Metal Nanoparticles
Tailored P(NMP)
Nanowires Sensor
5.1 Introduction

Necessity for efficient monitoring of ambient and workplace air quality has resulted in varied class of information acquisition entities in terms of gas sensors. Growing levels of industrialization and urbanization are continuously adding up pollutants to the atmosphere and most alarmingly, many of these pollutants can endanger human life even at sub-ppm level of occurrence in atmosphere [1]. Mostly alarmingly, such pernicious effects are often too low to be detected at early stage [2]. Thus reliable performance of a sensor in a complex reference of operation that prevails in the term of ambient atmosphere has always been the prime point of research in gas sensors. At the same time, requirements of a real time sensing device [3], for ex.- (i) high sensitivity towards trace level of analytes, (ii) low power consumption, (ii) facile integrability with existing electronics, (ii) small physical dimension, (ii) fast operation etc. are setting new challenges the every other day and has geared spectrum of efforts towards development of tailor-made sensor platforms. Sound understanding of underlying sensor mechanism for any sensor constitutes the key point to achieve expected performance.

Present status of understanding and operational maneuverability of nanostructured materials suggests that one dimensional [1-D] nanostructures are highly potent is addressing the challenges to emerge as new age sensing materials [4-5]. Apart from minimization of sensor dimension and requirement of low power electronics to be combined with, theirstructures offer high aspect ratio that result in charge carrier accumulation or depletion in the bulk of the structure [6] and thus they are highly sensitive to even minor
perturbations in ambient conditions. Among pronounced 1-D nanostructures [7-9], conducting polymer (CP) nanowires has succeeded to remain at the focus of interest for sensor-based applications. This class of materials exhibit unique tunable electronic properties [10-12] that enables acute shaping of band gap structure which is a prime requisite for gas sensing applications [13]. At the same time, ease of synthesis, and unparallel flexibility and processibility are the advantageous aspects with polymeric materials that are not easy attainable for its counterparts viz. SWNTs and metal oxide nanowires. Either in the form of single nanowires [14-15] or aligned [16-18] / dendritic nanowires matrix [19] between pre-patterned electrodes, conducting polymer nanowires have shown highly significant sensing capabilities.

A large variety of analytes/gases have been detected by conducting polymers till date, however, sensing mechanism mostly relies on charge transfer from analytes [14-15, 17, 20-23]. Selective screening of analytes, thus, remains a stiff hurdle for polymeric sensors. Several reports have demonstrated modified /functionalized polymers that have shown enhanced sensing towards particular analytes. Dixit et al have found that Fe-Al doped Poly(Aniline) (PANI) has specific affinity towards CO in contrast to HCN and NH₃ [24]. Paul et al have found that inclusion of ferrocene with poly (Pyrrole) effected in efficient carbon monoxide sensing [25], which had been attributed to the transfer of electron cloud near the carbon atom of CO to the Fe atom of ferrocenyl moiety. Surprisingly, in strike contrast to the above mechanism, Watcharalahakom et. al. have reported PANI based CO sensor [26] where they have suggested withdrawing of electron lone pair from –NH sites of PANI by CO. Such discrepancies in suggested mechanisms definitely warrants systematic studies for effective designing of selective sensing backbones based on conducting polymers.
Moreover, modification / functionalization of polymers are mainly based on thin film based structures. Recently, Pawar et. al. have demonstrated a PANI-TiO\textsubscript{2} nanofibrous film that shows selective behaviour towards ammonia. Selective nature of the sensor was attributed to creation of positively charged depletion layer on TiO\textsubscript{2} [27]. However, behaviour of the sensor with other analytes was not thoroughly discussed. A significant attempt towards post synthesis functionalization of polymeric nanowires has been reported by Shirsat et al [28], where the authors have demonstrated successful ppb level sensing of H\textsubscript{2}S with Au nanoparticles modified PANI nanowires matrix. Liu et. al. have employed similar sensing backbone to detect volatile sulfur compounds [29]. Significance of this particular approach is multifold – (i) metal nanoparticles enhance effective surface area that results in higher surface of interaction with the gas [30], (ii) catalytic affinity of several metals to particular gas /gases [31], (iii) ease of synthesis of metal nanoparticles on polymeric surface by electrochemical route [28], chemical route [29], thermal /e-beam evaporation [32] etc. (iv) chemical library of metals are well extensive. However, not much effort has been directed to explore this perspective for development of analyte specific sensors. Some encouraging outcomes, however, with different metal decorated SWNTs based gas sensors array has been reported by Star et al [32].

*From the standpoint of above facts, the next course of the investigations (i.e work documented in the present chapter) was directed towards post synthesis tailoring dendritic matrices of Poly (N-Methyl Pyrrole) [P(NMP)] nanowires with Fe nanoparticles. During synthesis of the nanowires matrices platform, already described route in chapter 4 was adapted with the solitary difference that the concentration of dopant (NaNO\textsubscript{3}) was...*
increased to achieve higher conductivity so that a significant device current could be achieved at low biasing conditions.

Till date, most of the investigations on metal nanoparticles decorated SWNTs/CPs have relied on noble metals due to their catalytic properties [33-35]. However, for the investigation, Fe was a particular choice keeping in view their vacant d-orbital that are prone to accept electrons [2] for elucidation of sensing mechanism. The choice of analytes were Ammonia (NH₃), Carbon Monoxide (CO) and Phospine (PH₃), all having electron donating capability and hence, particularly interesting for the metal chosen. P(NMP) was chosen due to its generic high conductivity of Pyrrole group and less susceptibility towards oxygen and humidity [36].

5.2 Experimental Details

5.2.1 Materials

Monomer N-Methyl pyrrole (>99%) was procured from ACROS-ORGANICS (Geel, Belgium). Sodium Nitrate (NaNO₃), Ferrous Sulphate (FeSO₄) and Potassium Chloride (KCl) (all chemicals were of analytical grade) were purchased from Rankem Ltd., India. The monomer was vacuum distilled prior to use and rest of the chemicals were used as received. HPLC grade water (Rankem) was used for all syntheses and Double deionized (DID) water was employed for rinsing purpose unless otherwise specified.
5.2.2 Sensor Substrate

Standard photolithography and lift off technique was employed to generate specific patterned Au contacts on a heavily doped Si substrate with 300nm SiO\(_2\) layer. The oxide layer was deposited by low pressure CVD followed by e-beam and thermal evaporation of 20nm Cr (adhesion layer) and 180 nm Au layer. The electrode patterns were defined with 3 \(\mu\)m gap between successive electrodes and width of the patterns were kept to be 200 \(\mu\)m. Substrates were immersed in piranha solution (70% conc. H\(_2\)SO\(_4\)/30% H\(_2\)O\(_2\)) followed by rinsing with double deionized (DID) water and dried under N\(_2\) flow before use.

5.2.3 Fabrication of Sensor Backbone

The bridging of Au micropatterns by P(NMP) nanowires network were accomplished electrochemically in a generic three- electrode geometry [37]. The Au pads were wire bonded [West Bond; 7476D] to a custom chip carrier and epoxy glue was stamped onto the bonded regions for reduction of effective surface area to c.a. 37, 254 \(\mu\)m\(^2\) (as confirmed under optical microscope). Working electrode was formed by externally shorting two successive Au electrodes. A Pt wire (CH Instruments; CHI115) and a chlorinated Ag wire (Ag/AgCl wire) served as counter and reference electrodes respectively. Deoxygenated aqueous solution of N-methyl pyrrole (monomer) and NaNO\(_3\) (dopant) served as electrolyte for the syntheses of nanowires matrix. The monomer and dopant were taken in a concentration ratio of 0.5 mM : 1.5 mM. A 0.2 \(\mu\)L electrolytic solution was placed onto the Au ‘finger-tips’ region. The counter and reference electrodes were precisely poised in contact to the electrolyte via probe-station (Ecopia; EPS1000). The typical two-step deposition
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The process consisted of 0.5 mA/cm² anodic current density applied for 20 min followed by 0.02 mA/cm² for 90 min to the working electrodes. The P(NMP) nanowires surface were tailored with Fe nanoparticles under identical electrochemical conditions as already described by cycling potential across the electrodes from a +0.2V to -0.4V (V/S Ag/AgCl) for five times at a scan rate of 20 mVs⁻¹. The electrolyte, in this case, consisted of metal salt FeSO₄ (0.5 mM) and supporting electrolyte KCl (1 mM) in aqueous media. A 0.2 µl drop of deaerated electrolyte was dispersed on the synthesized nanowires region before electrodeposition. All electrochemical syntheses were carried out by CHI 660C electrochemical work station (CH Instruments, Texas, USA). After synthesis, the devices were rinsed in DID water to remove excess metal salts and dried under nitrogen flow.

5.2.4 Characterization Techniques and Instrumentation

Morphological study of the synthesized sensor devices were carried out by Scanning Electron Microscopy (SEM, Jeol JSEM 6360). To ensure the formation of Fe nanoparticles tailored P(NMP) nanowires devices were subjected to energy dispersive x-ray spectroscopy (EDAX). Electrical characteristics (I/V characteristics) were determined by linearly sweeping potential across the devices from -1 V to +1 V and simultaneous recording of resulting current (linear sweep voltammetry; CHI660C). Transfer characteristics of the devices were studied in back gate modality with a Keithley 2400 source measure unit coupled with Aplab (India) PPD3003-S programmable power supply with Si as back gate. The channel current (I_DS) was recorded while sweeping the drain-source voltage (V_DS) between -15V to +15 V and keeping the gate voltage fixed at -1V.
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For maximum effective exposure of the sensors to analytes, the devices were placed under a small cylindrical quartz flow through cell (c.a. 8 ml vol.) and clamped. Atmospheric isolation was ensured with a sandwiched silicon-o-ring between the chip-carrier and cell. Prior to sensing studies, the sensors were exposed to continuous flow of zero air (>98.5%; 200 ml min⁻¹) unless a stable baseline was achieved. The sensors were tested under various concentrations of NH₃ (>99.99%, Fisher Scientific), PH₃ (99.9995+, Sigma Aldrich) and CO (≥99%, Sigma Aldrich) prepared by diluting the analytes in pre- determined volumetric ratio to the carrier (zero air) to obtain the concentrations (at a cumulative flow rate of 200 ml min⁻¹) for which the sensors were validated. The flow of carrier and analyte were regulated by Mass flow controllers (Alicat Scientific Inc., MC200).

For CHEMFET modality sensing, transport measurements were carried by sweeping the $V_{GS}$ from -15V to +15V at constant $V_{DS}$ of -1 at 0.25 ppm concentration of analyte in each case. Mode and methods of instrumental approach was same as that was applied for studying device transfer characteristics had been applied here. Dynamic sensing responses of the devices were studied by applying a constant 10µA (DC) current to the sensor and recording the potential across the sensor when they were exposed to various concentrations of analyte. During exposure of the analyte at a particular concentration, the sensors were allowed to achieve maximum response immediately followed by flooding with zero air for optimum recovery to complete one validation cycle. The signals were applied and recorded by a current/voltage source-measure unit (Keithley; 2400). Ohm’s law was applied to calculate sensor resistance.

All syntheses and measurements were carried out under general laboratory conditions unless otherwise specified.
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Temperature stability of Fe nanoparticles tailored P(NMP) nanowires based sensors were studied from room temperature to 95°C in an indigenously developed controlled environment chamber by recording the baseline resistance at every elevation step of 10°C. For estimating the stability of the same sensor, sensitivity (at 1ppm) was recorded for a span of 90 days (three months) at regular interval of 5 days.

5.3 Results and Discussion

5.3.1 Electrochemical Synthesis

Chronopotentiogram for the synthesis of P(NMP) nanowires devices by typical two step galvanostatic route [28] is shown in fig. 5.1. In the first step of deposition, a higher current density was applied for formation of polymeric nuclei that acted as seeds for growth of nanowires in the subsequent phase of deposition.

![Chronopotentiogram](image)

**Figure 5.1:** Chronopotentiogram of two step galvanostatic deposition of P(NMP) Nanowires
During the first step, potential across the working electrode (with respect to Ag/AgCl quasi reference electrode) was found to be in the range of c.a. 0.62 V. On lowering the current density in the second step, the potential of the working electrode decreased and gradually stabilized at c.a. 0.57 V indicating the formation of nanowires [38]. A lower polymerization potential could be observed in comparison to the polymerization potential observed for NaNO₃ doped P(NMP) nanowires formation in chapter 4 as the concentration of dopant had been increased.

5.3.2 Morphological Study and Elemental Analysis

SEM image (figure 5.2) of the Fe nanoparticles tailored P(NMP) nanowires shows formation of dendritic nanowires with abundant intertwines. The average diameter of the nanowires was found to lie in the range of 250-320 nm.

*Figure 5.2:* SEM images of Fe nanoparticles tailored P(NMP) nanowires
Surface of the synthesized nanowires were found to be smooth and uniform throughout. Similar morphology of electrochemically synthesized P(NMP) nanowires have been reported by the author [37]. Distribution of Fe nanoparticles on the surface of nanowires matrix were found to be uniform with average diameter of the nanoparticles lying in the range of 65-80 nm. As shown in figure 5.3, different peaks of EDAX spectrum corresponds to the elements C, O, N, Si and Fe for the Fe nanoparticles tailored P(NMP) nanowires and the SiO$_2$/Si substrate.

![EDAX spectrum of Fe nanoparticles tailored P(NMP) nanowires](image)

**Figure 5.3:** EDAX spectrum of Fe nanoparticles tailored P(NMP) nanowires

### 5.3.3 Electrical (I/V) and FET Transfer Measurements

The current-voltage (I/V) characteristics (figure 5.4) indicate formation of ohmic contacts with Au microelectrodes for both the pristine and surface tailored P(NMP) nanowires network. As suggested by the transfer characteristics (figure 5.5), both the devices
have exhibited p-type nature confirming that the surface tailoring did not affect generic nature of the polymeric network.

**Figure 5.4:** Room temperature I/V characteristics of P(NMP) nanowires before and after tailoring of Fe nanoparticles

**Figure 5.5:** FET transfer characteristics of P(NMP) nanowires before and after tailoring of Fe nanoparticles
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Thus, the ohmic contacts ensured work function of the P(NMP) nanowires network (both pristine and modified) to be lower than Au ($\phi_{\text{Au}} = 5.1$ eV) [39]. Further, the lower device current observed for Fe tailored network was indicative towards transfer of electrons from Fe nanoparticles to the polymeric backbone decreasing overall hole concentration. In fact, when a metal and a semiconductor is brought to contact, a charge transfer occurs till the Fermi levels of both are aligned (under equilibrium condition). Such phenomenon is acutely dependent on the work function of the metal and semiconductor and, equally, on the type of semiconductor (-p or -n) that decides if a schottky barrier or an ohmic contact will result [40]. As per observations, since, the semiconducting backbone was p-type in nature and electron donation took place from metal to the semiconductor, two crucial assumptions were allowed to be made- (i) that work function of P(NMP) nanowires network was greater than Fe ($\phi_{\text{Fe}} = 4.5$ eV). To the best of our knowledge, work function of P(NMP) is not reported in any literature. However, Poly(pyrrole) was reported to have work function of $5\text{eV}$; and (ii) that schottky barriers have been formed at the metal semiconductor interface. Formation of these schottky barriers occur since aligning the Fermi level at equilibrium asks for donation of electrons from metal to semiconductor (since work function of P(NMP) is higher than that of Fe) and those electrons are accommodated by a depletion region in which ionized acceptors are left uncompensated by holes [40]. Thus, a potential barrier is formed at the metal nanoparticles- semiconductor interface and magnitude of the same, as well envisaged, is proportional to the work function difference. The depletion regions, thus formed, acts as potential scattering sites [41-42] that reduces effective carrier mobility and results in overall lowering of device current. This elucidation was further supported by transfer characteristics that show a negative shift of the threshold voltage along with a downward tilt in the transfer curve of the Fe nanoparticles tailored device than that of
pristine P(NMP) nanowires. As discussed above, the shift could be well attributed to the donation of electrons from Fe nanoparticles to the P(NMP) nanowires that reduced effective hole-concentration on the polymeric backbone whereas the downward tilt was due to the formation of charge depletion sites that decreases carrier mobility.

5.3.4 Sensor Behaviour

Figure 5.6 shows the transfer curves recorded for the pristine nanowires device under ambient atmosphere and 0.25 ppm concentration of all analytes.

![PNMP Nanowire Transfer Curve](image)

**Figure 5.6**: FET transfer sensing characteristics of the pristine nanowires device, at 0.25 ppm concentrations of NH₃, PH₃ and CO separately.

Under PH₃ and NH₃ atmosphere, the threshold voltage was found to exhibit a negative shift in comparison to the threshold voltage of device under ambient condition due to the donation of electrons from analytes to the protonated P(NMP) i.e. P(NMP)H⁺ sites
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that reduced effective hole concentration. Since all the analytes under scanner were having lone electron pairs, the ‘differences in threshold voltage shifts’ needed further consideration. As revealed by the characteristics, maximum shift in device threshold voltage could be observed under NH₃ atmosphere. A considerably less negative shift could be observed under PH₃ atmosphere. Such behaviour of the sensor for PH₃ indicated towards a lower tendency of the same to donate electrons than NH₃. Towards finding an explanation for such behaviour of PH₃, atomic radius of Phosphorus (128pm) and Nitrogen (65pm) was considered. Higher atomic radius of Phosphorus atom results in lesser electron density on Phosphorus atom in PH₃ than that of Nitrogen atom in NH₃. Thus, inferior sensing behaviour of the sensor towards Phosphine finds a concrete justification. To explain the ‘surprising’ positive shift observed in CO atmosphere, it was considered that, while on one hand, the carbon atom of CO reduces its negative charge by donating its lone pair of electrons, there is equal possibility of overlapping of unfilled d-orbitals of carbon atom with the delocalized π-orbital of P(NMP) backbone, accepting electrons. In fact, under situations, CO can act as both electron donor and acceptor [31]. Behaviour of the sensor under CO atmosphere was definitely shaped by these opposite charge transfer phenomenon and the electron acceptor nature of CO played a dominant role. Equally, observed positive shift was found to be lesser than negative shift observed for NH₃. Further, absence of any characteristic tilt in transfer curves well allowed to infer that the analyte induced modulations in work-functions of either P(NMP) or Au, at the contact region, had not significantly modulated the contact properties. Basically, formation of ohmic contacts, as described earlier, offers a very small barrier for flow of charge carriers at the metal-semiconductor junction region [40] and from observations, it was ensured that under the exposure of analytes, contact properties were not varied significantly.
The transfer characteristics of the Fe nanoparticles tailored P(NMP) nanowires devices under ambient atmosphere and 0.25 ppm atmosphere of all investigated analytes is shown in figure 5.7 (a-c).
Unlike pristine devices, in this case, both ‘shift’ and ‘tilt’ in device transfer characteristics could be observed for all analytes. For ammonia again, maximum negative threshold voltage shift could be observed. Such behaviour was certainly attributed to the presence of Fe nanoparticles that offered vacant d-orbitals acting as potential electron accepting sites [2] and those electrons were transferred to the P(NMP) backbone to reduce overall hole concentration. Similar negative shift could also be observed for PH\textsubscript{3}; however, with respect to untailored device under same atmosphere, the extent of shift was not that profuse as ammonia. Such behaviour was well expected as per our earlier observations. Most trivial changes could be observed for CO, where a slight positive relative shift with respect to the pristine device (under CO atmosphere) was recorded. It is well accepted that Fe acts as favourable interaction site for CO [43] and hence donation of electrons to the Fe d-orbital

**Figure 5.7(a-c):** FET transfer sensing characteristics of the Fe tailored P(NMP) nanowires device, at 0.25 ppm concentrations of NH\textsubscript{3}, PH\textsubscript{3} and CO separately.
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was expected to be more profuse, albeit, the simultaneous electron acceptor property of CO resulted in comparatively lowest exhibited shift in threshold voltage. Further insight of above modeled figure was obtained on considering the ‘tilts’ observed in transfer curves. To explain the observed tilt behaviour, it was considered that for p-type semiconducting materials, donation of electrons to the valence band raises Fermi energy level and consequently lowers work function [44]. Similar by, Fermi level is raised in metal on increasing electron density at conduction band [45]. Considering the dimension scale of metal nanoparticles, Kauffmen et al. [41] have envisaged that metal Fermi level is only affected due to electron donation under similar conditions. However, such assumption would over-simplify the situation since the analytes got significant interaction sites with the P(NMP) backbone. Thus, a concurrent modulation in the work function of P(NMP) and Fe nanoparticles was considered for explaining the observed ‘tilt’ behaviour. Also, introduction of electrons results in electron-hole recombination at the nanoparticle/ nanocomposite interface sites. Had it been solely the recombination phenomenon that took place at the interface sites, the donation of electrons by ammonia had resulted in significant downward tilt in transfer curves. However, the upward tilt observed in that case clearly suggests that recombination was not the solitary reason for shaping the sensing phenomenon and relative modulation in work function of metal and semiconducting entity played crucial. As per our observations, this was the mechanism that had shaped the transfer characteristics of the present devices under ammonia atmosphere. A reasonable figure was modeled in a manner that the contact potential barriers were modulated in accordance to the electron donating tendencies of the analytes. Under that domain, ammonia, with highest electron donating tendency (as observed), had resulted in more significant lowering of work function of P(NMP) backbone at nano-schottky contact regions [46] whereas lowering of work function in metal nanoparticle was not that profuse. Hence,
contact potential at the interface sites decreased and allowed maximum electron transfer from Fe-nanoparticles to P(NMP) backbone, justifying the observed negative shift. At the same time, due to recombination at interface sites, significant downward tilt was expected. The upward tilt, on the contrary, indicated lowering of contact potential due to profound lowering of P(NMP) work function. Hence, it was confirmed that recombination effect did not play the dominant role in shaping interface properties. Due to lower electron donacity of Phosphine, the P(NMP) work function was not that significantly affected as ammonia and a lower upward tilt could be observed. The surprising downward tilt that could be observed for CO, found its root in electron accepting capability, again, as the dominating phenomenon that resulted in lowering of Fermi level in P(NMP) and simultaneous donation of electrons at metal conduction band that resulted raising in Fermi level of Fe. Such opposite phenomenon effected in overall increase in contact potential barrier and maximum downward tilt in device transfer characteristic.

Figure 5.8 (a&b) shows normalized changes in resistance ($\Delta R/R_0 = (R - R_0) / R_0$; where $R_0 =$ steady resistance of the sensor at certain concentration of analyte and $R =$ baseline resistance of the sensor) for the Fe nanoparticles decorated P(NMP) nanowires sensing backbone under different concentrations of the three analytes. For NH$_3$ and PH$_3$, device resistance was found to increase with introduction of analytes and decrease upon flushing with zero air. However, for CO, an opposite phenomenon could be observed with formidable weak sensor response. Best sensing behaviour was recorded for ammonia while for carbon monoxide, sensing behaviour was most inefficient. Thus, the recombination phenomenon at interface sites was found to play a less effective sensing mechanism in deciding overall device characteristic.
Figure 5.8: (a) Normalized response of the P(NMP) nanowires device, at general concentration window (5-40ppm) of NH₃, PH₃ and CO separately. Normalized response of the Fe tailored P(NMP) nanowires device, (b) at general concentration window (5-40ppm) and (c) lower concentration window (0.05-1ppm) of NH₃, PH₃ and CO separately.

Figure 5.9: comparison of the response time and recovery time of the Fe tailored P(NMP) nanowires device, at lower concentrations (0.05-1ppm) of NH₃
For ammonia (and even phosphine), the sensor exhibited quick response and recovery. For carbon monoxide, however, a sluggish behaviour was exhibited that was due to opposite electron transfer behaviour as discussed above. At higher levels of concentration of the analytes (beyond 100 ppm concentration for CO, 135 ppm for PH₃, and 155 ppm of NH₃) partial and slow recovery could be observed that indicated adsorption of analytes at the crossover sites of the nanowires. Response and recovery behaviour of the fabricated sensors, under all analyte atmosphere is given in figure 5.9.

![Graph a](image-a)

![Graph b](image-b)

![Graph c](image-c)
Figure 5.10: (a) Comparative performances of the P(NMP) nanowires device, at general concentration window (5-40ppm) of NH$_3$, PH$_3$ and CO separately. Comparative performances of the Fe tailored P(NMP) nanowires device, (b) at general concentration window (5-40ppm) and (c) lower concentration window (0.05-1ppm) of NH$_3$, PH$_3$ and CO separately.

Calibration plots for the pristine and Fe nanoparticles tailored P(NMP) nanowires devices are shown in fig 5.10 (a) and (b). Best sensing platform (i.e. Fe nanoparticles tailored P(NMP) nanowires based devices) showed a sensitivity of 31.3% with excellent linearity ($R^2 = 0.987$ as given by linear regression equation ) for ammonia concentration window of 0.05-1 ppm. A low concentration window for validation of the sensors was chosen since the interest was more evinced towards capability of the sensor towards low concentrations of analyte.
5.3.5 Temperature Stability of The Best Sensing Platform

Fig. 5.11 shows the baseline resistance of the Fe nanoparticle tailored P(NMP) nanowires matrix based sensor for temperature upto 95°C starting from room temperature.

Figure 5.11: Variation in baseline resistance with temperature of the Fe nanoparticle tailored P(NMP) nanowires matrix based sensor.

The value of the resistance decreased steadily as the sensor was introduced to increasing ambient temperature. Such behaviour was attributed to the semiconductor nature of the material. A deviation of 4.57 % from the initial baseline resistance could be observed at 75°C. However at 95°C, the deviation was recorded to be 13.46% indicating that limit of operating temperature for the sensor lies around 75° C.
5.3.6 Stability of the Best Sensing Platform

Very negligible drift could be observed (figure 5.12) in the performance of the sensor till 75 days with a maximum deviation of 4.03% from the initial sensitivity. Rapid fall in the sensor performance then after was recorded which was due to natural degradation of polymer.

![Graph](image)

**Figure 5.12:** Stability of the Fe nanoparticle tailored P(NMP) nanowires matrix based sensor.

5.4 Conclusions

According to expectation, increasing dopant concentration brought about a significant increase in device current level that was required for development of sensing backbone. Electrochemical route proved to be a facile technique for surface tailoring of Fe nanoparticles on P(NMP) nanowires matrices. Due to the relative positions of Fermi level in
Fe and P(NMP), schottky barriers were found to form at the nanoparticle/nanowires interface sites that had adverse effect on device carrier mobility. However, enhanced sensing behaviour could be achieved after Fe nanoparticles tailoring of nanowires surface. On exposure to three different entities (viz. ammonia, phosphine and carbon monoxide) having equivalent characteristics, the behaviour of the sensors were found to be pivotally dependent on electron donating tendencies of the analytes that shaped the recombination characteristics at nanoparticles/nanowires interface sites and equally modulated the work function in semiconductor and the metal. The sensing mechanism was critically decided by combinational effect with work function modulation as higher dominating role. The inferior performance of the sensor for CO was attributed to the simultaneous electron accepting nature of the analyte.

The observations clearly indicate that while choosing suitable metal for surface tailoring of semiconducting substances, a sensitive look into the work function of both the entities can be a well-mechanized route for probable efficient choice of the metal. At the same time, a novel perspective in terms of electron donating capability of analytes came into light that is definitely going to be a crucial ingredient for designing selective sensing elements. This is definitely a significant step keeping in view the plethora of polymeric sensors developed till date whose mechanism have been defined in terms of charge transfer.

A comparative sensing performance of the fabricated devices under three analytes of interest has been tabulated below.
<table>
<thead>
<tr>
<th>DEVICE</th>
<th>ANALYTE</th>
<th>DETECTION RANGE</th>
<th>LINEARITY</th>
<th>SENSITIVITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(NMP) Nanowires</td>
<td>NH₃</td>
<td>5-40 ppm</td>
<td>R² = 0.952</td>
<td>0.9%</td>
</tr>
<tr>
<td></td>
<td>PH₃</td>
<td>5-40 ppm</td>
<td>R² = 0.943</td>
<td>0.9%</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>5-40 ppm</td>
<td>R² = 0.998</td>
<td>0.5%</td>
</tr>
<tr>
<td>P(NMP) Nanowires/Fe</td>
<td>NH₃</td>
<td>5-40 ppm</td>
<td>R² = 0.997</td>
<td>4.2%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.05-1 ppm</td>
<td>R² = 0.987</td>
<td>31.3%</td>
</tr>
<tr>
<td></td>
<td>PH₃</td>
<td>5-40 ppm</td>
<td>R² = 0.998</td>
<td>3.8%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.05-1 ppm</td>
<td>R² = 0.984</td>
<td>17.6%</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>5-40 ppm</td>
<td>R² = 0.992</td>
<td>0.8%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.05-1 ppm</td>
<td>R² = 0.990</td>
<td>12.7%</td>
</tr>
</tbody>
</table>

# Response and Recovery Time has been shown for the best sensing platform only

- Analyte: Ammonia (OSHA PEL: 50 ppm; IDLH: 300 ppm)
- Analyte: Phosphine (OSHA PEL: 0.3 ppm; IDLH: 50 ppm)
- Analyte: Carbon Monoxide (OSHA PEL: 50 ppm; IDLH: 1200 ppm)
- Temperature maintained for general validation: 25° ± 2 C
- Cycles repeated for chemiresistive sensing: 5
- Measurements were taken in conformation to the formulations laid by IUPAC

So far the applicability of the developed sensor for real time application was concerned, the sluggish recovery (especially) at higher concentration of operation was a potent hurdle. Since, intertwines in the matrix was responsible for this (and also reported
in other contemporary literature), our next step was to pursue a solution of this problem. In addition, it was kept in account that analytes diffuse into the nanowires structure opposed fast recovery of such sensors. Structures with lower scale of cross section (that was hypothesized to render less diffusion and fast desorption), with less intertwines (that was thought to offer less adsorption at such sites obviously) was the need and that framed next course of investigation.
References


3. J. Li., Y.Lu., Q.Ye, L. Delzeit, M. Meyappan; Electrochemical and solid state letters, 2005, 8, H100


5. B.Ding, M.Wang, J.Yu., G.San; Sensors, 2009,9, 1609


10. A.G. Mac Diarmid; Synthetic Metals, 2002, 125, 11

11. H. Shirakawa; Synthetic Metals, 2002, 125, 3

12. A.J. Heeger; Synthetic Metals, 2002, 125, 23

17. X.B. Yan, Z.J. Han, Y. Yang, B.K. Tay; Sensors and Actuators B., 2007, 123, 107
25. S.Paul, N.N. Chavan, S. Radhakrishanan; Synthetic Metals, 2009, 159, 415


35. M. Penza, R. Rossi, M. Alvisi, E. Serra; Nanotechnology, 2010, 21, 105501


39. P.S. Abthagir, R. J. Saraswathi; Applied Polymer Science, 2001, 81, 2127
Chapter 5


41. D.R. Kauffman, A. Star; Nano Letters, 2007, 7, 1863

42. S. Mubeen, J.H. Lim, A. Srirangarajan, A. Mulchandani, M.A. Deshusses, N.V. Myung; Electroanalysis, 2011, 23, 2687

43. S. Paul, N. N. Chavan, S. Radhakrishnan; Synthetic Metals, 2009, 159, 415

