Synthesis and Characterisation of Nanomolecular Conjugated Polymer/DNA Complex for Gas Sensing

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Highlights

- PPy/DNA nanowires were synthesised and aligned on an oxidised silicon substrate and micro electrodes.
- The chemical properties of the PPy/DNA composite were investigated using different spectroscopic and microscopic techniques.
- Results revealed the formation of a supramolecular hybrid polymer containing DNA and polypyrrole.
- The conductance of the PPy/DNA film at 20 °C was of the order of 10-100 µS.
- The polymer nanomaterials were thermal stable.
- PPy/DNA can be deployed in gas sensor.

Graphical Abstract

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**Abstract**

This research work is concerned with the synthesis, chemical, structural and electrical characterisation of conductive polypyrrole DNA (PPy/DNA) templated nanowires for their possible application as gas sensors. The composite is based on conductive polymer (polypyrrole) created using a simple and low cost fabrication method that applied DNA as a template on which to carry out the polymerisation. The PPy/DNA nanowires are synthesised in solution and aligned on an oxidised silicon substrate and micro electrodes by the molecular combing method that relies on a combination of fluid flow and surface tension forces for chemical, structural and electrical characterisation respectively. The chemical properties of the PPy/DNA composite were investigated using different spectroscopic techniques such as Fourier Transform Infrared (FTIR) spectroscopy, Ultra Violet Visible (UV-Vis) spectroscopy and X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) were used to characterise the dimension. Results from the characterisation revealed the formation of a supramolecular hybrid polymer containing DNA and polypyrrole. The polypyrrole DNA templated structures, revealed an average height of 1.60 nm for free DNA and 9-10 nm for PPy/DNA. The conductance (using two-terminal conductivity measurement) of the PPy/DNA film at 20 °C was of the order of 10-100 µS. The results also demonstrate thermal stability of the polymer nanomaterials. The corresponding Arrhenius plot of the conductance of the PPy/DNA nanowires displays the temperature dependence of the conductance with activation energy < 1 eV. These results demonstrate the possible application of PPy/DNA in gas sensor.

**1. Introduction**

Unique properties of conductive polymer nanocomposites derived from the successful combination of the qualities of parent constituents into a single material have made them to attract a lot of research interests and applications in several electronic devices[1-2].

Polypyrrole is becoming increasingly important for it technological importance due to its considerable electrical, optical properties and high chemical and electrical stability at ambient conditions [3]. It is particularly, a good candidate for solar cells, electrochromic displays, sensors, and high power supercapacitors among others, within unique property of non-metallic temperature dependence conductivity [4]. It is relatively air-stable with good environmental stability [5]. In recent times, it have gained popularity as competent sensing materials for various organic vapours, hazardous gases and humidity. This is due to fast charge-discharge mechanism which is proportional to its structure, high conductivity caused by high charge density and physico-chemical properties which are not easily altered by an external impulse [6]. It can be stabilized by counter ions incorporation into the polymer matrix during synthesis process, because polarons and bipolarons are greatly considered as the charge carriers in it [7].

The focal point of this work focal is on the synthesis, chemical, structural and electrical characterisation of PPy/DNA templated nanowires for possible use as gas sensors. The PPy/DNA sensing elements will be based on nanowires created using a simple and low cost fabrication method that applied DNA as a template on which to carry out the polymerisation. The nanowires are synthesised in solution and aligned on an oxidized silicon substrate by the molecular combing method that relies on a combination of fluid flow and surface tension forces [8].

**2 Materials and Methods**

**2.1 Materials**

All chemicals, except otherwise stated, were purchased from Sigma-Aldrich Company Ltd. and are of Analar grade and used as procured. Magnesium chloride (MgCl₂.7H₂O,
99%) and ferrous sulfate heptahydrate (FeSO$_4$.7H$_2$O, 99%) were acquired from BDH Chemicals Ltd. Lambda DNA (λ-DNA, Cat no. N3011S) was purchased from New England Biolabs (UK) Ltd. and were both used as received. n-Si (100) wafers (3 inch diameter, 525±50 µm thickness, polished on one side, reverse-etched, phosphorus doped and 1-10 Ω cm resistivity), were purchased from Compart Technology Ltd. Si wafers was used as substrate supports for AFM and SEM imaging of samples. Platinum microband electrodes were supplied by Windsor Scientific Ltd (Pt-h Pt-MB400MB4000). Deionised water (18 M Ω cm resistivity) was obtained from a NANOpure® Diamond™ Life Science ultrapure water system equipped with a Diamond™ RO Reverse Osmosis System (Barnstead International).

2.2 Methods

2.2.1 Substrate Cleaning

n-Si (100) wafers was cut into ~1 × 1 cm$^2$ pieces using a diamond scribe and immersed in acetone for 50 min. The chips were then rinsed with copious deionised water and dried in a gentle stream of N$_2$ gas before further drying in an oven for 5-10 min. Final cleaning with FEMTO low pressure plasma system (Diener plasma system, Diener electronic GmbH + Co. KG. Germany), using oxygen plasma oxidation (90W, 15 sccm, 15 min) at 40% power was carried out.

2.2.2 Chemical Preparation of Polypyrrole/DNA Nanowires

This involved the thorough mixing of freshly distilled (under N$_2$) Py (5 µl; 3 mM), λ-DNA solution (20 µL; 500 ng µl$^{-1}$) and MgCl$_2$ (5 µl; 0.5 mM), FeCl$_3$ (5 µl; 1 mM), an oxidant, was added and the solution was mixed and incubated at room temperature as developed at the Nanoscience Laboratory, Newcastle University, UK.

2.2.3 Samples Preparation and FTIR Measurements

For all FTIR measurements in this work, about 5µL of the prepared PPy/DNA nanowires films were drop-cast on clean Si (100) substrate and left to dry for 1 h prior to measurements. FTIR spectra were acquired using a Shimadzu FTIR (IRAffinity-1S). Spectra were recorded in the range 400–4000 cm$^{-1}$, with 128 scans at 4 cm$^{-1}$ resolution and a clean Si (100) substrate was used as a background.

2.2.4 Samples Preparation and Ultraviolet–Visible Spectroscopy

For UV-vis measurements, 2 ml of aqueous CT-DNA (162.5 ng µl$^{-1}$) solution was mixed with 0.5 ml freshly prepared pyrrole solution in the presence of 0.5 ml MgCl$_2$ (0.5 mM). Then, 0.5 ml of FeCl$_3$ (1 mM) was added drop-wise to the solution. The solution was stirred and allowed to further react at room temperature for 1 h. UV-vis absorption spectra were recorded on a CARY 100 BIO spectrophotometer at room temperature. Water was used as the background. The absorbance values reported have been scaled to a standard path length of 1 cm by the instrument software.

2.2.5 Sample Preparation and X-ray Photoelectron Spectroscopy

Samples were prepared for XPS by drop-casting ~20 µl of solution onto a clean Si (100) substrate and then left to dry in air at room temperature in a laminar flow hood. A theta probe photoelectron spectrometer was used to collect photoemission spectra. The binding energies obtained in the XPS analysis were calibrated using Carbon (284.8 eV) as a reference. Photoemission spectra were fitted with a combination of mixed singlet components using the CasaXPS software version 2.3.16 from Casa Software Ltd (Teignmouth, UK).
2.2.6 Samples Preparation and AFM Measurements

Exactly 5 μl of samples were dropped cast on treated n-Si (100) wafers. The deposited samples were dried in a C-flow vertical unidirectional (Laminar) airflow cabinet (ENVAIR, UK) over night before AFM analysis. In this work, AFM data was acquired using MultiMode® 8 Scanning Probe Microscope (SPM) (Bruker, UK). The machine was operated in Tapping Mode™, using TESP (n-doped Si cantilevers, resonant frequency range of 230-410 kHz, force constant range of 20-80 N/m). The sensitivity of the cantilevers was determined with the assumption that there was no deformation of the tip and sample. Data acquisition was carried out using NanoScope® Version 8.1 software. For decreasing vibrational noise, an isolation table was used (Bruker, UK). All the AFM images are height images taken in tapping mode on Si/SiO₂ surfaces.

2.2.7 Samples Preparation and SEM Measurements

Exactly 5 μl of sample was dropped cast on treated n-Si (100) wafers and dried in a C-flow vertical unidirectional (Laminar) airflow cabinet (ENVAIR, UK) over night before SEM analysis. The SEM analysis were carried out using JEOL JSM-5610LV Scanning Electron Microscope and the samples were coated with few nanometers of gold film using sputter coater (Bio-rad SC500, Sputter coater) machine at Advanced Chemicals and Materials Analysis Laboratory, Newcastle University UK.

2.2.8 Current Voltage Characterisation

Two-terminal conductivity measurements were performed using Pt microband electrodes deposited on clean silanized Si/SiO₂ chips (Windsor Scientific Ltd, Berkshire, United Kingdom). The gap between each pair of Au electrodes ranged from 1-8 micrometers. A 2 μl drop of an aqueous solution of PPy/DNA nanowires was placed on these electrodes and aligned across the gap between the Au fingers by molecular combing. A Cascade Microtech Summit 110008-M model probe station with Agilent B1500A semiconductor device analyzer controlled by B1500A’s EasyEXPERT software was used for the I–V measurements.

3. Results and Discussion

3.1 FTIR Characterisation of PPy/DNA

FTIR investigations were carried out to confirm the polymerization of the monomer and mixing of polypyrrole with DNA during the synthesis process. Figure 1 is a joined transmission spectra plot of PPy/DNA and DNA, that shows in-plane vibration of cytosine and guanine peaks in both PPy/DNA (1519 cm⁻¹) and DNA (1535 cm⁻¹), that is a lower peak shift of 16 cm⁻¹ in the PPy/DNA. Similarly the transmission bands of the two compounds at 1659 cm⁻¹ (PPy/DNA), and 1690 cm⁻¹ (DNA), which are assigned to the Thymine (C₂ = O stretching) [9-10].

![Figure 1: Transmission FTIR spectra of PPy/DNA (blue) and DNA (orange). Total of 28 scans co-added and averaged, 4 cm⁻¹ resolutions. The spectra are offset for clarity.](image-url)
Table 1: Selected bands in DNA and PPy/DNA spectra and their assignments

<table>
<thead>
<tr>
<th>Wavenumber in DNA (cm⁻¹)</th>
<th>Wavenumber in PPy/DNA (cm⁻¹)</th>
<th>Peak Shift (cm⁻¹)</th>
<th>Assignment [13 – 14]</th>
</tr>
</thead>
<tbody>
<tr>
<td>744</td>
<td>714</td>
<td>-30</td>
<td>Ring deformation out-of-plane-bending</td>
</tr>
<tr>
<td>810</td>
<td>810</td>
<td>0</td>
<td>Deoxyribose, B-marker</td>
</tr>
<tr>
<td>1044</td>
<td>1072</td>
<td>+28</td>
<td>C-O deoxyribose stretch/ PO²⁻ symmetric stretching</td>
</tr>
<tr>
<td>1234</td>
<td>1289</td>
<td>+55</td>
<td>Asymmetric PO²⁻ stretch</td>
</tr>
<tr>
<td>1404</td>
<td>1466</td>
<td>+62</td>
<td>In-plane vibration of cytosine</td>
</tr>
</tbody>
</table>

In Table 1, various shifts in the peak position change can be seen in PPy/DNA spectrum when compared to the corresponding bands in the spectrum of free DNA. For instance, the ring deformation out-of-plane-bending (PPy/DNA, 714 cm⁻¹) peak, shifted to lower frequency when compared to the DNA (744 cm⁻¹) spectra. On the other hand, C-O deoxyribose stretch/ PO²⁻ symmetric stretching; asymmetric PO²⁻ stretch and in-plane vibration of cytosine (1044, 1234 and 1404 cm⁻¹ in DNA) were found to shift to high frequency in the PPy/DNA nanocomposite (1072, 1289 and 1466 cm⁻¹). Furthermore, both substances have same spectral values at 810 cm⁻¹ which correspond to deoxyribose, B-marker. Generally, bands observed in the 800-1800 cm⁻¹ region of the spectrum further confirm the presence of DNA in the hybrid material. Nucleobase vibrations as well as stretches associated with the phosphate backbone may be assigned to these features observed [11 – 12].

Previous similar works [15–16] have shown that templating PPy on DNA depends on the non-covalent interaction of the nascent polymer chains with the template. Watson et al. [15] states that the characteristic bands from the DNA structure are still apparent in the FTIR transmittance spectrum of DNA/iron oxide after sequential treatments with Fe³⁺/Fe²⁺ ions and NaOH. Though several notable shifts in their peak positions and intensities were observed as a consequence of the interactions between the DNA and iron oxide material which took place. For instance, the symmetric PO²⁻ vibration at 1097 cm⁻¹, the P-O/C-O stretches of the phosphate backbone at 1071 cm⁻¹ and the asymmetric PO²⁻ vibration at 1246 cm⁻¹ are all shown to be reduced in the intensity and shifted by 16, 6 and 34 cm⁻¹ to lower frequency, respectively which is similar to the results obtained in this work.

The FTIR spectra indicated that the PPy/DNA sample is not a simple mixture of DNA and polypyrrole (Ppy) but rather an intimate interaction of DNA with PPy in the hybrid polymer because of the several notable shifts in their peak positions and intensities observed even though the characteristic bands from the DNA structure are still apparent in the FTIR transmittance spectrum of PPy/DNA, which is an indication that not all the DNA was used in the templating.

3.2 UV-vis Characterisation of PPy/DNA

The extent of mixing of PPy and DNA in PPy/DNA was evaluated in this work by UV-vis absorption spectroscopy. As shown in Figure 2, a π → π* transition is likely to occurs in the pyrrole ring present in the pyrrole-alginate conjugate, allowing quantification of the amount of PPy/DNA by UV-vis absorption spectroscopy at 217 nm [17]. The result is similar to other researcher’s findings in which they suggested that, the changed π - bond chromophore of indene/pyrrole aromatic ring system in ClnPy nanomaterial is due to overlapping of phenyl π -conjugated unit and skeleton of pyrrole monomer and is possibly responsible for the blue shifted and broadened absorption peak. These additional absorptions suggest π - π* electron transitions in the band gap of the conjugated pyrrole ring system, existing in ClnPy polymeric
Fig. 2: UV-Vis spectra: PPy solution (blue); DNA (red) and PPy/DNA (purple)

The continuous variation of wavelength and intensity of UV-Vis bands may result from the copolymerization effect of PPy with DNA. That is to say, the polymer formed by oxidative polymerization of PPy with DNA is a complex mixture of two substances rather than the mixture of two homopolymers.

3.3 X-ray Photoelectron Spectroscopy (XPS) of PPy/DNA

To determine the elements and chemical-bonding state of the compounds in the PPy/DNA mixture, the X-ray photoelectron spectroscopy (XPS) analysis of the samples was studied with the binding energy obtained in the analysis calibrated using carbon (284.8 eV) as a reference.

The XPS survey spectra of PPy/DNA samples (Figure 3) exhibit the presence of the elements C, N, O, Cl (which originated from the oxidant used or from MgCl₂ that was used in the preparation), and (weakly) P. P2p signal at 133.2 eV, arising from the phosphorus in the phosphodiester backbone of the DNA and can be considered as an evidence for the presence of DNA in the sample material. Lack of the detection of iron in the survey spectra confirmed that the FeCl₃ was used only to drive the polymerisation without any

Fig. 3: XPS Survey scan chart of PPy/DNA nanowire at pass energy of 20 eV and the step size of 0.3 eV

Fig. 4: a) N₁s XPS Spectrum and b) C₁s XPS Spectrum of PPy/DNA nanowires
Fig. 5: AFM height images of bare DNA on Si/SiO$_2$ substrate: (a) network of DNA bundles with some rope like structures being formed (b) zoomed image of the rope like molecule.

Fig. 6: AFM height images of PPy/DNA complex: (a-b) nanowires film’s image showing (blue cycles) the polymer materials incorporated to the DNA material and aggregates of PPy/DNA(c) well aligned, polymeric nanomaterials with regular coverage extended across the substrate (d) high density Ppy/DNA films

oxidative damage to DNA.

Figures 4a and b revealed the N1s and C1s spectra of PPy/DNA complex. The C1s signal can be fitted by three different carbon species at 284.8, 286.6 and 288.3 eV. The first component at the lowest binding energy (284.8 eV) relevant to $\beta$ and $\alpha$ carbon atoms, revealed the first fascinating finding.

Actually, the comparison of this carbon atom areas showed that, due to over oxidation, the $\beta$ carbons in the film were less abundant than the $\alpha$ ones, which is an indication that the $\beta$ positions are involved in the polymer functionalization. The second peak at 286.6 eV is attributed to carbons of the polymer C=N or C-N$^+$; the third one at 288.3 eV to C=N$^+$ carbons and the peak much weaker at 284.8 eV to carbonyl C=O groups. The appearance of a C=O component may be associated with the over oxidation of PPy/DNA at the $\beta$ carbon site in the pyrrole rings [20-21]. The C (1s) component occurring between 286.1 and 286.4 eV can arise from a number of different sources.

Pfluger and Street [22] attributed this band in polypyrrole to disorder type carbons, which they defined as being cross linked, chain-terminating and non-$\alpha, \alpha'$ bonded carbons as well as partially saturated rings. There will also be a small contribution from unavoidable hydrocarbon contaminants, while Atanasoska et al. [21] have suggested that electrostatic interaction of ring in carbons with counterions will also have an effect. The C (1s) component between 288 and 289 eV is generally attributed to carbonyl or carboxyl species resulting from chain termination.

The PPy/DNA showed the expected principal C (1s) component at 284.8 eV arising from the pyrrole ring $\alpha$ and $\beta$ carbons and methylene groups within the pendant side chain. The N1s spectra (Figure 4b) indicate the presence of three peaks in the case of PPy/DNA. It contains a two signals at 399.9 and 399.1 eV which are characteristic of pyrrolyluminitrogens (NH-structure) and a high Binding Energy (BE) tail (BE = 401.6 eV)
to the positively charged nitrogen NH\(^+\) (bipolaron) [23].

The N (1s) region’s two peaks located at approximately 400.1 and 401.6 eV, with the major component being the lower binding energy signal. This is in general agreement with other XPS studies of different Polypyrrole species a number of which also show a small shoulder at \(\approx 397\) eV [24].

The main peak at 400.1 eV arises from the neutral pyrrole ring nitrogen, while the higher binding energy component is generally attributed to partially charged nitrogens within bipolaron sub-units. The presence of the shoulder at 399.1 eV depends, to some extent, on the experimental signal-to-noise ratio but also on the nanowires preparation conditions since it is more pronounced for neutral than as-prepared or oxidized Polypyrrole. Lei et al. [25] have attributed it to –C=N– defects in the pyrrole backbone, while Vigmond et al. [26] ascribed it to inter chain hydrogen bonding effects. In this latter interpretation, equal intensity peaks on either side of the principal N (1s) line are expected due to electron donation from one nitrogen to another.

Examination of the N1s peak provided evidence of the presence of DNA and polypyrrole in the sample material. Curve fitting of high resolution XPS spectra of the N1s region revealed two distinct peaks in the N1s envelope with binding energies at 399.5 and 401.4 eV (Figure 4b). Contributions to both of these peaks can be assigned to the presence of the DNA and polypyrrole.

Previous XPS studies of both free DNA and polypyrrole have reported that spectra of the N1s core level of these materials can be fitted to at least two separate components. The N1s core level of DNA, for example, has been reported to comprise of a lower binding energy peak (398.6–399.0 eV) arising from the contributions of sp2-bonded N atoms in the nucleobase base rings, and a higher binding energy peak (400.1–401.4 eV) attributed to the sp3-bonded N atoms in the nucleobase rings and -NH\(_2\) groups. In this study, a lower binding energy peak (399.1 eV) tends to dominate, arising from the N-H groups present in the constituent pyrrolyl rings of the polymer. The higher binding energy species (400.1–401.6 eV) arise from the presence of inequivalent nitrogen atoms in the polypyrrole structure, which occur as a result of their electrostatic interaction with the dopant anions present in the polymer structure [27-28].

The presence of the Cl in the sample was reveal by the presence of Cl\(_2\)p peak in the survey spectrum which is an indication that the anionic

Fig. 7: A histogram displaying the heights of 150 PPy/DNA nanowires

Fig. 8: SEM micrographs of undiluted and water diluted PPy/DNA coated with gold on Si/SiO\(_2\) surface: (a-b) thick film of PPy/DNA materials and (c-d) PPy/DNA nanowires images reveling network of individual wires after dilution with pure water.
charge of the DNA is not sufficient to compensate the cationic charge of the bound PPy/DNA, and that Cl\(^-\) anions are also present as dopants in the material. Finally, the survey scan shows the absence of Fe in the sample which indicates that it is not incorporated in the material to any significant extent. Consequently, these XPS spectra confirmed that PPy/DNA nanowires incorporating FeCl\(_3\) doping agents are obtained from the oxidation of pyrrole in aqueous solvents.

3.4 AFM Characterisation of PPy/DNA

AFM height images of bare DNA on pretreated Si substrate (Figure 5) reveals two dimensional network of DNA structures with average height of approximately 1.60 ± 0.01 nm; which is close to double stranded DNA chain height of 1.5–2.0 nm. The free DNA AFM height studies in our research work is considered as a control studies to prove that the PPy/DNA nanocomposite formed are due to the interaction of both the polymer materials and the DNA, as the PPy/DNA formed from the reaction have large AFM height compared with the free DNA height.

Figure 6 reveals the PPy/DNA nanowires AFM height images, that shows different morphologies with materials indicating both small number of bare DNA strands, (a-b) proving that not all of the DNA in the reaction is involved in templating, well aligned polymeric nanomaterials with regular coverage extended across the substrate (c) and high density PPy/DNA films (d).

Many researchers have reported work on AFM imaging of pyrrole polymer, that showed fractal dimensions calculated by electrochemical methods represent more chaotic and complex behaviour because some parts of porous media in the surface is not accessible to imaging devices. Therefore, some features of the surface were not included in AFM images [29-30].

From a more elaborate statistical analysis of the PPy/DNA AFM height as shown in Figure 7, the most common height was 9-10 nm range, which can be attributed to long standing time, that led to increase of the nanowires thickness as the agglomeration process is gradual and continues for days, generating even thicker ropes. Larger structures with diameter greater than 13 nm were also recorded indicating the continuation of the polymerisation reaction after the nanowires formation, which may be due to the wrapping/bundling of the PPy/DNA structures into larger rope-like assemblies formed in the solution [31].

3.5 SEM Characterisation of PPy/DNA

Figure 8(a-d) displayed the SEM micrographs of undiluted and water diluted PPy/DNA nanomaterials on treated silicon dioxide substrate, coated with gold using sputter machine. The PPy/DNA materials shows a dense film of the undiluted DNA template polymers. On the order hand, the water diluted PPy/DNA nanomaterials revealed a more loose or dispersed morphologies because of the dilution that may break their binding together. They did not show the presence of globular particles which can be due to the extent of polymerisation or mixing of the Polypyrrole and the DNA. The SEM images are similar to those reported in literature [32-33].

Generally, the SEM images from our studies imply the mixing of the polypyrrole with the DNA has a strong effect on the resulting templated nanomaterials’ morphology. The composites show a transformation in morphology from typical free DNA to thick films with the increase of polymer coating on the DNA, which are suitable for gas sensing test as they can easily allow the flow of current when aligned on a micro electrode.

3.6 Two-Terminal Current – Voltage (I-V) Characterisation of PPy/DNA

To check the instrument for comparison and proved that the current measured is from the PPy/DNA nanomaterials, measurements were made on a single platinum microelectrode point and free lambda DNA aligned
across the Pt electrodes. The result is shown in Figure 9. The curves for both the Pt electrode and the lambda DNA displayed Ohmic behaviour in the pA regime at close to zero bias, but the currents are very low and may include contribution from ion transport.

A significant contribution to resistance from electrical contact made between the polypyrrole nanowire and the Pt electrodes is possible, known as contact resistance which refers to the contribution to the total resistance of a material which comes from the electrical leads and connections as opposed to the intrinsic resistance of the wire, which is an inherent property, independent of the measurement method. Contact is also traditionally applied for the consideration of the metal to semi-conductor interface as a main contribution to this phenomenon. However, if the contact resistance is ignored, an estimate (lower bound) of the wire conductivity can be made [34].

To elucidate details of conduction mechanism and provide useful qualitative and quantitative information regarding current voltage behaviour, measurements of current-voltage over a range of temperatures were performed. This method relies on the alignment of the nanowires by molecular combing across two micro fabricated Pt electrodes on a thermally oxidized Si chip. Variable-temperature I-V studies of the two-terminal device were performed over a temperature range of 223 to 423 K in order to elucidate details of the conduction mechanism.

Current-voltage curves of PPy/DNA mesh of nanowires device were recorded under nitrogen at sequence of temperatures in the range of 223 to 423 K. In Figure 10 the resulting I-V curves are presented. As can be seen, the current-voltage curves show linearity at low bias voltages and exhibit a reproducible, linear response at a range of temperature while others were not completely linear, but have a linear region at low bias, which can be due to small tunnelling barrier at the Pt/polymer contact. In addition, they displayed an increase in current output with increase temperature which is consistent with results of similar measurements on PPy/DNA nanowires in other studies. The conductivity of any material changes with temperature and depending on the direction of this change it is possible to identify the nature of this material (metal, semiconductor and so on). The conductivity of an intrinsic semiconductor increases with increasing temperature, because more valence electrons are exited into the conduction band, whereas it decreases in the case of metals (because of electron-phonon scattering), but in polymers, the situation is different [35-36].

Many researchers have suggested that another way to view the metal/polymer or nan-

![Fig. 9: Current – Voltage plots for Pt and free lambda-DNA aligned across Pt electrodes as control.](image1)

![Fig. 10: Current-voltage (I-V) curves of a two-point contact PPy/DNA mesh of nanowires at a temperature range from 223K to 423K](image2)
owire/metal system is to consider the charge transport process in the same framework as that proposed for thin films of redox polymers. They behave very differently to inorganic semiconductors because of high doping level. Therefore, the ion transport cannot be explained by Nernst Plank equation [37-38].

Analysis of the temperature dependence of conductance in conjugated polymers gives a more in-depth of the conduction mechanism and is typically carried out through fitting conductance (G) values to the equation (1):

\[
\ln G - \ln G_0 = \left(\frac{E_a}{T}\right)\beta \quad ... \ 1
\]

This expression in equation 1, is used when describing the conductance behaviour of a conjugated polymer system through a variable range hopping (VRH) model. This in turn describes the low temperature conductance behaviour in strongly disordered systems where electronic states are localized. In this approach, the outcome is dependent upon the dimensionality of the system which is described by the parameter \( \beta = 1/(1+D) \), where \( 'D' \) is the dimensionality of the system [39].

Figure 11 shows the corresponding Arrhenius plot of the conductance of the PPy/DNA nanowire. The plot illustrates the temperature dependence of the rate constant and suggests simple electron hopping as the dominant mechanism for electron transport, shown through the exponential behaviour of the conductance upon increasing the temperature.

The slopes of the Arrhenius plots in Figure 11 were analyzed to determine the activation energies associated with the hopping of charge in these polymer nanowire sample. The PPy/DNA composite have activation energy (\( E_a = 11.1 \pm 0.50 \times 10^{-3} \text{J mol}^{-1} \) and \( \text{eV} = 0.115 \pm 0.0052 \)). In most conductive polymers if the process were limited by thermal excitation across the gap, the band gap is of order 3 eV that would predict \( E_a \) equal to 1.5 eV. Instead, in our studies, \( E_a \) is <1 eV. This because the process is thermally-assisted tunnelling between localized sites.

Several scientists have reported similar findings in their works. For example, Bobarova et al. [40] measured the conductivity of a single polypyrrole nanowire (50-60 nm in diameter) grown onto a device comprising Au microelectrodes (1 \( \mu \text{m} \) apart) and found it to be in the range 1-3 S cm\(^{-1}\). Houlton et al. [41] reported similar levels of conductivity for DNA-templated nanowires of polypyrrole. Using \( \text{FeCl}_3 \) as an oxidant, conductivity was determined to be in the range of 4 S cm\(^{-1}\), the same order as the conductivity of bulk polypyrrole powder (1.7 S cm\(^{-1}\)) prepared using \( \text{FeCl}_3 \) as oxidant. The electrical conductivity of the PPy/DNA nanowires in this study have signify their potentials in sensor application.

4. Conclusion

PPy/DNA nanowires were synthesised in solution and aligned on an oxidised silicon substrate and micro electrodes by the molecular combing method that relies on a combination of fluid flow and surface tension forces. The chemical properties of the PPy/DNA composite were investigated using different spectroscopic techniques such as Fourier Transform Infrared (FTIR) spectroscopy, Ultra-Violet Visible (UV-Vis) spectroscopy and X-ray Photoelectron Spectroscopy (XPS).
Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) were used to characterise the dimensions. Results from the characterisation revealed the formation of a supramolecular hybrid polymer containing DNA and polypyrrole. The conductance (measured using two-terminal conductivity measurement) of the PPy/DNA film at 20 °C was of the order of 10-100 µS. The results also demonstrate thermal stability of the polymer nanomaterials. The corresponding Arrhenius plot of the conductance of the PPy/DNA nanomaterials. The corresponding Arrhenius plot of the conductance with activation energy < 1 eV. These results demonstrate the possible application of PPy/DNA in gas sensor.

References


