CHAPTER 3

CHARGE DENSITY WAVE STATE
IN PURE AND COMPOSITE
POLYPYRROLE NANOTUBES

3.1.0 Introduction

Conducting polypyrrole is an ideal test bed for studying electron-electron interaction (EEI) where doping and disorder can be changed in chemical route. Polypyrrole nanotubes have shown several interesting features of charge density wave state like existence of gap voltage below certain voltage, power law behavior in current-voltage, resistance switching, negative-differential resistance (NDR), enhancement of noise power near threshold voltage, non-curie temperature dependence of dielectric constant etc. These are the manifestation
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of Wigner Crystal state in polypyrrole nanowires [104,105]. In this chapter we have presented results of studies to understand the effect of incorporated impurities in this quasi-one-dimensional system. Due to this reason we have incorporated gold nanoparticles in polypyrrole nanotubes using template based technique. Structure and morphology of these incorporated nano-particles have been studied using Transmission Electron Microscopy( TEM), Secondary Ion Electron Mass Spectroscopy (SIMS)as shown in earlier chapter. In order to find the effect of doping, disorder and charge state of gold, we have studied Hard X-ray Photoemission Spectroscopy (HAXPES) and Magneto-transport measurements. The results of these studies helped us to understand the effect of the gold incorporation on the charge density wave (CDW) state that controls the low temperature electronic transport properties of these composite nanowires.

3.2.0  Hard X-ray Photoemission Spectroscopy (HAXPES)

3.2.1  EXPERIMENTAL

The utilization of high energy x-ray beam during photoemission spectroscopy has few advantages, both for specimen excitation and its investigation. Using hard x-ray we can easily ionize inner shells of elements in target material. This is the guideline of ESCA (Electron Spectroscopy for Chemical Analysis), created by K. Siegbahn who was awarded the Nobel Prize for it in 1981. Examination of the emitted electron gives data on the ionized atom and its environment. According to the chemical environment of the "targeted"
3.2. Hard X-ray Photoemission Spectroscopy (HAXPES)

Figure 3.1: C 1s spectrum of (a) 50 nm PPy nanotubes, (b) 200 nm PPy nanotubes. The thick solid line is the fitted curve to the experimental data, assuming four peaks. The thin solid lines correspond to the individual components. (c) Comparison of C 1s spectra of polypyrrole nanotubes having diameters 200 nm and 50 nm respectively. The inset in (c) showing α, β position of carbon atom in pyrrole ring.

atom, change in photoemission peak are observed. Deeper electron shells could be arrived at by increasing the photon energy, the ionization of these electron shells prompting exceptionally metastable states over time scales shorter than a femto second. On the other hand, when studying condensed matter, producing high kinetic energy electrons allows their mean free path to be increased. Using HAXPES, it is possible to probe materials down to depths about 10 times greater than with standard photo-emissions mostly performed in the soft x-ray regime, which opens the way for the study of buried interfaces.

In order to find details electronic structure configuration we have done Hard X-
ray Photoemission Spectroscopy. HAXPES measurements of PPy and AuPPy nanotubes were carried out at the BW2 X-ray wiggler beamline of the DORIS III storage ring (DESY, Hamburg) choosing a photon energy of 3 keV. The total energy resolution estimated is 0.5 eV. Small photon energy drifts that may be induced by heat load variations on the double-crystal monochromator were taken care of by monitoring the position of the Au $4f^{7/2}$ line measured from a gold foil on the sample holder. Photoelectrons emitted in the plane of photon polarization at 45$^\circ$ relative to the polarisation vector were recorded using a SCIENTA SES-200 electron spectrometer. All spectra were fitted using the UNIFIT software.

### 3.2.2 RESULTS & DISCUSSIONS

**a. Carbon Spectra ($=\text{C}=\text{C}$)**

Figures 3.1(a) and (b) showing C 1s photoelectron spectra measured for PPy nanotubes with 50 nm and 200 nm diameter. Both C 1s spectra are broad and asymmetric and could be fitted by four peaks consistent with previous peak assignments for polypyrrole [106–109] in bulk and film samples. The lowest binding energy peaks centered around 284.6 eV and 283.6 eV correspond to $\alpha$ and $\beta$ carbon atoms, respectively, in the pyrrole ring [106–108] as sketched in the inset of Figure 3.1(c). However, it is well known that due to disorder and hydrocarbon impurities contributing to the XPS spectrum, the intensity of the $\alpha$-peak is generally enhanced. The third broad peak around 285.8 eV is known to arise due to disorder corresponding to non-ideal carbon attributed to chain termination, non $\alpha$-bonded carbon atoms, and carbon atoms in partially satu-
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(HAXPES)

Figure 3.2: C 1s spectrum of (a) 50 nm AuPPy nanotubes. (b) 200 nm AuPPy nanotubes. The thick solid line is the fitted curve to the experimental data, which is the sum curve of four peaks. The thin solid lines are the component peaks of the fitted curve.

rated rings. The peaks at higher binding energy of 288 eV may be attributed to an oxidation of the PPy nanotubes corresponding to the formation of carbonyl (-C=O), as has been found in oxidized films of PPy. The comparison of C 1s spectra for 50 nm (Figure 3.1(a)) and 200 nm PPy nanotubes (Figure 3.1(b)) shows that for the higher diameter nanotube there is an enhanced density of states around the β-carbon peak (Figure 3.1(c)). The peak intensity ratio C 1s(β)/C 1s(α) is found to increase from [107,108] 0.25 for 50 nm PPy nanotube to 0.47 for 200 nm PPy nanotube. Also, the area of the disorder related C 1s component around 285.8 eV reduces from 27% of the total C 1s spectrum area for 50 nm nanotubes to 19% for 200 nm nanotubes. This strongly indicates less disorder to be present in the larger diameter nanotubes. C 1s spectra for AuPPy nanotubes of 50 nm and 200 nm diameter are shown in Figure 3.2. It
was found that at a given diameter, AuPPy nanotubes have higher $C\, 1s(\beta)/C\, 1s(\alpha)$ peak ratio compared to pure PPy nanotubes. For 50 nm nanotubes, this ratio increases from 0.25 for PPy to 0.33 for AuPPy, while for 200 nm it increases from 0.47 to 0.6. Thus, there is a clear reduction of disorder in AuPPy nanotubes compared to bare PPy nanotubes.

b. Nitrogen Spectra (\(\equiv N^-\))

Figure 3.3 shows nitrogen N 1s spectra for PPy and AuPPy nanotubes. All spectra could be fitted with three components corresponding to amine-like N (\(-NH^-\)) atoms, imine-like N (\(\equiv N^-\)) atoms, and positively charged amine-like N (\(-N^+\)) atoms, typical of the polypyrrole spectrum [110,111] For PPy nanotubes, a pronounced shoulder is observed at lower binding energy around 397.7 eV corresponding to (\(\equiv N^-\)), which is larger compared to that in AuPPy. For 50 nm diameter nanotubes, the area of the (\(\equiv N^-\)) component is found to reduce from 2.4% of the total N 1s spectrum of PPy nanotubes to 1% for AuPPy nanotubes, while for 200 nm diameter it reduces from 4.3% for PPy to 2.1%. The reduced density of imine-like N atoms in AuPPy is due to the protonation of (\(\equiv N^-\)) atoms in the presence of chloroaauric acid to form (\(-NH^-\)) atoms, whereby $HAuCl_4$ releases H atoms that attach to (\(\equiv N^-\)) atoms. Such protonation of imine atoms to form amine-like N atoms in PPy films in the presence of acid solution is well-known [112]. This leads to reduction of gold atoms in the process. Similar protonation of nitrogen atoms results in reduction of gold from chloroaauric acid has been observed in PPy thin films [113]. Furthermore, it is found that the area of the (\(-N^+\))-component in the N 1s spectrum decreases for AuPPy [113].

The integrated intensity of (\(-N^+\))-ion varies from 19.4% (PPy) to 12.8% (AuPPy) for 50 nm nanotubes and from 19.8% (PPy) to 15.4% (AuPPy) for
3.2. Hard X-ray Photoemission Spectroscopy (HAXPES)

Figure 3.3: N 1s spectra of (a) 50 nm PPy nanotubes, (b) 50 nm AuPPy nanotubes, (c) 200 nm PPy nanotubes, (d) 200 nm AuPPy nanotubes, normalized to the peak intensity. The thick solid lines are the fitted curve to the experimental data, which is the sum curve of three peaks. The thin dotted lines are the component peaks of the fitted curve.

200 nm diameter material. A decrease of the -N\(^+\)-component has been ascribed to a reduction of the doping level in nanotubes [110], and the present data therefore suggest a reduction of the carrier concentration in gold incorporated nanotubes.

c. Gold Spectra(Au)

For AuPPy nanotubes, the Au 4f core level spectra reveal the well-known doublet structure corresponding to 4f\(^7/2\) and 4f\(^5/2\) at 84.0 eV and 87.7 eV binding energy [99] (Figure 3.4). However, each component exhibits a pronounced shoulder at higher binding energies. The spectra were thus fitted with two peaks, one corresponding to neutral Au\(^0\) and the other to positively charged state of Au. The data show that gold is mostly reduced to the neutral state.
but some are only partially reduced to positively charged state from chloroauric acid. Comparing the data obtained for 50 nm and 200 nm diameter AuPPy (Figure 3.4), it is obvious that the ratio of the charge states depends on the diameter and the amount of $\text{Au}^+$ is less in the 200 nm diameter nanotubes. From the x-ray photoelectron spectra of the PPy nanotubes we have found the information about the major constituents of PPy nanotubes are carbon and nitrogen and chlorine from the oxidizing agent, additionally gold lines are clearly observed for AuPPy nanotubes. The C $1s$-spectra for a given diameter of nanotubes shows that gold-incorporated nanotubes is less disordered in compared with pure polypyrrole nanotubes.

Figure 3.4: Au 4f spectra of (a) 50 nm AuPPy nanotubes. (b) 200 nm AuPPy nanotubes. The thick solid lines are the fitted curves to the experimental data, corresponding to the sum curve of two components. The thin lines are the component peaks of the fitted curve.
3.3. Variation of disorder in polypyrrole and gold incorporated polypyrrole nanotube:

3.3.0 Variation of disorder in polypyrrole and gold incorporated polypyrrole nanotube:

Conductivity

The electronic transport in a disordered solid is basically composed of two parts,
1. Transport in Extended states and
2. Transport in Localized states.

The contribution of the extended states to the conductivity is always dominates when there is a sufficiently large number of carriers in these states. This happens when Fermi energy lies above the mobility the edge $E_c$ or within few $k_BT$. The first case occurs in case of liquid and amorphous metals and in alloys. The second is important in impurity band of semiconductor, amorphous semiconductors or in conducting polymers at not too low a temperature. If the Fermi energy lies in the region of localized states, the conductivity contribution of the extended states can be calculated using Kubo-Greenwood formula and it is represented as

$$\sigma = \sigma_{E_c} \exp\left(-\frac{(E_c - E_F)}{k_BT}\right),$$

where $\sigma_{E_c}$ is the conductivity at mobility edge. Until now we didn’t consider any contribution of localized states below $E_c$ to the conductivity. It is fundamentally different in that, for $T = 0$, $\sigma_E$ vanishes below $E_c$. It is not possible for a charge carrier to diffuse from one localized state to another without any expenditure of energy. Transitions are only made possible by thermal vibration of the lattice and it is called phonon assisted hopping. In disordered solids, the energy of the the localized states are spread over a wide range. Adjacent localized states can have widely different energies. But in any case the energy difference must be supplied by a phonon for the phonon assisted hop-
ping or for activation to occur. At low temperature when the energy supplied by the phonon is less than the energy need for activation of an electron to the nearest-neighbor, the transition probability become so small that the transition to further removed states, which involves the expenditure of a lesser amount of energy, become more likely this introduces variable range hopping mechanism (VRH). The principle behind Variable range Hopping is an optimization of transition rates: Transitions between two sites are affected exponentially both by the distance and by the energy that separate the sites. (In this it differs fundamentally from hopping of ions over a barrier, say in a regular glass, where only barrier energies determine exponentially the transition rates). The fact that a lower temperature $T$ makes it harder to overcome the energy separation can be partly compensated by hopping over larger distances, where a lower energy site is more easily found, resulting in variation of hopping range with temperature. The result of an optimization is an activation energy that decreases with decreasing $T$. Mott showed that in three dimensions and at a constant density of states the optimization leads to a $T$-dependent conductivity

$$\sigma(T) = \sigma_0 \exp\left[-\frac{T_0}{T}\right]^x$$

(3.1)

where $T_0$ is called Mott’s characteristics temperature, and the exponent $x = 1/(1+d)$. In three dimension $d = 3$ and the corresponding conductivity

$$\sigma(T) = \sigma_0 \exp\left[-\frac{T_0}{T}\right]^{1/4}$$

(3.2)

For 3D VRH, $T_0$ is represented as

$$T_0 = \frac{18.1\alpha^3}{k_B N(E_F)}$$

(3.3)
3.3. Variation of disorder in polypyrrole and gold incorporated polypyrrole nanotube:

Figure 3.5: (a) $\sigma$ vs $T^{-\frac{1}{4}}$ plot, showing 3D-VRH behaviour of 200 nm PPy, 50 nm PPy, 200 nm AuPPy, and 50 nm AuPPy at low temperature. The solid line shows 3D-VRH fitting. The value of $T_0$ indicated in each graph corresponds to Mott's temperature. (b) $\sigma$ vs $T^{-1}$ plot showing thermally activated behaviour (solid line) at higher temperatures.

[114] $\alpha$ is inverse of localization length and $N(E_F)$ is the density of states at Fermi level. At high temperature the energy of phonon is enough to supply the energy for nearest neighbor hopping and conductivity become activated.

Magnetotransport

In presence of a magnetic field the energy spectrum of a free electron in transverse direction is represented by $E_n = (n + \frac{1}{2})\hbar \omega$ where $\omega = \frac{eH}{mc} = \frac{h}{m\lambda}$ is called Larmor frequency and $\lambda$ is called magnetic length which is represented as $\frac{c\hbar}{eH}$. This length scale corresponds to the narrowest length of electron localization due to magnetic field. Typically, a positive magnetoresistance is expected for hopping conduction; applying a magnetic field results in a contraction of the overlap of the localized state wave functions and thus an increase of the needed average hopping length [115,116]. This corresponds to a large positive magnetoresistance at sufficiently low temperatures. The theory of positive MR has been developed for two cases, namely, without and with electron-electron
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interactions. In both cases the weak-field magnetoresistance with strong temperature dependence can be expressed as follows:

\[
\ln\left(\frac{\rho(H)}{\rho(0)}\right) = t\left(\frac{L_C}{L_H}\right)^4 \frac{T_0}{T} \propto H^2 T^{-Y}
\]

(3.4)

, where \(t, Y\) are constants, the magnetic length \(L_H = \left(\frac{\hbar}{eH}\right)^{1/2}\), \(\hbar\) is the Planck’s constant, and \(c\) is the velocity of light. For 3D-VRH, \(t = \frac{5}{2016}\), and \(y = \frac{3}{4}\) (for 1D-VRH, \(t = 0.0015\), and \(y = \frac{3}{2}\)). Alternatively in case of 3D VRH, weak field magneto resistance can be represented as

\[
\ln\left(\frac{R(B)}{R(0)}\right) = t_1\left(\frac{B}{B_C}\right)^2 \left[\frac{T_0}{T}\right]^{\frac{1}{4}}
\]

(3.5)

, where \(t_1 \approx 0.1\) and \(B_C\) is the higher limit of weak magnetic field zone. \(B_C = \frac{\hbar \alpha^2}{2\pi e^2 T_0^{1/4}}\). In high magnetic field limit (above \(B_C\)) the magneto-resistance follows \(B^{-(d+1)}\) law up to certain extent, where \(d\) is the dimension of the material.

3.3.1 Results & Discussions

Temperature dependent conductivity (\(\sigma\)) measurements of the PPy and AuPPy nanotubes of 50 nm and 200 nm diameter is shown in Figure 3.5. As it is clear from the figure that at low temperature conductivity of the system following 3D-VRH behavior. \(ln(\sigma)\) vs \(T^{-\frac{1}{2}}\) fits well in the low temperature region(shown in Figure 3.5a). For the PPy nanotubes, the VRH behavior is found to prevail up to 28 K and 95 K for 200 nm and 50 nm nanotubes, respectively, in case of AuPPy nanotubes, this behaviors exists up to 35 K and
3.3. Variation of disorder in polypyrrole and gold incorporated polypyrrole nanotube:

Figure 3.6: (a) ln\left[\frac{R(B)}{R(0)}\right] \text{ vs } B^2 plot showing, $B^2$ dependence (solid line: corresponds to fit) of magneto-resistance at low magnetic field. All the data are taken at a temperature of 25K which is within the 3D-VRH region of charge transport in the nanotubes. (b) ln\left[\frac{R(B)}{R(0)}\right] \text{ vs } B^{1.3} plot showing $B^{1.3}$ behavior (solid line) of magneto-resistance at high magnetic field.

199 K for 200 nm and 50 nm nanotubes respectively. At higher temperature this system is following activated type behavior, shown in Figure 3.5b. From the fitting, values of Mott characteristics temperatures $T_0$ was obtained to be 6.25X10^6 K, 1.34X10^7 K, 2.18X10^7 K, and 1.47X10^8 K for 200 nm PPY, 50 nm PPY, 200 nm AuPPY, and 50 nm AuPPY nanotubes respectively.

Our aim is to find out the value of localization length and density of states at Fermi level. In order to find the localization length have done magnetoresistance measurement. The $\ln\left[\frac{R(B)}{R(0)}\right] \text{ vs } B^2$ plot (Figure 3.6a) and $\ln\left[\frac{R(B)}{R(0)}\right] \text{ vs } B^{1.3}$ (Figure 3.6b) taken at 25 K in the 3D-VRH region of PPY and AuPPY nanotubes clearly show $B^2$ and $B^{1.3}$ dependence of magneto-resistance at low and high magnetic field, respectively. $B_c$ is defined by the maximum magnetic field upto which the magneto-resistance follow $B^2$ dependence, it is called the critical magnetic field. Combining Figure 3.6a, b and using equation 3.4 we have find out values of critical magnetic fields ($B_c$) for all these samples, were found to be 0.9 T, 1.0 T, 0.5 T, and 0.4 T for 200 nm PPY, 50 nm PPY, 200 nm AuPPY, and 50 nm AuPPY.
Diameter of nanotube | $T_0$ (K) | Localization length ($\alpha^{-1}$) | $N(E_F)$ $eV^{-1} cm^{-3}$ | $B_c(T)$
--- | --- | --- | --- | ---
200 nm | 6.25X10^6 | 14 ± 0.28 nm | 1.21X10^{16} | 0.9
50 nm | 1.34X10^4 | 12.08 ± 0.24 nm | 8.834X10^{15} | 1.0
Au200 nm | 2.18X10^4 | 16 ± 0.32 nm | 2.3X10^{15} | 0.5
Au50 nm | 1.47X10^5 | 14.16 ± 0.28 nm | 4.999X10^{14} | 0.4

Table 3.1: Results of data analysis for samples 200 nm PPy, 50 nm PPy, 200 nm AuPPy and 50 nm AuPPy; $B_c$ deduced from $B^{1/3}$ vs ln[$R(B)/R(0)$], $\alpha^{-1}$ calculated using $B_c$, $T_0$ extracted from the fitting of 3D-VRH graph (conductance vs $T^{-1/4}$), using the value of $T_0$ and $\alpha^{-1}$ we have calculated $N(E_F)$

nanotubes respectively. Using these values of $B_c$ and corresponding values of $T_0$ in equation 3.5, we obtain localization lengths. All these values for 200 nm PPy, 50 nm PPy, 200 nm AuPPy, and 50 nm AuPPy nanotubes, are shown in Table 3.3.1. This clearly indicates that the localization length decreases as the diameter of nanotubes decreases, while it increases on incorporation of gold for a given diameter of the nanotube. The localization length is directly related to the amount of disorder in the nanotubes [110] and decreases with the increase of disorder. Thus, the disorder increases as the diameter of nanotubes decreases, while it decreases on incorporation of gold for a given nanotube diameter. This observation is consistent with the C 1s photoemission data.

Using the values of $\alpha$ and the corresponding $T_0$ in equation 3.3, we obtain the values of $N(E_F)$ as shown in Table 3.3.1. In the case of PPy films and nanowires, it is known that a change in the doping level leads to the change in the density of states at the Fermi level $N(E_F)$ [110, 117]. Our result shows reduction in doping level on reduction of the diameter of PPy nanotubes as well as on gold incorporation.
3.4. Charge Density Wave (CDW) like behavior in Polypyrrole and gold-polypyrrole nanocomposite nanotube:

3.4.0 Charge Density Wave (CDW) like behavior in Polypyrrole and gold-polypyrrole nanocomposite nanotube:

In a system of low electron density when the kinetic energy of electrons is dominated by columbic interaction between them, then these electrons get positional ordering and it is called Wigner crystallization [10]. There is a condition for formation of Wigner crystallization in a system which is directly depends on the electron-electron separation (a) and effective Bohr radius (aB) of the carrier. This strength of interaction is defined as $r_S = \frac{a}{2a_B}$. Peoples have defined the values of $r_S$ for different systems, $r_S \simeq 36$ for clean unbound system, $r_S \simeq 7$ for disordered unbound system and for a bound system it is $r_S \simeq 4$ [118–121]. The decrease of $r_S$ in disordered system is due to the breaking of continuous translational invariance that stabilize the crystalline state. It has been predicted theoretically that 1D Wigner crystal has the same property of the $4k_F$ charge density wave [18]. It has been shown earlier that Wigner crystal can form in quasi-one-dimensional system or in disordered nanowires [21,38,122,123]. Disorder in these systems act as pinning centers of this correlated-electronic state. In case of strong impurity pinning, the carrier transportation occurred through the variable range Hopping. For weak pinning, conduction occurs following a power law behavior. If we increase the applied bias from below the threshold value, then certainly conductivity increases due to the de-pinning of Wigner crystal state. This state is called the sliding charge density wave state that manifests resistance switching in current-voltage measurement [105].

Polypyrrole is a conjugated polymer (alternative double and single bonds) where Peierls distortion occurs due to electron-phonon interaction which results alternative double and single bond. As a result, potential-well arises where elec-
Figure 3.7: (a) & (b) showing current voltage characteristics of polypyrrole and gold-incorporated polypyrrole 100 nm diameter nanotube at 5 K temperature. Showing three distinct zones; gap voltage ($V_G$), power law and switching above threshold voltage ($V_{Th}$).

Electrons can be localized. Therefore they behave like an insulator in the neutral state and become conducting after doping [124]. For low doping level, carriers can get trapped in these potential wells at low temperature results in Wigner Crystallization (WC) [104]. It has shown earlier that WC state can occur in low doped polypyrrole nanotubes which manifests all behaviors of CDW state, as predicted earlier by Schulz [18]. Here we have studied the effect of external impurity on the Charge Density wave state of Polypyrrole nanotubes. For this we have successfully incorporated gold in polypyrrole nanotubes, and studied the results of low temperature electronic transport measurements.

### 3.4.1 Current-Voltage Characteristics (I-V)

The current voltage characteristic of gold incorporated polypyrrole nanotubes follow ohmic behavior at room temperature. At low temperature Current-Voltage characteristics of gold incorporated polypyrrole shows three distinct regions, shown in Figure 3.7(b). Upto the voltage $V_G$ there is not much in-
3.4. Charge Density Wave (CDW) like behavior in Polypyrrole and gold-polypyrrole nanocomposite nanotube:

crease in current with the increase of voltage, $V_G$ is called the gap voltage. Above $V_G$, current increases rapidly with the increase of voltage and following a power law behavior in $I \propto V^{1+\beta}$, where $\beta$ is an exponent. The power law in I-V behavior continues up to a voltage called threshold voltage ($V_{Th}$) above which the system goes to a highly conducting state. Above $V_{Th}$ the current in the system is limited by source meter compliance. Once the system goes to a high conducting state, if we reduce the value of applied bias below the $V_{Th}$ the system does not return back to low conducting state, unless we reduce the applied bias below $V_{Re}$ (return voltage). Thus the system shows a hysteresis loop in the I-V curve. These three distinct zones in polypyrrole nanotubes are one of the characteristics of Charge Density Wave (CDW) state. All the three zones in PPy and AuPPy are clearly shown in Figure 3.7a and 3.7b.

**a. Gap Voltage ($V_G$)**

Chemically synthesized polypyrrole nanotubes with low doping at low temperature shows a gap ($V_G$) in I-V characteristics. This arises due to presence of electron-electron interaction (EEI) in the correlated electrons. Conducting polypyrrole is a disordered material, where several ordered metallic zones are separated by disorder barrier. Coulomb blockade phenomena can not explains the gap voltage. In case of coulomb blockade phenomena, if the charging energy for these nano-particles is greater than the energy supplied by the thermal energy then a gap voltage arises. Below which no conduction occurs. With the increase of temperature the threshold voltage decreases. Suppose there is $N$ number of identical nanoparticle in a chain and $V_T(0)$ is the threshold field for conduction. At any finite temperature $T$ the threshold voltage can be related by the equation $V_T(T) = V_T(0) - Nk_B T/e$, so the variation of threshold voltage will be linear in $T$ [125]. Here in our representation we are using the notation
Figure 3.8: (a) & (b) Temperature dependence differential conductance of 100 nm polypyrrole (PPy) nanotube and gold-polypyrrole (AuPPy), the gap voltage decreasing with the increase of temperature.

$V_G$ in place of $V_T$. In case of gold-incorporated nanotubes $V_G$ decreases with $T$ and it varies strongly in exponential manner.

Figure 3.8 shows $dI/dV$ vs $V$ plot, from which it is clear that $V_G$ in case of gold-incorporated nanotube is much higher than the polypyrrole nanotube of same diameter and at same temperature. In case of PPy nanotube $V_G$ vanishes just above 20 K, whereas in case of AuPPy nanotube it vanishes above 35 K. We have plotted the temperature variation of $V_G$ in Figure 3.9 for 100 nm PPy and AuPPy which showing that $V_G$ following an exponential dependence with temperature. This phenomena can easily be explained by the correlated electrons pinned by disorder [104,125,126] and opens up a gap.

b. Power law and Luttinger liquid like behavior

In 1D the electronic transport properties are strongly affected due to the presence of strong electron-electron interaction (EEI), conventional Fermi liquid theory breaks down and Luttinger Liquid (LL) theory comes into play due to the short range repulsive force [127]. When there is long range Coulomb
3.4. Charge Density Wave (CDW) like behavior in Polypyrrole and gold-polypyrrole nanocomposite nanotube:

interaction dominates then we found the Wigner Crystal (WC) behavior [18]. In 1D system the existence of temperature dependence power law of conductance \( dI/dV \propto T^\alpha \) and power law in I - V \( I \propto V^{1+\beta} \) arises (depending on \( eV \ll k_B T \) or \( eV \gg k_B T \)), due to power law behavior of the tunneling density of states near Fermi level \( (E_F) \). To a certain degree this behavior correlates with a LL theory for transport in 1D systems, which implies that both: tunneling along LL state through impurity barriers and tunneling between the polymer chains with LL state provides the conduction of a set of coupled LL state. Existence of power law behavior in I-V and conductance-temperature, existence of single Master curve in \( I/T^{1+\alpha} \) vs \( eV/k_B T \) plot are the signature of LL state. In Figure 3.10a we have presented the current-voltage characteristics of 100 nm PPy nanotubes which exhibit power law behavior with an exponent(\( \beta \)) value 5.25 at 5 K temperature. The conductance vs temperature plot which is shown in the inset of Figure 3.10a, clearly showing that conduc-

Figure 3.9: (a) & (b) Temperature variation of gap voltage for 100 nm polypyrrole (PPy) nanotube and gold-polypyrrole (AuPPy), the gap voltage decreasing exponentially with temperature.
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Figure 3.10: (a) Showing the power law dependence of $I \propto V^{1+\beta}$ with $\beta$ value 5.25 at lowest temperature 5 K, inset showing temperature dependence of conductance following power law with $\alpha = 3.74$, (b) plot of $I/T^{1+\alpha}$ vs $eV/k_B T$ at different temperature showing data at different temperature does not fit well a single Master curve.

tivity also following power law in the temperature range between 25 K to 200 K, with an exponent ($\alpha$) value 3.74 (the details of the variation of conductivity w.r.t. temperature and applied bias presented in chapter 5). The value of $\beta$ and $1+\alpha$ are not equal. We have presented in Figure 3.10b $I/T^{1+\alpha}$ vs $eV/k_BT$ plot for current-voltage data of 100 nm PPy nanotubes collected at different temperature which clearly showing that they are not collapsing on a single Master Curve. So the inequality of these two exponents and the lack of single Master curve does not support LL theory. Polypyrrole is a conjugated polymer (alternative double and single bonds) where Peierls distortion arises due to the presence of alternative double and single bond. Because of the peierls distortion they are insulated in the neutral state and become conducting after doping [124]. For low doping level carriers get trapped in these potential well and at low temperature it can formed Wigner Crystal (WC). At low bias when these correlated states are pinned and localization length is smaller than the separation between the impurity states, the conduction occurs via interchain
3.4. Charge Density Wave (CDW) like behavior in Polypyrrole and gold-polypyrrole nanocomposite nanotube:

Figure 3.11: (a) Showing the power law dependence of $I \propto V^{1+\beta}$ with $\beta$ value 8.7 at lowest temperature 5K, inset showing temperature dependence of conductance following power law with $\alpha = 8.2$, (b) plot of $I^{1+\alpha}$ vs $eV/k_B T$ at different temperature showing data at different temperature does fit well a single Master curve.

hopping [128] and 3D- VRH arises. With the increase of bias, tunneling become more probable along the polymer chain due to the directionality imposed by the bias and tunneling density of states in WC follows power law [18,118,129] and values of the exponent varies between (3-6) [32]. For a classical 1D WC pinned by impurities one should expect the VRH regime at low temperature with an exponential temperature dependent of conductivity $G(T)$ [29,130]. For weakly pinned Wigner crystals tunneling density of states shows a power law behavior with the applied bias [131]. In case of gold-incorporated polypyrrole nanotube also showing power law in I-V and $\sigma$-T as shown in Figure 3.11a and 3.11b. The value of $\beta$ is found to be 8.7, which is much higher compared to pure polypyrrole nanotube of same diameter. In this case also the correlation between the two power law does not exist as $\beta \neq 1 + \alpha$. In case of WC the power law exponent of current- voltage increases as we reduce the disorder in the system [32]). In case of gold-polypyrrole (AuPPy) nanotube we have found that due to gold incorporation process the disorder in the system has decreased [132] as shown...
in HAXPES section and the increase of $\beta$ is consistent with the reduction of disorder. Gold incorporated nanotubes used to show power law behavior in $\sigma$-$T$ at higher bias compared to polypyrrole nanotubes of same diameter because due to gold incorporation, number of disorder or pinning sites reduces but the value of pinning potential increases, which results in higher applied bias for weakening the pinning sites for the movement of correlated electrons along chain direction.

c. Switching behavior

Gold-polypyrrole composite and bare polypyrrole nanotube used to show a sharp transition (resistive switching) to a highly conducting state above a certain threshold voltage ($V_{Th}$). After the switching transition, the low conducting state is recovered when the bias voltage is reduced below a certain voltage ($V_{Re} < V_{Th}$). Current-voltage (I-V) characteristics, thus exhibit hysteresis and was found to be symmetric for both positive and negative bias (Figure 3.12a). In Figure 3.12a, the open circle data correspond to polypyrrole (PPy) and filled circle corresponds to gold-incorporated polypyrrole (AuPPy) nanotube. For 100 nm diameter AuPPy sample, if we increase the bias voltage above 28.35 V ($= V_{Th}$) at 25 K temperature, the current through the nanowires increases abruptly and the current gets limited by the current compliance of the source meter, which is set to 10 mA. If we decrease the voltage below 1.6V ($< V_{Re}$), then the nanotube switches back to a low conducting state giving a large hysteretic I-V characteristics. The corresponding values of $V_{Th}$ and $V_{Re}$ for 100 nm PPy, 0.375 V and 0.09 V and for 100 nm AuPPy, 27.35 V & 1.43V respectively. Much higher hysteresis of AuPPy nanotubes as compared to nanowires of PPy makes these nanotubes better materials for memory device application. Moreover, larger hysteresis allows the resistance switching to survive at much higher
3.4. Charge Density Wave (CDW) like behavior in Polypyrrole and gold-polypyrrole nanocomposite nanotube:

Figure 3.12: (a) Comparison of switching between 100 nm polypyrrole (PPy) and gold-polypyrrole (AuPPy) nanotube, inset showing current biased switching of 100 nm AuPPy nanotube (b) Variation of hysteresis and threshold with temperature for 100 nm AuPPy nanotube.

Temperature. The area under the hysteresis was found to be independent of scan speed with which data were taken. The hysteresis \( V_{Th} - V_{Re} \) was found to decrease with the increase of temperature. The change in resistance due to switching was found to be more than three orders of magnitude as shown in Figure 3.12. Systematic measurement showed that the switching threshold bias remains constant at any particular temperature over a large number of voltage cycles. The switching threshold \( V_{Th} \) was found to be very sharp, and we have seen that if the bias is kept few mV below the \( V_{Th} \), switching never occurs. But this sharpness decreases with the increase of temperature. The sharpness of switching as well as hysteresis is better in gold incorporated polypyrrole nanowires than that obtained in PPy system, as shown in Figure 3.12a. In the upper inset of Figure 3.12a, we have shown a typical hysteresis data of AuPPy sample obtained in current bias condition that exhibit features of switched state in better clarity. The nature of the obtained data is similar to the published [104] data of PPy nanowire. As the applied bias crosses the
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Figure 3.13: Variation of (a) Threshold voltage and (b) hysteresis with the increase of temperature for 200 nm and 100 nm nanotubes.

$V_{Th} (=27.35 \text{ V})$, the value of resistance drops and measured voltage across the wires becomes 17.00 V (refer upper arrow in the upper inset of Figure 3.12a). Further increase in current reduces the voltage further giving a zone of negative differential resistance (NDR) expected in a charge density wave system (CDW) [105]. Lower arrow in this figure indicates the return path, the system remains in NDR state as the current is reduced, and we obtain a hysteresis until $V_{Re}$ is reached. It is clear from the data (see Figure 3.12(a)) that the hysteresis loop is much larger for the gold-polypyrrole system compared to that in bare polypyrrole nanotubes. With increasing temperature, the threshold voltages as well as hysteresis loop decrease (Figure 3.12). For pure polypyrrole nanotubes of 200 nm diameter, the switching behavior reduced substantially above 30 K, but for gold embedded polypyrrole nanotubes of 200 nm diameter the switching is observed even above 90 K (refer Figure 3.13(a)). In the case of 100 nm diameter polypyrrole nanowires, the switching remains up to 65 K. But gold incorporated nanotubes exhibit switching transition even above 120 K (shown Figure 3.13(a)).

We observed a large change in resistance of 3-order of magnitude and
absence of change in temperature was not observed during the switching process, ruling out switching due to Joule heating. For such bias current (voltage), an increase in temperature 100 K is needed to change the resistance by two orders of magnitude, to observe switching due to Joule heating. From Figure 3.12(b), it is clearly seen that with the increase of temperature the hysteresis loop \((V_{Th} - V_{Re})\) decreases for both 200 nm and 100 nm diameter tubes. The data in Figure 3.12(b) also show that switching transition and corresponding hysteresis cannot be due to any charge trap phenomenon, because in case of charge trap phenomenon hysteresis loop should decrease with the decrease of temperature. Reversibility in hysteresis confirms that the switching transition is not due to any redox reaction.

**Ruling out filamentary conduction:**

The observed switching is not due to filamentary conduction. If switching is due to the formation of conducting filament, then the switching to low resistive state will occur when the conducting filament will extend from one electrode to another electrode \([133–135]\). So if the separation between these electrodes increases then one needs larger bias voltage to establish a filamentary path between them. However, we have observed that for larger diameter nanowires which are longer but the switching threshold voltage is small than low diameter short nanowires. The data shown in Figure 3.13(a) clearly showing that with increase of tube diameter threshold bias \((V_{Th})\) decreases at any particular temperature. It is to be noted here that the lengths of nanotubes having 200 nm diameter were 1.2 times higher compared to those having 100 nm diameter as used membrane of different thicknesses. As a result, for a particular applied bias voltage, the 200 nm nanotubes get lower field compared to 100 nm diameter tubes. If the switching was due to dielectric breakdown, then for a
particular temperature we should have obtained higher threshold voltage in 200 nm diameter tube as compared to that in 100 nm tube. The opposite behavior observed here rules out the possibility of dielectric breakdown as the cause of switching transition. If the switching is due to the formation of conducting filament, then the switching threshold should not show systematic variation on the diameter of the nanowires [133] rather should depend on the length of the nanowires. It is also noted that after gold incorporation the threshold voltage has increased.

If the switching transition in these system is due to the formation of conducting filament then incorporation of gold nanoparticle will enhance the formation of filamentary path and the switching threshold should decrease. Also in the case of filamentary conduction noise in the high resistive state is higher than the low resistive state [133], whereas we see an enhancement of noise in the low resistive switched state [105].

The observed switching transition cannot be explained by movement of Oxygen ion (often observed in filamentary conduction) or on the basis of a redox reaction because in these case the change in conductance is permanent whereas, we see a reproducible switching transition even after several thermal cycling. In order to rule out conducting path formation due to movement of doping ion (Cl\(^-\)) we have done SIMS of the sample before and after electronic transport measurement (switching measurement) along the length of the entire nanotube. We didn’t found any significant change of doping along the length of the nanotube (Cl\(^-\) profile and Cl/N profile), as shown in Figure 3.14.
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Figure 3.14: Amount of various elements in the polypyrrole nanowires along the length, before (upper) and after switching (lower) transition. After switching transition data were shifted for clarity. The profile of Cl/N along the nanowires remains same before and after switching transition.

Ruling out Fuse-AntiFuse conduction:

A switching process in which the switching procedure does not depend on the polarity of the voltage and current signal is called unipolar (or symmetric). This type of switching occurs generally due to filamentary formation in metal-insulator-metal (MIM) structure [136]. The system switched from high-resistance state (OFF) into the low-resistance state (ON) when a threshold voltage ($V_{SET}$) is applied, as sketched in Figure 3.15(a). The current is limited by the compliance current of the control circuit. The system remains in the low resistive state (ON) state until we pass high current through the system. The system switched back to off-state (‘reset’) at a higher current ($I_{RESET}$) and a voltage below the set voltage ($V_{RESET}$). As shown in Figure 3.15(a) the blue-line corresponds to the switching path from OFF state to ON state and
Figure 3.15: (a) A typical Uni-polar resistance switching behavior in FUSE-ANTIFUSE (filamentary) type switching transition, $V_{SET}$ is the threshold voltage for switching to low-resistive state and $V_{RESET}$ is the RESET voltage below which the system become switched to high-resistive state ($I_{SET} < I_{RESET}$) (Switching to high and low resistive state independent of bias polarity). (b) Typical Bipolar-switching behavior, where $V_{SET}$ and $V_{RESET}$ occurs at opposite bias polarity (c) V-bias switching behavior in Polypyrrole-nanotube ($V_{SET} > V_{RETURN}$) (d) current driven switching in our system.

the orange line corresponds to switching back from OFF state to ON state. In contrast, bipolar-switching (or anti-symmetric) occurs when the system set to an ON state at one voltage polarity and the reset to the OFF state on reversed voltage polarity (Figure 3.15(b)). The structure of the system must have some asymmetry, such as different electrode materials or the voltage polarity during the initial electroforming step, in order to show bipolar switching behavior. Our system of course used to show Unipolar type behavior as for SET and RESET it don’t need to change the bias polarity. In our system switching is symmetric.
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and unipolar, but the main difference between our system and fuse-antifuse type switching is that after the switching to the ON state the system can be switched back to the OFF state just by reducing the bias ($V_{\text{RETURN}} < V_{\text{SET}}$) Figure 3.15(c). In this case we don’t need to increase the current above compliance current, which is necessary to fuse the filamentary type conducting state for returning it back from ON to OFF state in case of fuse-antifuse type transition. This phenomenon is also clear from the current bias measurement of our system (see Figure 3.15(d)), that the $I_{\text{SET}}$ is higher than $I_{\text{RETURN}}$. In our system the resistive switching model can not be explained by fuse-antifuse mechanism.

The observed switching transition reported here is consistent with that predicted for charge density wave system [137]. In structurally disordered materials (e.g., polymer and polymer-metal hybrids), characteristics of coherent CDW state can only appear due to the formation of an electron crystal known as Wigner crystal (WC) [18,29,104]. The formed WC remains pinned by the impurities present in the system and under a sufficient bias sliding motion starts which takes the system to a low resistive state through a switching transition [104] and the value of the threshold voltage depends on the pinning strength. By introducing gold homogeneously in the polypyrrole nanowires, we could effectively increase the pinning strength in the system that results in the increase of threshold voltage of switching transitions. The temperature domain of WC state is expected to increase with increasing pinning strength. [138,139]

The survival of switching transition above 90K in case of 200 nm and above 120K for 100 nm diameter nanowires clearly suggests that the presence of gold in polypyrrole has increased the temperature domain of WC state and associated resistance switching transition.
There are two possible reasons for the stabilization of the CDW state in gold-incorporated polypyrrole nanotubes. As the screening carriers are less in gold-incorporated nanotubes for this reason electron-electron interaction reduces less at a particular temperature compared to pure polypyrrole nanotubes. And second reason is that in gold-incorporated nanotubes disorder is less and localization length is large which results in much stronger electron-electron interaction in gold-incorporated nanotubes. As a result we get the manifestation CDW state in AuPPy nanotubes up to much higher temperature compared to polypyrrole nanotubes.

3.5.0 Conclusion

Here we have presented the preparation and characterization procedure of a metal-polymer composite nanotubes. The morphology of these nanotubes was studied using SEM, TEM, EDS. HAXPES technique was used to extract information about the doping and disorder of these nanotubes. Magneto-transport measurements were also carried out and the results clearly support the HAXPES data. The analysis of N 1s spectra and transport measurements reveal reduced carrier and disorder in AuPPy nanotubes compared to PPy nanotubes of same diameter. From the electronic transport measurements we have found that pinned CDW state exist in both PPy and AuPPy nanotubes. The pinned CDW states starts sliding when the applied bias increased above some threshold voltage ($V_{\text{th}}$) which manifests as resistive switching in current-voltage measurement. With the reduction of nanotubes diameter disorder increases which causes higher threshold field for sliding of the pinned CDW state. But for same diameter, the increase of threshold voltage in gold-incorporated nanotubes
probably due to existence of stronger pinning centers. The existence of stronger pinning centers arises probably due to the low doping in gold-incorporated nanotubes which causes lesser screening. With the increase of temperature, pinning centers are get screened by activated carriers, which results in weakening of these pinning centers and the threshold voltage for sliding decreases. But the decrease of threshold voltage with the increase of temperature is very fast in pure polypyrrole nanotubes compare to gold-incorporated one. The number of free carrier generated in a system at a particular temperature is directly related to the doping in the system and the doping is less in gold-incorporated one. The reduction of disorder and doping in the system increases the stability of CDW state in gold-incorporated one.
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