure 7)). The decrease in selectivity can be attributed to the evolving morphology of PANI from a mixture of sheet-like

entities and entangled chains to a layered sheet-like morphology with the decrease in wt.% of In_2O_3 dopant from 5 wt.% to 1.25 wt.% in PANI.

The sheet-like morphology might have a higher surface to volume ratio and more “sites” for the analytes to diffuse and attach to the polymer compared to the mixture of sheet-like and entangled chain structures. But the additional sorption sites in the former morphology might not be specific to any particular gas analyte like formaldehyde; other larger molecules like benzene might also diffuse more readily.^[21] This led to a decrease in the specificity of PANI towards formaldehyde with a decrease in wt.% of In_2O_3 from 5 wt.% to 1.25 wt.% (Figure 7 and Table 2). It must also be noted that an increase in selectivity was observed upon a decrease in wt.% of In_2O_3 from 10 wt.% to 5 wt.%. Therefore, it would be reasonable to say that PANI with 5 wt. % of In_2O_3 seems to be an “optimal” material based on selectivity grounds (of F over B) since it exhibits a good balance of sheet-like and entangled chain morphology.

3.3 Stability Aspects

Sensitivity and selectivity are the two main characteristics that one requires for proper evaluation of gas sensing materials for any target gas analyte. Sensitivity is the only characteristic usually evaluated in the literature (although most of the literature papers report a percentage of change in resistance, without translating it necessarily to ppm of analyte sorbed). Selectivity and stability characteristics are hardly ever discussed. Stability of sensing materials is the third characteristic, with a ‘looser’ definition, involving the effects of environmental factors on sensing materials. A sensitive and selective but not stable sensing material might restrict the applications of the

related sensor, and/or give unreliable results. The most important factors for stability studies are the effects of temperature and ageing. To evaluate the sorption of selected polymeric material with varying temperature, PANI samples were exposed to F 10 ppm (source) and the temperature was varied by heating the flask containing the sensing material (and monitoring the temperature via a temperature sensor) from $\sim 25^{\circ}\text{C}$ to $\sim 60^{\circ}\text{C}$.

PANI with 5% In_2O_3 was observed to sorb about 2.5 times more formaldehyde when exposed to F 10 ppm source at higher temperature compared to room temperature as shown in **Figure 8**. The increase in sorption can be attributed to the relaxation of the PANI chains on increasing temperature. The relaxation of PANI chains allowed F to interact with and access more active sites of the sensing material. Increased sorption of formaldehyde on PANI with 5% In_2O_3 at temperature levels above room temperature also indicates that PANI with 5% In_2O_3 is stable and does not lose its ability to detect formaldehyde at higher temperatures.

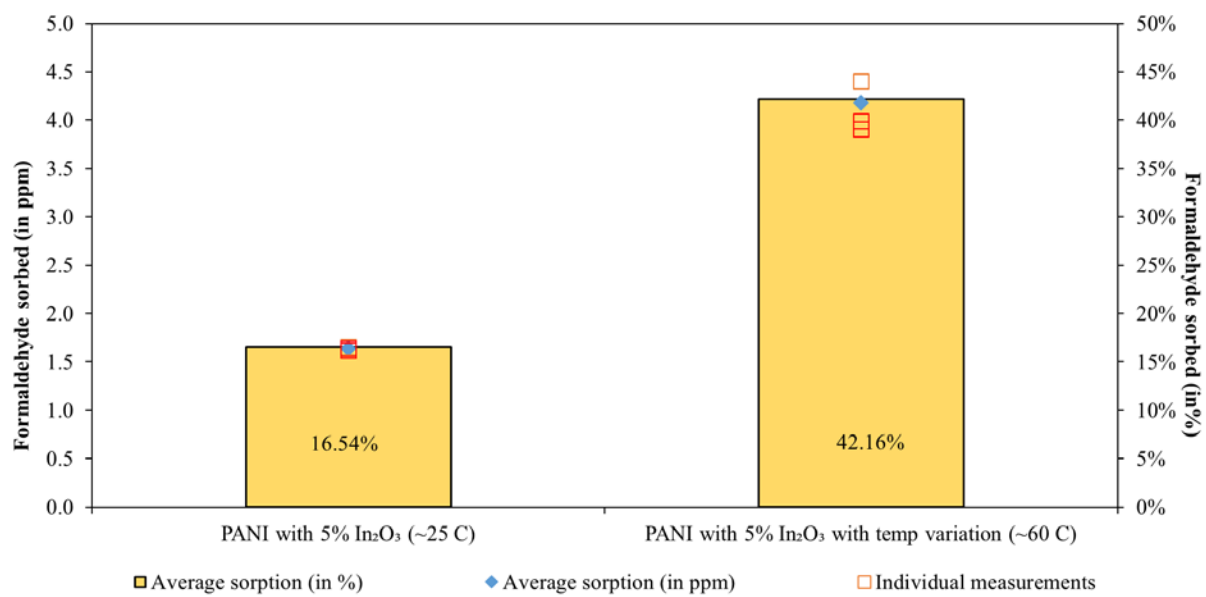


Figure 8: Formaldehyde sorption for PANI with 5% In₂O₃ with constant and varying temperature conditions; (Source: 10 ppm formaldehyde in nitrogen)

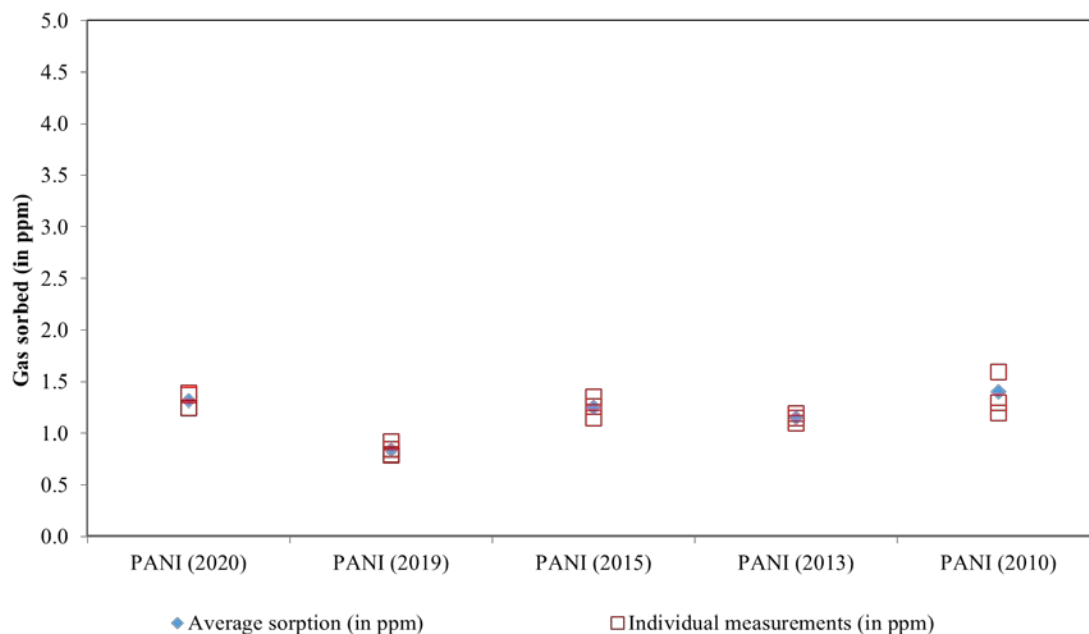


Figure 9: Levels of PANI sorption over a decade

Finally, ageing effects were studied by examining PANI prepared using the exact same synthesis protocol and recipe components over a decade by different operators in our lab. **Figure 9** displays the results from this comprehensive ageing study. Figure 9 indicates that all five PANI samples sorbed an average of ~1.4 ppm of gaseous analyte and ageing had almost no effect on PANI sorption.

4. Conclusions

From this evaluation study of PANI and doped PANI with a different weight percentage of In_2O_3 , the following concluding remarks can be made:

Based on sensitivity studies, it is evident that PANI with 1.25% In_2O_3 seems to sorb the most formaldehyde from a 10 ppm source. The good sorption capability of PANI with 1.25% In_2O_3 can be attributed to its unique surface sheet-like layered morphology. Based on selectivity studies, it is evident that PANI with 5% In_2O_3 and PANI with 2.5% In_2O_3 seem to be potentially better selective materials for sensing formaldehyde based on selectivity results of F over B (5/5 ppm). In addition, PANI materials synthesized and tested over a decade seem to have stable performance.

The interesting observation was made that sensitivity and selectivity trends are reverse of each other. Therefore, it is a trade-off between sensitivity and selectivity for an “optimal” material to be selected for a specific application. Since selectivity and sensitivity trends are reverse of each other, “optimal” materials can be selected based on the specific application of the sensor. For instance, in the case of sensing formaldehyde for indoor air quality, the sensor needs to be very sensitive since the goal is to detect trace concentrations of formaldehyde. In other cases, it might be more important for a sensing material to be selective with reasonable sensitivity towards formaldehyde to avoid false-positive response signals.

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Table of Contents Entry

Polymeric sensing materials capable of detecting formaldehyde gas in minute quantities find application in fields such as indoor and outdoor environment monitoring and as surrogate gas for warfare agent detection. However, most of the studies reported in literature used either inorganic metal oxides or organic polymeric materials synthesised via complex synthesis. Furthermore, to the best of authors knowledge, this is the first time indium oxide doped polyaniline is being used for detection of formaldehyde gas.

Sensing Materials

Bhoomi Het Mavani and Alexander Penlidis

Indium Oxide Doped Polyaniline for Detection of Formaldehyde

