Spectroscopic, microscopic and electrical characterization of nanoscopic polyindole DNA-templated nanomaterials

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Abstract
There has been an increasing demand for inexpensive, accurate, movable and reliable nanomaterials for nanoelectronics devices and other applications. Deoxyribonucleic acid has robust nature, therefore it self-fabrication with indole can produce highly organised functional nanostructures that are of great interest for chemical industry applications. This research work is concerned with the synthesis, spectroscopic, microscopic and electrical characterisation of hybrid polyindole (PIn) DNA templated nanowires. Polyindole (PIn) has been templated on λ-DNA via oxidative polymerisation of indole using FeCl₃ to produce conductive PIn/DNA nanowires. The formation of PIn/DNA nanowires were verified by FTIR, UV-vis and XPS spectroscopy techniques. AFM, SEM and TEM techniques were used to characterise the nanowires dimensions. AFM studies revealed an average height of 1.60 nm for free DNA and the PIn/DNA nanowires have diameters in the range 2–15 nm with the dominance of 3–4 nm mean diameter range. The electrical properties of PIn/DNA nanowires as drop-cast films were investigated by two-terminal current voltage (I-V) measurements on a probe station. The nanowires were drop-cast (5 μL of as-prepared dispersion) onto platinum microband electrodes. The conductance of these films at 20 °C was of the order of 10⁻¹⁰⁻¹µS. In addition, the conductance of PIn/DNA nanowires exhibits Arrhenius behaviour (Ea = 0.80 ± 0.06 eV) as a function of temperature. The above results have revealed the potentials of the PIn/DNA nanowire in nanoelectronics applications.

Keywords: Polyindole, Nanomaterials, Template, Characterisation, DNA

1 Introduction
In recent times, there has been an increasing demand for inexpensive, accurate, movable and reliable nanomaterials for nanoelectronics devices and other applications. Conductive polymers (CPs) such as indole are being explored as promising materials for such applications, due to their ability to form good basis for premise chemical sensors either as a sensing element or as a matrices to deactivate specific analytes [1]. Their charge transport properties are based on chemical redox reactions and provide various chemo-electrical signal transduction mechanisms. Combining them with other functional materials has provided opportunities to tailor their major morphological and physicochemical properties; improve sensitivity and selectivity at low temperature that often result in enhanced sensing performance. These correspond to one of the greatest advantages of using CPs as the sensing material [2].

It was reported that while electro polymerisation of indole which have substituent on the benzene ring produced polymers and indole while derivatives with substitution at the pyrrole ring do not electropolymerised [3]. Therefore, it is considered that polymerisation does not involve coupling via the benzene ring. But work by Wadatkar and co-workers, [4] showed that coupling of 5-substituted indole trimers take place at the ring nitrogen.
Deoxyribonucleic acid has robust nature, therefore it self-fabrication with indole can produce highly organised functional nanostructures that are of great interest for chemical industry applications. Its utilization as template to direct the self-fabrication or supramolecular polymerization of artificial molecules is a bioinspired concept in chemistry approach, as control over its length and sequence permits the achievement of ideally monodisperse and sequence-controlled polymers [5-6].

In this research work we report the production of conductive polymers/DNA nanomaterials based on polyindole DNA templated nanowires that were fabricated by rapid and cost-effective wet chemistry method. The chemical properties of the nanowires were investigated using different spectroscopic techniques such as Ultra-Violet Visible spectroscopy, X-ray Photoelectron Spectroscopy and Fourier Transform Infrared spectroscopy, Electron microscopy (SEM and TEM) and Atomic force were employed to characterise the nanowire dimensions. These techniques demonstrated the formation of a supramolecular hybrid polymer comprising conductive polymers and DNA.

2 Experimental

2.1 Chemicals and Materials

All chemicals were purchased from Sigma-Aldrich Company Ltd. Lambda DNA (λ- DNA, Cat no. N3011S) was purchased from New England Biolabs (UK) Ltd. n-Si (100) wafers were purchased from Compart Technology Ltd. Platinum microband electrodes were supplied by Windsor Scientific Ltd (Pt-MB4000) and Copper grids (HC300Cu) for TEM were purchased from EM Resolutions Ltd. UK. Deionised water (18 MΩ cm resistivity) was obtained from a NANOpure Diamond Life Science ultrapure water system equipped with a DIamond RO Reverse Osmosis System.

2.2 Substrates Cleaning

n-Si (100) wafers was cut into ~1 x 1 cm² pieces using a diamond scribe and immersed in acetone for 50 minutes. The chips were then rinsed with copious deionised water and dried in a gentle stream of N2 gas before further drying in an oven for 5 - 10 minutes. Final cleaning with FEMTO low pressure plasma system, using oxygen plasma oxidation (90W, 15 sccm, 15 min) at 40% power was carried out.

2.3 Polymerisation of Indole in DNA-Containing Solutions

Polyindole DNA templated (PIn/DNA) nanowires were chemically synthesised using FeCl₃ as an oxidant; by adding 5 μL of freshly prepared indole (C₈H₇N) solution (6.24 mM) to 20 μL of λ-DNA (500 ng μL⁻¹) in the presence of 5 μL of MgCl₂ (0.5 mM), then 5 μL of FeCl₃ (1 mM) drop-wise into the solution. The solution was thoroughly mixed and allowed to react for at least 1h at room temperature prior to analysis [7].

2.4 Samples preparation for Fourier Transform Infrared Spectroscopy

For all FTIR measurements in this work about 5μL of the prepared PIn/DNA nanowires films were dropcast on clean Si (100) substrate and left to dry for 1h 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.
2.5 Samples preparation for Ultraviolet–Visible Spectroscopy
For all UV-vis measurements, samples solution was made using calf thymus DNA (CT-DNA). Typically, 0.125 mL freshly prepared samples solution was added to 0.5 mL of CT-DNA solution (162.5 μg mL\(^{-1}\), 10mM Tris-HCl pH 8 + 1 mM ethylene diaminetetraacetic acid (EDTA)) in the presence of 0.125 ml of (0.5mM) MgCl\(_2\). Then, 0.125 mL of FeCl\(_3\) (1 mM) was added drop-wise to the solution. The mixture was stirred and allowed to react at room temperature for at least 1 h. UV-vis absorption spectra were recorded on a CARY 100 BIO spectrophotometer at room temperature. Diluted sample volume of 1.5 μL was used with water background. The absorbance values reported have been scaled to a standard path length of 1 cm by the instrument software.

2.6 Samples preparation for 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) Backgrounds were subtracted by the Shirley method [8].

2.7 Samples Preparation for Transmission Electron Microscopy
Samples (5 μL) were cast dropped on copper grids and placed on a laminar flow hood to dry for 5 h. Transmission electron microscopy experiments in this research were carried out with Philips CM100 TEM (FE1) using Holey carbon films in a mesh of Copper grids as substrate and camera images were acquired with AMT CCD (Deben).

2.8 Samples Preparation for Scanning Electron Microscopy
Five micro liters (5 μL) of samples were cast dropped on treated n-Si (100) wafers. The deposited samples were dried in a C-Flow vertical unidirectional (Laminar) Airflow cabinet over night before SEM analysis. The SEM analysis was carried out using JEOL JSM-5610LV Scanning Electron Microscope and some samples were coated with few nanometers of gold film using sputter coater (Bio-rad SC500, Sputter coater) machine.

2.9 Electrical Measurements
Two-terminal conductivity measurements were conducted using Pt microband electrodes deposited on clean silanized Si/SiO\(_2\) chips. A 2 μL drop of an aqueous solution of Pn/DNA nanowires was placed on these electrodes and aligned across the gap between the Au fingers by molecular combing. A Cascade Microtech 110008-M probe station with Agilent B1500A Semiconductor Device Analyzer controlled by B1500A’s EasyEXPERT software was used for the measurements. Prior to electrical testing, the two-terminal device undergoes a heating/cooling cycles from 223 to 423 K by using a heating/cooling chuck, under nitrogen gas supply to drive up any water bound to the Pn/DNA nanowire. All the electrical measurements were carried out under dry nitrogen without illumination in the shielded sample compartment of the probe station. Current-voltage measurement from 223 to 423 K was performed on the probe station using a thermal chuck system. For each of the electrical tests, the current was measured for applied voltages from -2 to 2 V in steps of 0.2 V.
The slopes of the Arrhenius plots in Figure 11 were analysed using equation (1) to determine the activation energies associated with the hopping of charge in the Pln/DNA nanowire samples.

\[ \ln G = \ln G_o - \frac{E_a}{k_B T} \]  

(1)

The slopes are \(-E_a/k_B\) for \(E_a\) in J and \(-eE_a/k_B\) where \(e\) is the charge on a proton, \(k_B\) is the average kinetic energy and \(E_a\) is in eV.

3 Results and Discussion

3.1 FTIR Characterisation

FTIR spectra in the spectral range 3600–600 cm\(^{-1}\) were used to identify the polymerisation of polyindole and its interaction with DNA. Comparing the IR transmittance spectra of indole and polyindole (Figure 1) a weak peak can be observed at 1362 cm\(^{-1}\) in the indole spectrum which is characteristic of the C-\(\text{H}\) rocking mode; the peak shifted to 1366 cm\(^{-1}\) in the Pln spectrum [9]. Similarly, the peak observed at 1694 cm\(^{-1}\) in the indole spectrum is a result of \(-\text{C} = \text{C} -\) ring modes which shifts to 1674 cm\(^{-1}\) in indole polymer. Other bands observed include one at 1516 cm\(^{-1}\) in indole due to \(-\text{C} \equiv \text{C} -\) ring modes which shifts to 1674 cm\(^{-1}\) in indole polymer. Other bands observed include one at 1516 cm\(^{-1}\) in indole due to \(-\text{C} - \text{C} -\) stretch (in-ring)/N-H bend that shifts to 1500 cm\(^{-1}\) in Pln spectra and another broad peak at 964 cm\(^{-1}\) in indole that is attributed to N –H wag/C-H bend, the peak shift to 972 cm\(^{-1}\) in Pln. Two sharp peaks at 675 cm\(^{-1}\) seen in both indole and Pln, are due to C - H bending vibrations [10 – 11].

![FTIR Transmission spectra of indole and polyindole](image)

**Figure 1.** FTIR Transmission spectra of indole (orange i.e. top graph line) and polyindole (blue i.e. second graph line) 128 scans co-added and averaged, 4 cm\(^{-1}\) resolution.

From the same Figure 1, peak at 1099 cm\(^{-1}\) in polyindole is usually assigned to C-N stretch of aliphatic amine, spectra band 837 cm\(^{-1}\)is due to vibration of =CH\(_2\) out-of-plane wagging vibrations in the polymeric matrix and the band located at 648 cm\(^{-1}\) is attributed to the cis CH=CH bending vibration modes; all of which were absent in indole spectra [12]. These changes in peaks positions in indole and polyindole have indicated the polymerisation of the monomer to polyindole.

According to literature [13] there are three main possibilities for the structure of poly(indole) – coupling via the 1, 2, or 3-positions. It is thought that polymerisation does not involve coupling via the benzene ring. But in another work by Mount and co-workers [14], they showed that coupling of 5-substituted indoletrimers takes place at the ring nitrogen. The structure of polyindole is more complex than that of other conductive polymers, such as polypyrrole, because of the different coupling schemes that are
possible. However, the presence of the N-H stretching band in the Pln spectrum suggests that the 1-
position (N) is not involved in coupling [15].

![Figure 2. FTIR Transmission spectra of Pln/DNA (orange) vs. controls spectra of DNA (green) and Pln (blue). The spectra are off set for clarity.](image)

Figure 2 compares FTIR transmission spectra of DNA, Pln and Pln/DNA in region between 600 and 1800 cm\(^{-1}\). Several changes observed in the DNA nucleobase region (1200-1700 cm\(^{-1}\)) of the spectra upon DNA/Pln formation indicate that the polymer also interacts with the nucleobases. For instance, peaks at 1219, 1465, 1550, 1597 and 1690 cm\(^{-1}\) present in free DNA were absent in Pln/DNA spectra.

Previous works [16–17] have shown that templating conductive polymer on DNA relies on the non-
covalent interaction of the nascent polymer chains with the template. Watson et al. [18] 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 Fe\(^{3+}\)/Fe\(^{2+}\) ions and NaOH, though several notable shifts in their peak positions and intensities are observed as a consequence of the interactions between the DNA and iron oxide material which take place.

Careful examination of the fingerprint region reveals that some of the DNA related bands are slightly
shifted relative to the pure DNA spectrum as can be seen in Table 1.

| Wave number in DNA (cm\(^{-1}\)) | Wave number in Pln/DNA (cm\(^{-1}\)) | Peak shift (cm\(^{-1}\)) | Assignment [19-21] |
|----------------------------------|-------------------------------------|-------------------------|--------------------|
| 964                              | 941                                 | -23                     | C-C deoxyribose stretch |
| 1087                             | 1157                                | +70                     | symmetric PO\(_2\) stretch |
| 1219                             | Not observed                        | -                       | Asymmetric PO\(_2\) stretch |
| 1319                             | 1366                                | +47                     | C-N stretch of cytosine/guanine |
| 1465                             | Not observed                        | -                       | In-p lane vibration of cytosine |
| 1550                             | Not observed                        | -                       | stretching vibration of purine ring (N7) |
| 1690                             | 1682                                | -8                      | Thymine (C2 = O stretching) |
For example the C – C deoxyribose stretch, at 964 cm$^{-1}$; the PO$_2^-$ symmetric stretches of the phosphate backbone at 1087 cm$^{-1}$; the asymmetric PO$_2^-$ stretch at 1219 cm$^{-1}$ and C-N stretch of cytosine/guanine at 1319 cm$^{-1}$ shows a major increase in their intensities and shifted by -23, +70 and +47 cm$^{-1}$ to lower and higher frequencies respectively. The peak, centred at 1091 cm$^{-1}$ comprises several unresolved components. The rich chemical functionality presented by the DNA offers several types of sites that allow it to bind a range of materials. The anionic phosphodiester backbone and the nucleobases of the nucleosides for instance provide routes to seed the DNA with other chemical species. The negatively charged backbone can bind cationic species via electrostatic interactions, whilst the nucleobase groups are capable of coordinating with metal cations.

It can be concluded that changes in the peak position and intensity of FTIR transmittance spectrum indicated that the PIn/DNA sample is not a simple mixture of DNA and PIn but rather an intimate mixing of DNA with PIn in the hybrid polymer.

3.2 UV-vis Characterisation

The UV-vis absorption spectra of PIn, free DNA, PInDNA and PIn/DNA - DNA recorded in aqueous solution are shown in Figure 3. The UV absorption spectrum of a freshly prepared solution of PIn shows the characteristic sharp and broad n−π* and π−π* absorption peaks at 216 and 274 nm respectively, typical of indole and both correspond to the polymer chain transition [22].

Free DNA has a characteristic broad absorption band at 260 nm and compared to the optical spectra of PIn, this absorption peak appears to be broader and slightly shifted to higher wavelength at 280 nm in PIn/DNA solution, a combination of these peaks due to the presence of some unreacted monomer is observed. In addition, the PIn and PIn/DNA spectra have a peak at about 273 nm and substantial tails extending into the visible region; these aspects of the spectra are very similar to previous reports for polyindole. These features are not present in the monomer but are characteristic of this type of polymer and originate from the extended conjugation and the midgap states in the doped polymer formed during oxidative polymerisation [23].

![Figure 3. UV-vis absorption spectra at different stages of the synthesis process: absorption spectra of aqueous 6.24 mM PIn (red); free DNA (green) and PInDNA (blue)](image-url)
Previous studies have shown that, $\pi-\pi^*$ bands of polymers in different solvents also show a hypsochromic shift with increase in dielectric constant of the solvent and the exciton band due to the inter/intra chain charge transfer is because of absorption from the highest occupied molecular orbital (HOMO) band centered on the benzenoid units to the lowest unoccupied molecular orbital (LUMO) band centered on the quinoid units [24-25]. In conclusion, it can be said that PIn/DNA is supramolecular structure containing DNA and PIn.

3.3 X-ray Photoelectron Spectroscopy studies

XPS survey spectra of PIn/DNA samples (Figure 4) revealed the presence of the elements C, N, O, Cl (which originated from the oxidant used or from MgCl$_2$ that was used in the preparation), and (weakly) P. Presence of DNA in the sample material was obtained from the P2p signal at 133.2 eV, arising from the phosphorus in the phosphodiester backbone of the DNA. Iron was not observed in the survey spectra which confirm that the FeCl$_3$ was used only to drive the polymerisation without any oxidative damage to DNA.

![Figure 4. XPS Survey scan chart of PIn/DNA nanowire at pass energy of 20 eV and the step size of 0.3 eV. Some higher resolution spectra were recorded with pass energy of 40 eV and a step size of 0.1 eV. The N1s and C1s spectra of PIn/DNA samples examined in this study are presented in Figure 5a and b respectively.](image)

Three main peaks are observed in the N1s spectrum of PIn/DNA (401.7, 400.0 and 399.1 Ev). Previous workers have observed two components in the N1s spectra of DNA alone: the lower binding energy component at 398.8 eV and another at 400.6 eV. The lower energy peak is attributed to neutral nitrogen
atoms. The component at 400.0 is observed for peptidic N atoms and is also typical of the N atoms in the pyrimidines of DNA [26].

While it is likely that the two lowest energy peaks in the N1s spectra of PIn/DNA contain similar contributions from the DNA, there will also be a contribution to these features from the N atoms of polyindole according to the extent of protonation and doping level. This is in agreement with previous reports on polyindole [27] in which it was proposed that the higher binding energy components are due to nitrogen atoms that bear a positive charge and are in chemically or structurally in equivalent environments.

The N1s peaks at 399.1 and 400.0 eV are typical of both polyindole and DNA. However, the third feature at 401.7 eV in the spectrum is definitely not present in the N1s spectrum of DNA and can be assigned to polyindole alone. N1s spectra of polyindole have similarly been reported to contain a major peak at 400.6 eV and a higher binding energy signal at 402.5 eV; these were attributed to (−NH+ (polaron)) and (≡NH(bipolaron)), respectively [28]. Therefore, the third component in PIn/DNA samples with a binding energy of 401.7 eV is assigned to positively charged nitrogen atoms associated with the charge carriers in PIn.

The C1s spectrum can be resolved into four different components centred at 284.7, 286.3, 287.6, and 288.6 eV. Four components have also been observed in C1s spectra of pure DNA by previous workers, although the peak at 284.9 eV is dominant in pure DNA. Two of the lowest binding energy components are assigned to C−H, C−C, and C−N species from PIn and DNA. The third peak at 287.6 eV is attributed to carbons in functional groups of the type, C≡N or C−N+, mainly from PIn because this feature is more intense relative to the 286.3 and 284.7 eV components in PIn/DNA samples than in pure DNA. Since the fourth peak at 288.6 eV is comparable to that at 284.7 eV in these samples, but is very weak in pure DNA, it is assigned to C≡N+ carbons in PIn. In general, the XPS spectra of PIn/DNA show large contributions from species assigned to PIn.

3.4 Morphological characterisation of PIn/DNA nanowires

3.4.1 AFM studies

The morphology of the PIn/DNA nanowires was characterized using AFM by aligning them on Si/SiO₂ surface. The water diluted images revealed network of DNA bundles with some rope like structures. The formation of well-defined stable DNA structures on the surface, toroid’s, rods, bended molecules and so on is well studied by researchers, for example, Japaridze et al. [29] always observed shortening of DNA molecules upon drying, when they deposited DNA using divalent cations, which was consistent in magnitude with a partial B- to A-form conformational transition [29]. But in our work, both MgCl₂ addition and substrate pre-treatment have effects on the structures formed.

The mechanism of the network formation in DNA is still not yet understood, although it has been noticed that the formation depends on variety of factors, for instance, type and concentration of DNA and counterions in the solution, surface properties and network treatment after formation. Proposed mechanisms for network formation from cyclic DNA include overlapping of the circles where divalent charged positive ions are serving as salt bridges not only between it and the surface, but also between its chains. A similar mechanism for network formation by overcrossing of linear DNA chains is proposed to
involve double strand splitting and triple strand organisation, while junction formation has been observed in short DNA networks of short strands [30-31].

The effective deposition and alignment of DNA-based nanowires onto surfaces is highly dependent upon the hydrophobicity of the substrate surface; hydrophilic surfaces such as freshly cleaved mica and silicon dioxide have been proven to cause nanowires to coil up or align in random directions. When the Pln/DNA nanowires were imaged on treated Si/SiO₂ (Figures 6a-d) nanostructures were clearly seen which show a regular and smooth structure with complete and continuous coverage of the duplex DNA by the polymer material. The nanostructures have shown relatively similar morphologies to other polymer nanowires prepared using DNA as a template [32-33].

![Figure 6 Pln/DNA AFM height images: (a) hexagonal network of Pln/DNA films (b) AFM height profile of the aligned nanowires (c) dense Pln/DNA film (d) thread like Pln/DNA with branches and some spherical shape.](image)

Although complete, regular and smooth appearance of the Pln/DNA nanowires was achieved at shorter reaction time in comparison with the earlier mentioned examples of polymer nanowires, a large number of agglomerated materials were also observed on the substrate surface. Santos et al. [34] explained the mechanism that leads to height formation in ambient AFM and employed them to describe how the apparent height of DNA molecules is affected by their local hydrophilicity/hydrophobicity in relation to the supporting surface.

Further statistical analysis of the 150 Plm/DNA nanowires (figure 7) size have indicated the dominance of 3-4 nm diameter range of wires. Larger structures with diameter greater than 13 nm were also recorded indicating the continuation of the polymerisation reaction after the nanowires formation.
Figure 7. A histogram displaying the heights of 150 Pln/DNA nanowires.

3.4.2 TEM Studies
In Figure 8 Pln/DNA composite TEM images were displayed showing the mesh/network like morphology (a-b) and floccule-like structures with semi-spherical white un-templated polymers (c-d), all the images showed the DNA-templated Pln/DNA nanowires to be one dimensional structure with different thickness as seen in their AFM images. As can be seen the surface of the nanowires structures were not all smooth, which indicted characteristic structures that can provide large surface that may enhance the performance of the conductive network formation for charge transport when the particles are compacted and can be good for gas sensing test.

Figure 8. Pln/DNA TEM images: (a-b) Pln/DNA nanowires network (c-d) images showing floccule-like structure with semi-spherical white un-templated polymers. Scale bar = 100 nm

3.4.3 SEM Studies
From Previous studies, bare DNA SEM images reveals a thick ordered film of the material while in the diluted form the images have a network like shape with white spot of some undiluted DNA materials,
which may be due to the DNA being more free in the diluted form that network of the free DNA can be seen clearly in contrast to the tick film in the undiluted form [34].

![Figure 9. Free and water diluted Pln/DNA sputtered with gold, SEM images: (a-b) thick films (c-d) individual thick structures of diluted samples. Scale bar = 5 nm.](image)

The diluted Pln/DNA SEM images (Figures 9c-d) show individual thick material structures that are likely because of aggregation its particles.

Mudila et al. [35] reported that, when a Lewis acid, adds to the N atom in the indole, it is on C3 atom of the ring, which in turn affects both the conductivity and polymerisation reaction of the indole compound. In Chhattise et al. [36] work, the synthesized polyindole reveals the formation of irregularly shaped particles with size ranging from 0.2 to 6 micron. The high resolution image depicts the presence of spherical particles with smooth surface which they believed are fused together to form chunk like morphology of the compound. The surface morphology of Pln powder sample with 0.6 M of FeCl3 was analyzed by FE-SEM the results shows macro-granular structure believe to be due to the aggregation of small globular structures. The irregular structure of particles has reflects its definite amorphous morphology. This is different from our Pln/DNA images that reveal thick films of the materials [37].

### 3.5 Electrical Characterization of Pln/DNA nanowires

To test if the device is conductive between electrodes and surface (short-circuit) the probe needles were positioned at points 1-1,1-2 and 1-3 on the micro electrode surface and I-V sweepings in the range -5 to +5 V at a constant temperature of 20 °C was measured.
Figure 10. Current–Voltage plots for Pln/DNA: (a) plots acquired by placing the probe needles at different pairs on the microelectrode chip (b) Pt and free lambda-DNA plots as control (c) plots of the sample at room temperature (d) curves of a two-point contact Pln/DNA at temperature range from 223 K to 423 K.

Figure 10a shows the I-V curve of the device from the sweeps at different probe needles point, the plots are noisy and show negligible current (<1pA) around zero bias indicating high resistivity. To check the instrument for comparison and proved that the current measured is from the Pln/DNA, measurements were made on a single platinum microelectrode point and free lambda DNA aligned across the Pt electrodes. The result is displayed in Figure 10b; 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.

Additionally to test the claim that the Pln/DNA-templated nanowire’s bridges are responsible for the electrical conduction, a 2 μL drop of an aqueous solution of Pln DNA-templated nanowires were placed on these electrodes and aligned across the gap between the Pt fingers by molecular combing. Current-Voltage sweepings, in the range of -5 to +5 V at a constant temperature of 20 °C were measured.

As shown in Figure 10c, the Pln/DNA bulk nanomaterials show a significant current when compared to Pt and DNA. The control measurements support the assertion that the Pn/DNA bridges are responsible for the electrical conduction, therefore they have electrical conductivity.

The conductivity of any material changes with temperature and based on the direction of this change the nature of this material can be identified. The conductivity of an inherent 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.
Current-voltage studies over a range of temperatures were performed to provide useful qualitative and quantitative information regarding I-V behaviour and to elucidate details of conduction mechanism. 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 Pln/DNA mesh of nanowires device were recorded under nitrogen at sequence of temperatures in the range of 223 to 423 K. In Figure 10d the resulting 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. In addition, displayed an increase in current output with increase temperature, which is same as results of similar measurements on PIn/DNA and PPy/DNA nanowires in other studies [38].

Many researchers have suggested that another way to view the metal/polymer or nanowire/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 [39].

Using equation 1, the activation energy (Ea) for the Pln/DNA nanowires was $1.08 \times 10^{-20}$J which is equivalent to $6.76 \times 10^{-02} + 0.52$eV. The band gap of most conductive polymers is of order 3 eV that would predict Ea equal to 1.5 eV if the process were limited by thermal excitation across the gap. Instead, in our studies Ea is $<$1 eV and lower than similar studies ($0.35 \pm 0.002$ eV) which may be because the process is thermally assisted tunneling between localized sites. Many researchers believed that the conduction pathway and therefore level of conductance in conductive polymers is dependent upon their
planarity and anisotropy ratio; the doping percentage; the alignment of the polymer chains; conjugation length and the purity of the sample [40].

4 Conclusion

Polyindole (Pln) has been templated on λ-DNA via oxidative polymerisation of indole using FeCl3 to produce conductive Pln/DNA nanowires. The formation of Pln/DNA nanowires were verified by FTIR, UV–vis and XPS spectroscopy techniques. AFM, SEM and TEM techniques were used to characterize the nanowires dimensions. AFM studies revealed an average height of 1.60 nm for free DNA and the Pln/DNA nanowires have diameters in the range 2–15 nm with the dominance of 3-4 nm mean diameter range. The electrical properties of Pln/DNA nanowires as drop-cast films were investigated by two-terminal current voltage (I-V) measurements on a probe station. The nanowires were drop-cast (5 μL of as-prepared nanowire dispersion) onto platinum microband electrodes (10 μm gap, 10 μm width). The conductance of these films at 20 °C was of the order of 10-100 μS. In addition, the conductance of Pln/DNA nanowires exhibits Arrhenius behaviour (Ea = 0.80 ± 0.06 eV) as a function of temperature. The above results have revealed the potentials of the Pln/DNA nanowire in nanoelectronics applications.

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