Afropolitan Journals

ISSN: 2762-4585X www.afropolitanjournals.com

Nanostructured DNA-Templated Polyimidazole Nanowires for Volatile Organic Compounds Sensors

Yahaya M.I.

Department of Chemistry, Sokoto State University, Sokoto, Nigeria.
Corresponding author: ymansur64@gmail.com

Abstract

This research paper presents the synthesis of polyimidazole deoxynucleic acid, templated (Plm/DNA) nanowires through a simple wet chemical method and measuring their potentials for volatile organic compounds (VOCs) sensing at room temperature. Conductive polymers (CP) like imidazole and their derivatives have continuously been used as active layers in chemical gas sensors. Even though lots of researches have been conducted on the potential application of CP as gas sensor, more investigations needs to be carried out in order to explore many of their suitable properties for application in gas sensing Templating CP with DNA have proving to be a method of improving their electrical capabilities and subsequent application in nanosensor. The sensor response shows a linear relationship with VOCs gas concentration. Chloroform and hexane take the longest time (105 s) to respond and the least response time of 73 Secs and faster recovery (49 Secs) were observed for methanol while ethanol (89 Secs) has the longest recovery time among the analytes. Generally, all the analytes have a response ratio in the range of 0.72 – 1.02, which is an indication of good response/repeatability. Methanol (0.99) has a low but consistent baseline for the Plm/DNA nanowires. The highest baseline drift value (>1) was observed in acetone, chloroform and ethanol. The remaining analytes have lower values that are lower than 50. The observed VOCs gas-sensing response to Plm/DNA nanocomposite sensor have shown higher repeatability, selectivity, long-term stability, and fast response-recovery characteristics which is a step forward toward their applicability in environmental monitoring sensor and nanoelectronics industry.implications for the field.

Keywords: Sensor, Polymer, Polyimidazole, Sensitivity, Repeatability.

Introduction

Polymer sensors play an important role in environmental surveillance and are important components of the current sensor devices. There are two main polymer materials that have a major impact on nanosensors devices. Artificial polymer vesicles or polymersomes are the first type which are based on the self-assembly of polymers. Wrapping up of components as well as the functionalisation of the vesicle membrane are possible because of their characteristic structure. (Nawrot and Malecha, 2020; Gualandi, et al., 2021); Fink, 2016; Wolfbeis, 2003) Their major advantage lies in their great tunability accessible through the structure of the polymers. Planar polymer membranes are the second class of polymer material that can be formed from different types of polymers: nanoporous, conducting or block- copolymer. They serve as an excellent alternative to study biological membranes. (Wessling and Volk. 1986; Das et al., 2019)

CP (CPs) are polyconjugated compounds with conventional organic polymer electronic properties and at the same time retaining those similar to metals . Since the success in changing the electrical properties of some CP to remarkably high electrical conductivity via halogenation, several other conjugated polymers have been converted from an insulator into an extremely conductive condition. (Idrissi et al., 2018; Wei, et al., 2019)

Chain conformational changes, redox reactions, ion adsorption/desorption, volume/weight changes or charge transfer/screening are among the sensing mechanisms in CP, like Imidazole. The above features, along with chemical sensitivity, room temperature operation, and tunable charge transport characteristics, have initiated CP as a great class of chemical transducers. Additionally, their synthetic routes are compatible with several functionalization schemes, including covalent bonding to the monomer, entrapment during synthesis, and surface chemistries, which can transmit a high degree of selectivity and are conducive to several sensor procedures. They have the advantage in achieving high sensitivity and selectivity by virtue of their chemical and structural diversity. They also have low-temperature synthesis/processing, large area manufacture, flexibility, and cost effectiveness. As a result, they are suitable for sensor application. (Schlechter (2003; Lin et al., 2022)

The DNA molecule has special potential in template materials used for the assembly of functional materials and the sedimentation of substances due to the intrinsic properties; advantages of recognition and self-assembly potential, outstanding programmability and rich chemical functions. With the evolution of structural DNA nanoscience, specifically designing DNA nanostructures and using them as templates to deposit substances makes shapes of nanomaterials converted from DNA nanostructures possible. Straight DNA nanostructures have long been favourable materials for bottom-up manufacture of nanoscale conducting wires. Several construction strategies, including tile-and scaffold-based assemblies, for 1D linear structures have been outlined to date. The proposal of DNA polymerisation overcomes the intrinsic low conductivity of DNA and allows conductive wires to be constructed in nanoscale which have shown significant beneficial application in sensing, nanoelectronics, bioimaging, catalysis and other fields owing to their size, composition, and morphology-related physicochemical characteristics. (Wei et al., 2019; Anindya, 2020; Svetlov and Nudler, 2018)

Monitoring of VOCs environmental levels is of utmost importance in many application areas such as indoor air quality, industrial safety, environmental monitoring, fire detection, health applications among others due to strict environmental regulations and increasing health perturbation. (Yuan et al., 2022) This motivated our research that synthesised polyimidazole DNA-templated nanowires through low cost chemical method (by oxidising imidazole polymer with iron oxide and mixing it with DNA to form their hybrid nanocomposite) and measuring their potentials for VOCs sensing.

Materials and Methods

PIm/DNA nanowires Synthesis

PIm/DNA nanowires were synthesised as explained in our previous work (Yahaya. 2020) . Typically, 5µL of freshly prepared imidazole (solution (3mM) was added to 20µL of λ-DNA (500 ng µL^{-1}) in the presence of 5µL of $MgCl_2$ (0.5mM), then 5µL of $FeCl_3$ (1mM) was added dropwise into this solution. The solution was thoroughly mixed and allowed to react for at least 2 h at room temperature.

Sensor Set up and Testing

Polyimidazole DNA-templated nanowire films gas sensing test experiments were carried out by depositing 5 µL of the nanocomposite between Platinum nanoelectrodes. The dry and wet air flow was controlled by Brooks's mass flow instrument at room temperature. The gas characteristics of the PIm/DNA nanowire was analysed by recording their electrical responses when exposed to different gas mixtures (dry air and vapour of the VOCs) that were passed at different flow rate. Amperometric detection with Palmsens.com software was used to acquire the sensing data. The schematic diagram is described in figure1.

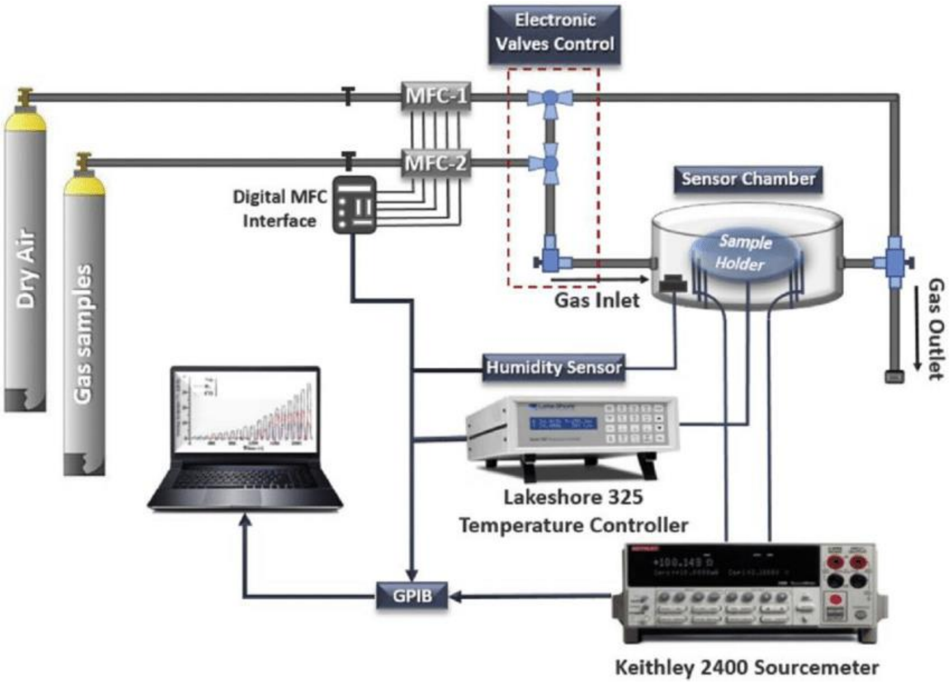

Figure 1: The schematic diagram of the gas sensing measurement system (Reprinted with permission from. Karaduman et al., (2019)

Results and Discussion

The gas characteristics of the PIm/DNA nanowires were investigated by recording their electrical responses when exposed to different gas mixture that were passed at different flow rate.

The response of the sensor was defined as:

$$\frac{\Delta R}{R_0}\% = \frac{\left(R_{exposure} - R_O\right)}{R_0} \times 100\% \qquad (1)$$

where ΔR is the change in resistance of the device before exposure to the analyte for long enough that R (resistance) has reached a steady-state and Ro (reference) value of the sensor. In the case where a steady-state resistance is not reached, it is usual to choose the value for ΔR to be equal to that after a particular time of exposure. (Yang, 2022).

Concentration Dependence of VOCs Gas Sensing

Data displayed in Figure 2 shows the response/signal output in relation to the concentration of the DNA-templated polymer nanomaterials, the chart has a linear relationship - as the concentration of the bulk nanowires increases the output also increases. Chemical sensors convert the concentrations of analytes to other detectable physical signals, such as absorbance currents. The active sensing material of the sensor interacts with the analyte when exposed to the vapour of the analyte, which causes the physical property changes of the sensing material. The interactions between the analytes and sensing materials are multiform, according to different analytes and different active materials.

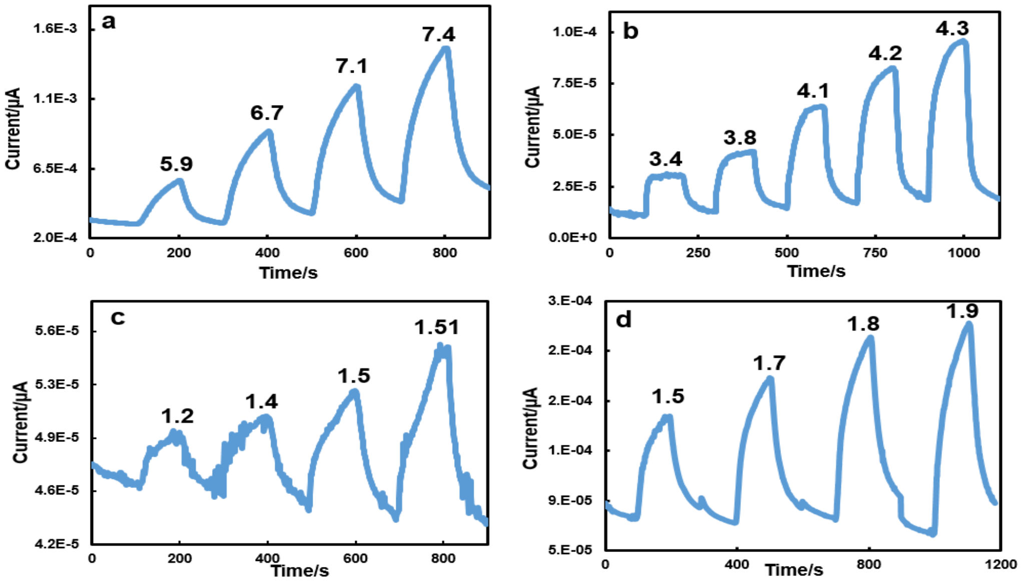

Figure 2: Current as a function Plm/DNA concentration charts in mmol/dm^{-3} at 290 K: a) four cycles of acetone sensing (b) five cycles of methanol sensing (c) four cycles of propanol sensing and (d) three cycles of acetone sensing.

The linear relationship in our work is similar to a study by Bissell et al., when they attempt to relate analyte volatility across a wide range of compounds to resistance changes in a series of polymers. It has been demonstrated that, for analyte functional classes, the electrical resistance changes of various conducting polymer sensors conform to a linear relationship with vapour concentration, producing a fixed amplitude of sensor response at an analyte-saturated vapour pressure. (Sperlich and Toroń. 2019)

The relationship can be due to the basic driving force for signal in amperometric gas sensors that were based upon an analyte concentration gradient across a gas barrier between the bulk matrix and the sensing electrode. This mechanism justifies the linear dependence between sensor signal and vapour concentration since a diffusion-limited current is formed under steady-state conditions. The driving force for the analyte diffusing across the barrier was described as the actual partial pressure gradient. (Bissell et al., 2002; Landolt, 2001).

Response and Recovery Time

Figure 3 displayed the representation graph of response-recovery time. The response time is defined as the time it takes for conductance/resistance of the gas sensor to increase to 90% of the maximum conductance/resistance when a specific amount gas was introduced into the sensor test chamber (written as t_{r90}).

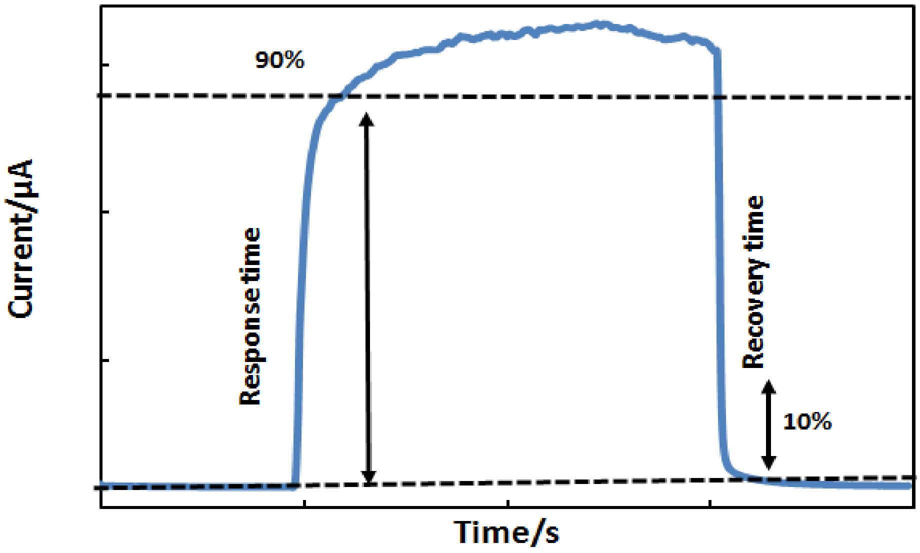

Figure 3: Representation graph of response-recovery time

The recovery time (t_{d90}) is the time required for a ninety (90%) reduction in conductance when the gas is turned off and air pumped into the chamber (i.e., the time to reach 10% conductance/resistance in volatile organic compounds vapour) The repeatability as described in figure 3 of the Plm/DNA nanowires film sensor based on response and recovery times ($\mathbf{t_{90}}$) were studied, after their exposure to the different analyte vapour. (Hong and Hoang 2021).

Figure 4 displayed the response and recovery time for the Plm/DNA nanomaterials towards the different VOCs tested, from the chart chloroform and when exposed to the Plm/DNA bulk nanowires hexane tooks the most prolong time (105 s) to respond then ethanol (104 s). Propanol and acetone responded at 96 and 91 seconds respectively. The least response time of 73 s was observed for methanol vapour when it was exposed to Plm/DNA nanowires.

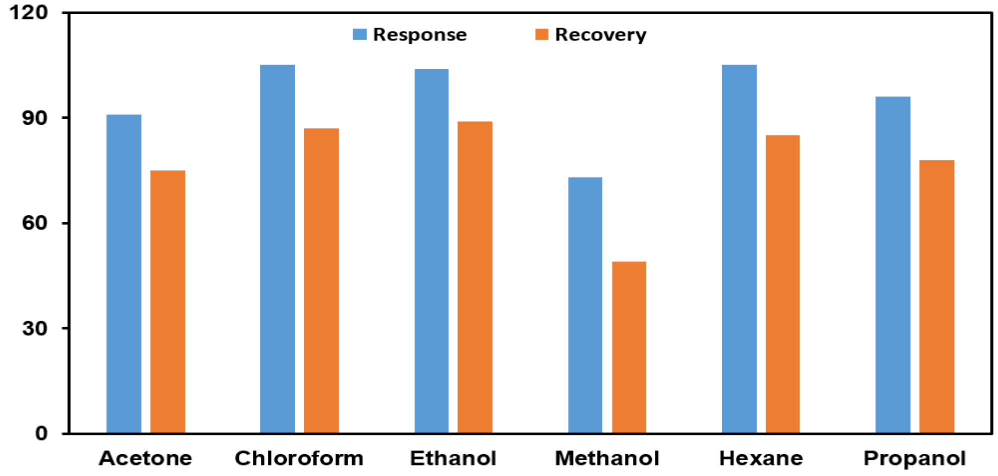

Figure 4: Response and Recovery times for Plm/DNA nanomaterials:

In the same figure 4, the recovery time for the different analytes when they were exposed to bulk polymer nanowires were displayed. Methanol (49s) recovered faster than all the other analytes while ethanol (89s) had the longest recovery time among the analytes. Chloroform (87s), hexane (85s) and propanol (78s) followed in descending order. Acetone was recovered in less than one and a half minutes (75s). Overall, recovery time is very fast in comparison with the response time. The expeditious and straightforward recovery makes the Plm/DNA nanostructures suitable for practical applications in VOCs sensing.

The performance of 1-D nanostructured sensors depends greatly on the chemical composition, sensor fabrication method, surface morphology, operating temperature/humidity, microstructure, processing approach and crystallinity. The results of the response and recovery can be explained in terms of the conductive polymer configuration which have been used to measure shifts in work function caused by the adsorption of a range of VOCs. The response of a conductive polymer film is determined by the electrochemical deposition conditions and, in particular, the electrolyte/solvent system used. (Shi, et al., 2021)

Measurements of the change in optical absorption spectra on exposure to organic vapours and the work-function switch, reveal a little but reversible charge transfer when a gas is adsorbed at the surface of the polymer. Partial electron transfer may increase or reduce the concentration of the charge carriers in the polymer backbone and, hence, polymer conductivity; the direction is determined by the relative magnitude of the electronegativity of the vapour and the work function of the polymer. Li, et al., 2001; Janata and Josowicz,. 2003).

Repeatability and Sensitivity

Figure 5 illustrates the general typical current transients of Plm/DNA nanowire device, sensing sensitivity and repeatability at a constant biassed voltage. In due course of time, the current is turn on in the presence of VOCs vapour and turn off to baseline current when the vapour is turn off in the presence of air.

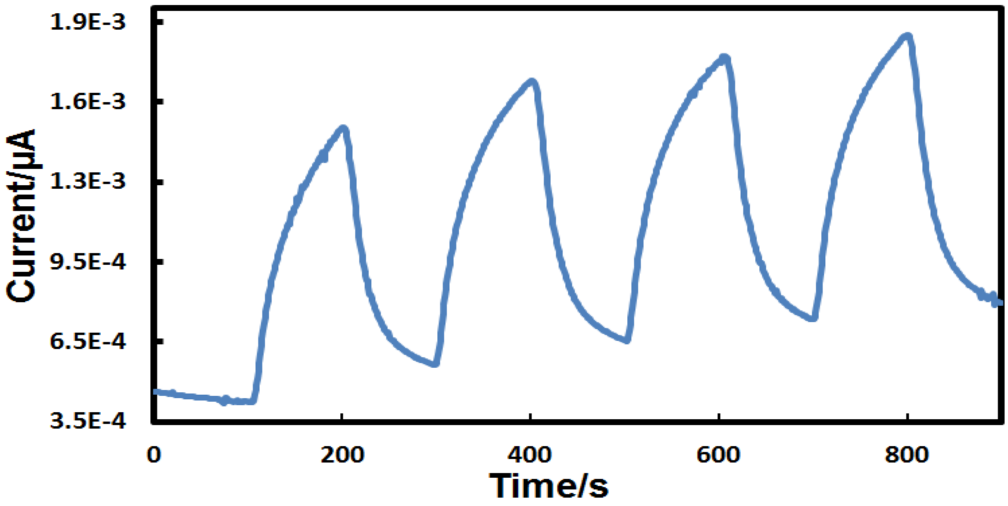

Figure 5: Representation graph of sensitivity and repeatability of Plm/DNA nanowires-array based gas sensor towards different volatile organic compounds vapour at different Kelvin temperatures.

To check the repeatability of the nanowires sensing test for the different analytes, the response and baseline ratios of the different volatile compounds were calculated and presented in figure 6. The response ratio (change in current in the presence of the analyte vapour) was calculated using the formula in equation 2 below:

$$Response\ ratio\ = \frac{\Delta I_n}{\Delta I_1} \qquad (2)$$

Where,

In is the change in current of the last cycle response for the sensing test for an analyte and **I1** is the initial change in current for the first cycle response. A ratio value of close to 1 indicates a good response or repeatability, which is a desirable sensor characteristic. The response ratio was calculated for four (n = 4) sensing cycles for all the analytes. Generally, all the analytes have a response ration in the range of 0.72 – 1.02, which is an indication of good response/repeatability.

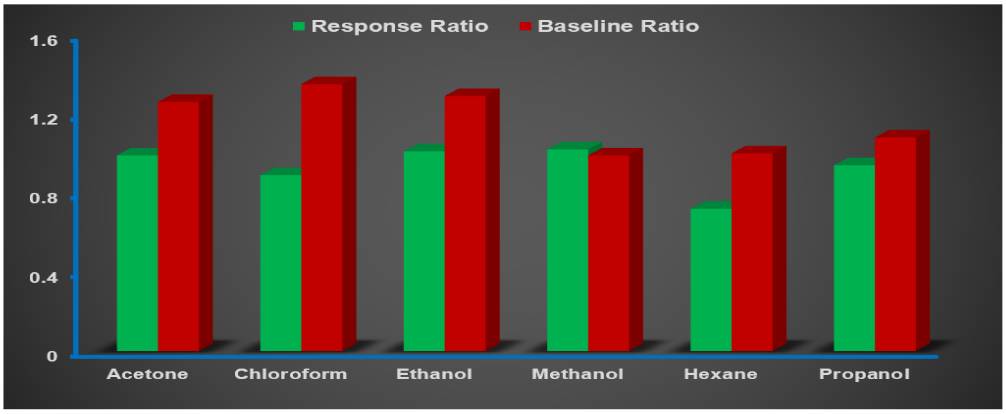

Figure 6: Current response and baseline ratios chart for the VOCs sensing with Plm/DNA

nanowire.

In same figure 6, the baseline consistency during the sensing test at different cycles for the analytes vapour were analysed using the background ratio formula in equation 3:

$$Background\ ratio\ = \frac{B_n}{B_1} \qquad (3)$$

Where, B_n is the baseline value in the last response/recovery cycle for the sensing test for an analyte and B_1 is the initial baseline value. Methanol (0.99) has a low but consistent baseline for the Plm/DNA nanowires from the chart. The highest baseline drift value (>1) was observed in acetone, chloroform and ethanol. Generally, the baseline is stable for all the VOCs sensed.

Sensitivity is the ratio of the incremental change in the sensor's output (Δy) to the incremental change of the measure input (Δx). The slope of the calibration curve, y = f(x), can be used for calculation of sensitivity. (Soleja et al., 2020) Figure 7 display the slopes of the calibration curve of the Plm/DNA nanowires towards different VOCs sensed. The responses most likely are due to adsorption of the molecules on the composite and then changes in the polymer conformation.

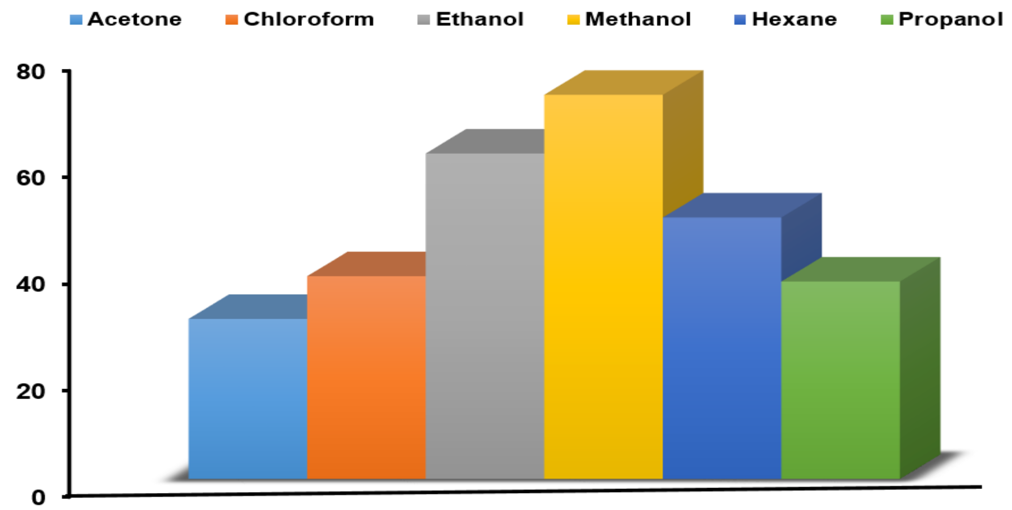

Figure 7: Slope of the calibration curves for the different VOCs illustrating the sensing behaviour of the prepared Plm/DNA nanowires samples under different analyte gas environments at room temperature. The change in electrical resistance of the prepared samples with the analyte gas exposure is converted into the sensitivity (S) by the formula $S = \Delta R/Ro$.

From the chart in figure 7, methanol and ethanol have the highest values respectively. The remaining analytes have lower values that are lower than 50. Sensitivity may be due to physical interactions between the analytes gases and the sensing Plm/DNA nanowires films, involving it adsorption or swelling. Even though these interactions do not change the oxidation levels of the conducting polymers, it can influence the properties of the sensing materials. (Krawczyk et al., 2021; Qu et al., 2019). The results reveal good repeatability and sensitivity of the Plm/DNA sensor towards VOCs.

Sensing Mechanism

Chemical sensors change the concentrations of analytes to other detectable physical signals, like absorbance, currents, acoustic or mass variables. Upon exposure to the vapour of an analyte, the active sensing material of the sensor will be combined with the analyte, which brings about the physical property variation of the sensing material. The reactions between the analytes and sensing materials are multiplexed, according to different analytes and different active materials. (Wang, et al., 2021; Narducci, 2022)

Absorbing of the analyte molecules on the surface of sensing film is widely used in explaining gas sensing. In reality, absorption is the first step in all the sensing methods. The absorption of organic gases on CP has been studied by several scientists. Bartlett’s group presented a basic model for polymer gas sensors which consists of a thin uniform polymer film lying on the top of a pair of coplanar electrodes supported by an insulating substrate. They assumed that the absorption process is described by the Langmuir adsorption isotherm. (Farbod and Norouzi 2021; Bai and Shi 2007)

The mechanism of CP nanowires sensing can be explained in terms of the interactions between gas molecules and CP films. Firstly, chemical reactions between analytes and conducting polymers were used to explain the mechanism. The physical properties of conducting polymers strongly depend on their doping levels, which can be change by chemical reactions with many analytes. For instance, the sensing mechanism in acetone can be described due to hydrogen bonding and dipole-dipole interactions, beside the chemical reaction and weak interactions. (Tun and Chen, 2021)

A model of a dielectric effect on electron hopping has been proposed to explain the conductive polymer sensing mechanism, in which polymer conductivity is determined by electron hopping between polymer chains or over intrachain defects and the hopping rate is altered by the dielectric property of the vapour. Other models have reported physical effects on conductivity as a result of polymer swelling by the organic vapours. It has also been recognized that variation in the extent of sorption of different vapours by the polymer may lead to significant differences in sensor performance. (Lee, 2007; Charlesworth et al., 1993) In our studies we believed that the mechanism of Plm/DNA sensing is by absorption of the analyte molecules on the surface of sensing film.

Conclusions

A polyimidazole DNA templated composite VOCs sensor has been developed by a simple oxidative wet chemical polymerization method that employed DNA as a template. The developed sensor showed good repeatability, selectivity, fast response/recovery, and long-term stability on exposure of VOCs at room temperature. In addition, sensor response also showed a linear relationship with VOCs concentration. The obtained results are in good agreement with reported work with enhanced gas sensor response properties and is a way forward towards sensor application in indoor monitoring and nanoelectronics industry.

Conflicts of Interest

The author declares that there is no conflict of interest regarding the publication of this paper.

Funding Statement

No funding statement to acknowledge.

References

Anindya, R. (2020). Single-stranded DNA damage: Protecting the single-stranded DNA from chemical attack. *DNA Repair*, *87*, 102804. https://doi.org/10.1016/j.dnarep.2020.102804

Bai, H., and Shi, G. (2007). Gas Sensors Based on Conducting Polymers. *Sensors*, *7*(3), 267-307. https://doi.org/10.3390/s7030267

Bissell, R., Persaud, K., and Travers, P. (2002). The influence of non-specific molecular partitioning of analytes on the electrical responses of conducting organic polymer gas sensors. *Physical Chemistry Chemical Physics*, *4*(14), 3482-3490. https://doi.org/10.1039/b201292h

Charlesworth, J., Partridge, A., and Garrard, N. (1993). Mechanistic studies on the interactions between poly(pyrrole) and organic vapours. *The Journal Of Physical Chemistry*, *97*(20), 5418-5423. https://doi.org/10.1021/j100122a038

Das, S., Kumar, V., and Yokozeki, T. (2019). Strain sensing behaviour of multifunctional polyaniline-based thermoset polymer under static loading conditions. *Polymer Testing*, *77*, 105916. https://doi.org/10.1016/j.polymertesting.2019.105916

Farbod, M., and Norouzi, E. (2021). Microstructure, mechanical and electrical properties of Al/carbon nanotubes composite. *Fullerenes, Nanotubes And Carbon Nanostructures*, *30*(6), 603-606. https://doi.org/10.1080/1536383x.2021.1986016

Fink, J. (2016). *Metallized and magnetic polymers*. Wiley.

Gualandi, I., Tessarolo, M., Mariani, F., Possanzini, L., Scavetta, E., and Fraboni, B. (2021). Textile Chemical Sensors Based on Conductive Polymers for the Analysis of Sweat. *Polymers*, *13*(6), 894. https://doi.org/10.3390/polym13060894

Hong, H., and Hoang, T. (2021). Using Palladium Nanocubes on ZnO Nanostructures in Hydrogen Gas Sensor for Fast Response and Recovery Time. *Journal Of Nanoscience And Nanotechnology*, *21*(4), 2495-2499. https://doi.org/10.1166/jnn.2021.19118

Idrissi, M., Meyer, C., Zartner, L., and Meier, W. (2018). Nanosensors based on polymer vesicles and planar membranes: a short review. *Journal Of Nanobiotechnology*, *16*(1). https://doi.org/10.1186/s12951-018-0393-7

Janata, J., and Josowicz, M. (2003). Conducting polymers in electronic chemical sensors. *Nature Materials*, *2*(1), 19-24. https://doi.org/10.1038/nmat768

Karaduman Er, I., Çağirtekin, A., Çorlu, T., Yildirim, M., Ateş, A., and Acar, S. (2019). Low-level NO gas sensing properties of $$\hbox {Zn}_{1-x}\hbox {Sn}_{x}\hbox {O}$$ Zn 1 - x Sn x O nanostructure sensors under UV light irradiation at room temperature. *Bulletin Of Materials Science*, *42*(1). https://doi.org/10.1007/s12034-018-1714-z

Krawczyk, M., Suchorska-Woźniak, P., Szukiewicz, R., Kuchowicz, M., Korbutowicz, R., and Teterycz, H. (2021). Morphology of Ga2O3 Nanowires and Their Sensitivity to Volatile Organic Compounds. *Nanomaterials*, *11*(2), 456. https://doi.org/10.3390/nano11020456

Landolt, D. (2001). Modern Electroplating, fourth edition, Edited by M. Schlesinger and M. Paunovic, The Electrochemical Society Inc, Pennington, NJ, Wiley, New York, 2000. ISBN 0-471-16842-6; 868 pp.; £96–95. *Electrochimica Acta*, *46*(9), 1385-1386. https://doi.org/10.1016/s0013-4686(00)00721-0

Lee, S. (2007). *Controlled Electrochemical Synthesis of Conductive Polymer Nanostructures and Electrochromism Property Study*. University of Maryland (College Park, Md.).

Li, G., Josowicz, M., and Janata, J. (2001). Electrochemical modulation of the electronic properties in conducting poly(phenylene sulphide phenylene amine). *Synthetic Metals*, *125*(3), 273-278. https://doi.org/10.1016/s0379-6779(01)00403-9

Lin, J., Liatsis, P., and Alexandridis, P. (2022). Flexible and Stretchable Electrically Conductive Polymer Materials for Physical Sensing Applications. *Polymer Reviews*, *2*, 1-60. https://doi.org/10.1080/15583724.2022.2059673

Narducci, R. (2022). Ionic Conductive Polymers for Electrochemical Devices. *Polymers*, *14*(2), 246. https://doi.org/10.3390/polym14020246

Nawrot, W., and Malecha, K. (2020). Biomaterial Embedding Process for Ceramic–Polymer Microfluidic Sensors. *Sensors*, *20*(6), 1745. https://doi.org/10.3390/s20061745

Qu, Z., Li, N., Na, W., and Su, X. (2019). A novel fluorescence "turn off−on" nanosensor for sensitivity detection of acid phosphatase and inhibitor based on glutathione-functionalized graphene quantum dots. *Talanta*, *192*, 61-68. https://doi.org/10.1016/j.talanta.2018.09.009

Schlechter, M. (2003). *Conductive polymers* (1st ed., pp. 20-26). Business Communications Co.

Shi, J., Lei, X., and Natsuki, T. (2021). Review on Carbon Nanomaterials-Based Nano-Mass and Nano-Force Sensors by Theoretical Analysis of Vibration Behaviour. *Sensors*, *21*(5), 1907. https://doi.org/10.3390/s21051907

Soleja, N., Agrawal, N., Nazir, R., Ahmad, M., and Mohsin, M. (2020). Enhanced sensitivity and detection range of FRET-based vitamin B12 nanosensor. *3 Biotech*, *10*(3). https://doi.org/10.1007/s13205-020-2073-1

Sperlich, P., and Toroń, B. (2019). An Ultrasonic Fabrication Method for Epoxy Resin/SbSI Nanowire Composites, and their Application in Nanosensors and Nanogenerators. *Polymers*, *11*(3), 479. https://doi.org/10.3390/polym11030479

Svetlov, V., and Nudler, E. (2018). Reading of the non-template DNA by transcription elongation factors. *Molecular Microbiology*, *109*(4), 417-421. https://doi.org/10.1111/mmi.13984

Tun, H., and Chen, C. (2021). Isosteric heat of adsorption from thermodynamic Langmuir isotherms. *Adsorption*, *27*(6), 979-989. https://doi.org/10.1007/s10450-020-00296-3

Wang, S., Meng, W., Lv, H., Wang, Z., and Pu, J. (2021). Thermal insulating, light-weight and conductive cellulose/aramid nanofibers composite aerogel for pressure sensing. *Carbohydrate Polymers*, *270*, 118414. https://doi.org/10.1016/j.carbpol.2021.118414

Wei, P., Leng, H., Chen, Q., Advincula, R., and Pentzer, E. (2019). Reprocessable 3D-Printed Conductive Elastomeric Composite Foams for Strain and Gas Sensing. *ACS Applied Polymer Materials*, *1*(4), 885-892. https://doi.org/10.1021/acsapm.9b00118

Wei, Y., Liu, M., Han, W., Li, G., Hao, C., and Lei, Q. (2019). Charge Injection Characteristics of Semi-Conductive Composites with Carbon Black-Polymer for HVDC Cable. *Polymers*, *11*(7), 1134. https://doi.org/10.3390/polym11071134

Wessling, B., and Volk, H. (1986). Post-polymerization processing of conductive polymers: A way of converting conductive polymers to conductive materials?. *Synthetic Metals*, *15*(2-3), 183-193. https://doi.org/10.1016/0379-6779(86)90022-6

Wolfbeis, O. (2003). Organic Conductive Polymers in Analytical Chemistry. *Microchimica Acta*, *143*(2-3), 73-73. https://doi.org/10.1007/s00604-003-0076-3

Yahaya, M. (2020). Synthesis and characterization of nanostructured DNA-templated polyimidazole nanowire. *IOP Conference Series: Materials Science And Engineering*, *805*(1), 012008. https://doi.org/10.1088/1757-899x/805/1/012008

Yang, S. (2022). Quantitative Calibration of Three-Wavelength Road-Condition Sensor Using a Dual-Wavelength Response Ratio. *IEEE Access*, *10*(2), 16512-16517. https://doi.org/10.1109/access.2022.3149778

Yuan, C., Cheng, W., and Huang, H. (2022). Spatiotemporal distribution characteristics and potential sources of VOCs at an industrial harbour city in southern Taiwan: Three-year VOCs monitoring data analysis. *Journal Of Environmental Management*, *303*, 114259. https://doi.org/10.1016/j.jenvman.2021.114259