Cross Analyte Study: Metal Nanoparticles Tailored P(NMP) Functionalized SWNTs Sensor
Chapter 7

7.1 Introduction

The excellent characteristics offered by 1-D nanostructures have revolutionized several conventional concepts towards better evolving technologies. All corners of modern technology, including (but not limited to) composite macrostructures, electronics, optoelectronics, non-conventional energy sources, field emission devices, medicine etc., in recent times, have found to be reframed under the limitless capabilities of these class of materials [1-3] and sensors do stand as a flagship of this all emerging change [4-6]. Gas sensors, especially, have found a giant leap with the advent of 1-D materials since various traditional sensor modes were subject to a trade-off between sensor performance parameters e.g. sensitivity, selectivity vs. response time and portability, however, nanodimensional sensors are capable to provide overall device enhancement [7].

Several characteristics of gas sensors in terms of sensitivity [8-11], response and recovery behaviour [12], physical footprint [13], power consumption [14], operating temperature [15-16] etc. have been improved drastically by employing 1-D nanomaterials as principal transducing element. Also, facile techniques for site specific synthesis/deposition of these materials on micro/nanofabricated platforms are capable to result in high integration sensor arrays [17-20] with an ultimate attempt to mimic human olfaction system. And there stands the toughest hurdle for even the most efficient sensor backbone developed till date. Unfortunately, lower dimensional features do not offer any selective characteristic to the materials and this limitation inhibit these materials (mostly in their pristine form) to be used as selective sensory elements for tailor-made applications [21-25].
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Unlike many other form of chemical sensors, gas sensors are always a challenge for designers because the operational background of a gas sensors is the ambient atmosphere, a highly complicated mixture of innumerable gaseous elements and particulate matters. Such situation is really tough to deal with since many the constituents of air bear similar physical and chemical characteristics. Imitation of olfaction system is a far story, till date very few sensors have been developed that show significant sensing affinity to a particular gaseous analyte under simultaneous action of interfering agents.

As already discussed, two of the most efficient sensing platforms that are under high research attention for their structural/ electrochemical characteristics i.e Single Walled Carbon Naotubes (SWNTs) [26-29] and Conducting Polymers (CPs) [30-33] are sensitive to mainly electron donating/withdrawing gases. Charge transfer process constitutes the fundamental transduction mechanism [34-38] for these materials. Although, there are several scattered reports on other sensing phenomenologies [39-42], less interest have been found to be evinced in those directions mostly due to dearth of reproducible results.

Utilizing the charge transfer as principal sensing mechanism, as it could be seen in Chapter 5 and with few contemporary reports, surface tailoring of polymeric sensors with metal nanoparticles show selective enhanced behaviour [43-44] to particular analyte. SWNTs decorated with metal nanoparticles have also shown selective behaviour to certain analytes. Penza et al. [45-46], Star et al. [47] have shown sensing behaviour of metal nanoparticles decorated pristine SWNTs/ MWNTs for sensing of mixture of analytes. However, there has been very few reports on polymer functionalized SWNTs based structures tailored with metal nanoparticles for gas sensing applications.
From our observations in chapter 6, 3μC charge deposited P(NMP) functionalized SWNTs were found to be a prolific backbone for NH₃ sensing. In the final phase of our experimentation work, it was the particular aim to inculcate selective behaviour to such backbone. From our earlier observations that Fe nanoparticles decorated P(NMP) nanowires based sensor had shown a selective behaviour to NH₃, in present case, the P(NMP) functionalized SWNTs structure was surface tailored with Fe nanoparticles for probable selective sensing of NH₃ under CO as interfering entity. Also, the same backbone was surface tailored with Au nanoparticles with the idea that electrons from completely filled d-orbitals of Au might donate electrons to vacant d-orbitals of carbon atom in CO and equally, due to such filled d-orbitals of electron transfer from NH₃ to Au nanoparticles might be least probable. Behaviour of that particular sensor for sensing CO, under the interference of NH₃. Most interestingly, these sensors were fabricated on a single Si/SiO₂ substrate (1cm × 1 cm). Outcomes were highly encouraging and suggested potential of such background for realtime complex sensing applications.

7.2 Experimental Details

7.2.1 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 are of analytical grade) was purchased from Rankem Ltd., India. Tetrachloroauric acid (HAuCl₄, 3H₂O; ≥99.9%) was purchased from Sigma Aldrich ( Switzerland). The monomer was vaccum 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.

### 7.2.2 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 20 nm Cr (adhesion layer) and 180 nm Au layer. The electrode patterns were defined with 3 µm gap between successive electrodes and width of the patterns were kept to be 200 µm. 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 further use.

### 7.2.3 Fabrication of Sensor Backbone

Ultrasonic dispersion of COOH-SWNTs in N-N dimethyl formamide was carried out at a concentration of 0.01 mgmL$^{-1}$. Centrifugation of the SWNTs suspension was carried out at 14000 RPM for 90 min to get rid of residual agglomerates of SWNTs. A 0.1 µl drop of final decanted suspension was placed on top of Au microelectrodes at the 3 µm trench region. SWNTs were aligned dielectrophoretically by applying 1 V$_{RMS}$ at 4 MHz frequency across microelectrodes. Resistance of the networks was optimized by varying the deposition time. In order to reduce the contact resistance between electrodes and SWNTs (and to remove possible residual DMF), the devices were annealed at 300°C for 1 hr under a reduced
atmosphere (continuous flow of 5% H₂ in N₂). Finally, SWNT networks with resistance lying in a pre-optimized range (90 kΩ+/− 02 kΩ) were used for functionalization and subsequent sensing. For electrochemical functionalization of aligned SWNTs surface by P(NMP) at ambient temperature, 2 µl of an aqueous solution of 0.05 M of NMP and 0.15 M of NaNO₃ was dropped on the top of SWNT aligned structures. Potentiostatic deposition was carried out at (+0.7V) versus Ag/AgCl wire (chlorinated Ag wire) as reference electrode, while the Au pads and a Pt wire (CHI 115) acted as working and counter electrodes respectively to constitute a three electrode configuration. The deposition charge was kept fixed at 3 µC. Two different sites on a single Si/SiO₂ substrate (1cm × 1cm) were created for simultaneous monitoring of sensor performance.

For surface tailoring of the functionalized structures, same electrochemical set-up (as described above) was employed. Fe nanoparticles on the surface of the functionalized structures were synthesized by cycling potential across the electrodes from +0.2V to -0.4V for two times at a scan rate of 20 mVs⁻¹. The electrolyte, in this case, consisted of metal salt FeSO₄ (0.5mM) and supporting electrolyte KCl (1 mM) in aqueous media. Similarly, For Au nanoparticles synthesis, electrolyte solution was made up of HAuCl₄ (0.5mM) and KCl (1 mM) and synthesis was carried out by cycling potential in a range of +0.2V to -0.5V (v/s Ag/AgCl) for 5 cycles at a scan rate of 20 mVs⁻¹ in each case. All electrochemical syntheses were carried out by CHI 660C electrochemical workstation (CH Instruments, Texas, USA). After synthesis, the devices were rinsed in DID water to remove excess metal salts and dried under nitrogen flow.
7.2.4 Characterization Techniques and Instrumentation

Electrochemical functionalization of aligned SWNTs were carried out by CHI 660C electrochemical workstation (CH Instruments; Texas, USA). The surface morphology of the fabricated devices were examined using a Field Emission Electron Microscope (FESEM; Hitachi S4800). To ensure the formation of Fe and Au nanoparticles tailored P(NMP) functionalized aligned SWNTs structures were subjected to energy dispersive x-ray spectroscopy (EDAX). The current voltage (I-V) characteristic of the devices were studied using the same electrochemical workstation by linearly sweeping potential from -1V to +1V. The FET characteristics were studied by a Keithley 2400 source-measure unit coupled with an Aplab (India) PPD3003-S programmable power supply operated in constant voltage sourcing mode. Drain to source voltage ($V_{DS}$) was kept fixed at 1V and gate potential was swept between -15V to +15V.

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$^{-1}$) to obtain a stable baseline for sensors. The sensors were tested under various concentrations of NH$_3$ (>99.99%, Fisher Scientific), CO (>99.99%, Sigma Aldrich) and their binary mixtures 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 V. Mode and methods of instrumental approach was same as that was applied for studying device transfer characteristics has 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 that particular 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.

Temperature stability of the Fe and Au nanoparticles tailored sensing platforms were studied from room temperature to 100°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 sensors, sensitivity (at 0.5 ppm) was recorded for a span of 100 days at interval of 5 days.
7.3 Results and Discussion

7.3.1 Morphological Study and Elemental Analysis

Typical Field emission scanning electron microscope (FESEM) image Au nanoparticles tailored P(NMP) functionalized aligned SWNTs are shown in figure 7.1. The average diameter of the functionalized SWNTs were found to be around c. a. 25 nm for the coating of P(NMP) is found to be highly consistent and uniform. Average diameter of Fe and Au nanoparticles were estimated to be around 15-20 nm respectively. As shown in figure 7.2 (a & b), different peaks of EDAX spectrum corresponding to the elements C, O, N, Si, Fe and Au are for the Fe and Au nanoparticles tailored P(NMP) functionalized aligned SWNTs.

![Figure 7.1](image_url)

**Figure 7.1:** Typical FESEM image of Au nanoparticles tailored P(NMP) functionalized aligned SWNTs
Figure 7.2: EDAX spectrum of (a) Fe (b) Au nanoparticles tailored P(NMP) functionalized aligned SWNTs
7.3.2 Electrical (I/V) and FET Transfer Measurements

Figure 7.3 shows current-voltage (I/V) characteristics for Fe and Au nanoparticles tailored P(NMP) functionalized (at 3 µC deposited charge) aligned SWNTs devices. For purpose of comparison, characteristic of device without surface tailoring is also provided. The pristine device had shown characteristic ‘S’ nature (as also observed in chapter 6) that indicates Schottky nature of the contacts and also imply a higher work function of the functionalized backbone than Au (contact material) [48].

![I/V Characteristic Graph]

**Figure 7.3:** I/V characteristics of P(NMP) functionalized aligned SWNTs before and after tailoring of Fe and Au nanoparticles

Further, lowest device current was recorded for Fe tailored device. Such observation was attributed to the formation of higher extent of depletion layer at the Fe nanoparticle/functionalized structure interface sites than the case of Au nanoparticles tailored device. Rationalization was done considering the work function difference of the devices.
Since Fe is having a lower work function than Au, transfer of electrons to functionalized backbone is more profuse. Thus, the extent of decrease in effective hole concentration on the functionalized backbone results in low device current. Also, the scattering sites created due to the formation of depletion layers is more potent for Fe tailored devices that deteriorates charge carrier mobility which is an additional entity in deciding device conduction behaviour.

![Graph showing FET transfer characteristics of P(NMP) functionalized aligned SWNTs before and after tailoring of Fe and Au nanoparticles.](image)

**Figure 7.4:** FET transfer characteristics of P(NMP) functionalized aligned SWNTs before and after tailoring of Fe and Au nanoparticles.

Transfer characteristics of the devices (figure 7.4) showed negative shifts in device threshold voltages with respect to the untailored device for Fe and Au nanoparticles tailored devices. Maximum negative shift for the Fe nanoparticles tailored device indicated highest transfer of electrons to the functionalized backbone. Also, downward tilt in device characteristic was
highest for Fe nanoparticles tailored device which was certainly due to creation of more potential scattering sites in case of Fe than Au nanoparticles. Thus, decreased carrier mobility decided the ‘tilt’ behaviour in respective device characteristics.

### 7.3.3 Sensing Behaviour

Study of sensing characteristics of the fabricated sensors were formulated as per hypotheses that Fe tailored backbone would be offering better sensing capabilities for NH$_3$ and Au nanoparticles based device would be a better option for CO sensing. Accordingly, sensing behavior of the Fe nanoparticles tailored device were carried under pure NH$_3$ atmosphere and NH$_3$ atmosphere with interfering CO. For that purpose, under pure atmosphere, the device was validated for 0.5 ppm NH$_3$ and keeping the NH$_3$ concentration prevailing, CO was allowed to act as an interferer at concentrations of 0.25 and 0.5 ppm respectively. Finally, the sensor was exposed to pure CO (0.5 ppm). For the other device i.e. Au nanoparticles decorated backbone, the device was validated for pure CO (at 0.5 ppm) and binary mixtures of CO (0.5ppm) and NH$_3$ (0.25 ppm and 0.5 ppm respectively) where CO concentration was kept consnt and NH$_3$ acted as infereing gas. As earlier, the device was finally exposed to pure NH$_3$ (0.5 ppm).

Transfer characteristics of the Fe nanoparticles tailored P(NMP) functionalized aligned SWNTs based sensors are shown in Fig. 7.5. Under pure NH$_3$ atmosphere (0.5 ppm), the device threshold voltage exhibited a negative shift of c. a. 2.4V with respect to ambient atmosphere condition and a slight upward tilt (with respect to device under ambient atmosphere, i.e datum for the study) was observed. The observations were in line with Fe
nanoparticles tailored P(NMP) nanowires structures (sensing modality in chapter 5) only with higher device current and more profuse negative shift. Such better behaviour, certainly, was due to the presence of SWNTs in the backbone that rendered a high conduction pathway at the P(NMP)-SWNT interface.

Also, with respect to the 3 µC charge deposited P(NMP) functionalized SWNTs sensor (described in chapter 6), the sensing behaviour was better; a definite indication of the active role of Fe nanoparticles. The ‘shift’ was attributed to the donation of electrons from ammonia to the sensor backbone (PNMPH+ i.e. protonated P(NMP) sites). While the ‘tilt’ was certainly defined by the Fermi level modulation of the functionalized backbone due to donation of electrons to the backbone from ammonia directly and transferring of electrons [49] that are

Figure 7.5: FET transfer sensing characteristics of 3µC charge deposited Fe nanoparticles tailored devices under pure NH₃ atmosphere (0.5 ppm), pure CO atmosphere (0.5 ppm) and binary mixture of NH₃ and CO
donated to the vacant d-orbitals of Fe nanoparticles [50]. Recombination effect at the Fe 
nanoparticle/functionalized structure interface site, as earlier, was not found to be a dominant 
mechanism. When the sensor was subjected to a binary mixture of 0.25 ppm CO and 0.5 ppm 
NH₃, the device threshold voltage suffered a slight positive shift in threshold voltage in 
comparison to the device threshold voltage recorded for pure ammonia atmosphere. Although 
CO is reported to as an electron donor, the observation clearly indicated the domination of 
electron accepting role of CO by overlapping of unfilled d-orbitals of Carbon atom with the 
delocalized π-orbital of P(NMP) backbone. Most surprisingly, the significant downward tilt 
that was observed in transfer characteristic of Fe nanoparticle tailored P(NMP) nanowires 
device (described in chapter 5) under CO exposure, was absent here. No significant variation 
in tilt behaviour (under 0.5 ppm ammonia + 0.25ppm conc. of CO atmosphere) in 
comparison to pure NH₃ atmosphere was, thus, most certain indication to the fact that 
electron donation by NH₃ prevailed as the principal phenomenon even at 33% occurrence (by 
concentration) of the interferer. When the concentration of CO was enhanced to 0.5 ppm in 
presence of 0.5 ppm concentration of ammonia (i.e. 50% occurrence of interferer by 
concentration) further positive shift in threshold voltage with respect to the earlier case 
(CO/0.25 ppm + NH₃/0.5 ppm) was observed. Nevertheless, the positive shift in the device 
threshold voltage, under presence of CO, never overshoot the datum status (ambient 
atmosphere threshold voltage), which was a concrete evidence for selective behaviour of the 
sensor towards NH₃ in presence of CO. However, slight downward tilt in comparison to 
earlier observations could be noted that was due to higher concentration occurrence of CO. 
Under exposure to pure CO atmosphere, the device threshold voltage exhibited a slight 
positive shift (with respect to datum) with significant downward tilt in respect to pure NH₃ 
atmosphere, however, the tilt was very trivial.
Figure 7.6 shows transfer characteristics of the Au nanoparticles tailored P(NMP) functionalized aligned SWNTs based sensors. Under pure CO atmosphere (0.5 ppm), the device threshold voltage exhibited a positive shift of 2.9V with respect to ambient atmosphere condition.

![Figure 7.6: FET transfer sensing characteristics of 3µC charge deposited Au nanoparticles tailored devices under pure CO atmosphere (0.5 ppm), pure NH₃ atmosphere (0.5 ppm) and binary mixture of NH₃ and CO.](image)

Such positive shift was a clear indication of the electron accepting behaviour of CO that dominated over the electron donating capability. Basically, in presence of Au nanoparticles with completely filled d-orbitals, electrons are allowed for transfer to unfilled carbon d-orbital from Au conduction band as well as from P(NMP) backbone. Now, removal of electrons - (i) from metal conduction band effects in lowering of metal Fermi level [51]; and (ii) from (PNMP) valence band effects in lowering of semiconductor Fermi level [52] (since...
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the material is p-type in nature). Under such situations, a significant downward tilt, in comparison to the device behaviour under ambient atmosphere, could be observed which was due to enhanced potential barrier at Au nanoparticle/functionalyzed structure interface sites. Such observations are well supportive to the fact that semiconductor work-function was more severely modulated. On exposing the sensor to a binary mixture of 0.25 ppm NH₃ (33% presence in concentration) and 0.5 ppm CO, device threshold voltage, most expectedly, was found to suffer a negative shift than the threshold voltage recorded for pure CO atmosphere. For 50% occurrence of NH₃ (i.e. for 0.5 ppm NH₃+ 0.5 ppm CO), the negative shift was more profuse, however, such shift did not overshoot the ambient atmosphere threshold voltage, which was an absolute indication of superiority of the backbone towards CO sensing. In spite of our earlier observations that NH₃ is more efficient electron donor to P(NMP) than CO as electron acceptor, such inferior behaviour towards NH₃ was certainly attributed to the presence of Au nanoparticles. Observations allowed to ascertain that Fermi level of functionalized structure, under the action of interferer NH₃, were raised above the Fermi level of Au. Implication of such happening is deep-rooted since schottky contacts at the nanoparticle/ functionalized structure interface site were transformed to ohmic contacts, paving a facile way for concurrent tunneling/transferring of electrons from functionalized backbone to Au nanoparticles and subsequently, the electron donating capability of NH₃ was surpassed. Under exposure of the sensor to pure NH₃ atmosphere, slight negative shift in device threshold voltage with a slight upward tilt than that could be observed for unexposed Au decorated device; behaviour certainly attributable to the electron donating nature of ammonia.
Figure 7.7 shows normalized changes in resistance ($\Delta R/R_0 = (R-R_0) / R_0$; where $R_0 = \text{steady resistance of the sensor at certain concentration of analyte}$ and $R = \text{baseline resistance of the sensor}$) for the P(NMP) functionalized (at 3µC deposited charge) SWNTs tailored with Fe and Au nanoparticles for sensing of pure NH$_3$ and CO at different concentration of analyte.

![Normalized response graph](image)

**Figure 7.7**: Normalized response of the Fe and Au nanoparticles tailored P(NMP) functionalized aligned SWNTs, at concentration window 0.005-0.5 ppm of NH$_3$ and CO.

Simultaneous recording of the responses of two sensors for all analyte (pure as well binary mixtures) atmosphere were recorded and shown in figure 7.8 (a & b). As clearly indicated by the normalized responses, selective behaviour of Fe nanoparticles tailored device towards ammonia and Au nanoparticles tailored device towards carbon monoxide was evident. For the Fe nanoparticle tailored backbone, sensor resistance was found to increase on exposure to NH$_3$ and most expectedly, response was diminished with increasing concentration of CO.
However, even for 50% (by concentration) presence of CO as interferer, the sensor response decreased by only 40% of the response for pure NH₃.

**Figure 7.8:** (a) Responses for Ammonia (pure as well binary mixtures) atmosphere of the Fe nanoparticles tailored P(NMP) functionalized aligned SWNTs. (b) Responses for Ammonia (pure as well binary mixtures) atmosphere of the Au nanoparticles tailored P(NMP) functionalized aligned SWNTs.
For the Au nanoparticle decorated device, sensor resistance was found to decrease on exposure to CO and response was diminished with increasing concentration of NH$_3$. In that case, even for 50% (by concentration) presence of NH$_3$ as interferer for the Au nanoparticles tailored device, the sensor response was deteriorated by a maximum factor of 39.3% only. Most encouragingly, although NH$_3$ and CO both are potent electron donors, they had shown opposite behaviour towards the sensing backbone they were intended for. Saturation behavior was dominant beyond 100 ppm concentrations of CO and 15.5 ppm concentrations of NH$_3$. Response and recovery behaviour of the fabricated sensors, under all concentration of analyte atmosphere is given in figure 7.9 (a & b).
As clearly indicated by the normalized responses, selective behaviour of Fe nanoparticles tailored device towards ammonia and Au nanoparticles tailored device towards carbon monoxide was evident. Finally, calibration plots (figure 7.10) for the Fe and Au nanoparticles tailored sensors towards pure NH₃ and CO show excellent selective nature of the sensors towards respective target analytes. Also, the lower detection limit for NH₃ is also found to get enhanced than untailored functionalized SWNTs backbone (10 ppb; as observed in chapter 6).
7.3.4 Temperature Stability of the Best Sensing Platform

Figure 7.11(a & b) shows the baseline resistance of the Fe and Au nanoparticles tailored sensing backbones for temperature upto 100°C starting from room temperature. The value of the resistance decreased steadily as the sensors were introduced to increasing ambient temperature. Such behaviour was attributed to the semiconductor nature of the materials. A deviation of 12% from the initial baseline resistance could be observed at 75°C for the Fe nanoparticles tailored device and 14% of deviation was recorded for Au
nanoparticles tailored device at 75°C. Drastic characteristic deterioration of the Fe nanoparticles tailored device could be observed at 85 °C and for Au nanoparticles tailored device, this value was again 85 °C.

Figure 7.11: Variation in baseline resistance with temperature of the (a) Fe and (b) Au nanoparticles tailored P(NMP) functionalized aligned SWNTs
7.3.5 Stability of the Best Sensing Platform

Very negligible drift could be observed (figure 7.12) in the performance of Fe nanoparticles tailored sensor till 70 days with a maximum deviation of 5.07% from the initial sensitivity. The above figures for Au nanoparticles tailored sensor were 75 days and 8% respectively. Rapid fall in the respective sensor performance after those durations were recorded and attributed to the natural degradation of polymeric layer of functionalized structure.

![Graph a: SWNT/PNMP/Fe](image1)

![Graph b: SWNT/PNMP/Au](image2)

**Figure 7.12:** Stability of the (a) Fe and (b) Au nanoparticles tailored P(NMP) functionalized aligned SWNTs
7.4 Conclusions

The best part of the above experiments was the fact that the sensors were designed with certain hypothesis and behaviour of the same were highly in inclination to the preliminary assumptions. Polymer functionalized SWNTS based sensors, if surface tailored with suitable metal nanoparticle, can be excellent selective sensing backbones. For the present case, Fe nanoparticles tailored P(NMP) functionalized SWNTs backbone showed a sheer inclination to NH₃ while the same principal backbone showed an affinity to CO when surface tailored with Au nanoparticles. Most encouragingly, simultaneous action of the sensors towards pure and binary mixtures of the analytes are well indicative of the screening capability of respective sensors. Observations suggest that using simple electronics, the devices could be well applied for selective sensing of NH₃ and CO under mixed atmosphere real time operating conditions. The Fe nanoparticle decorated sensor showed an excellent lower detection limit of 0.005 ppm for NH₃ (the analyte for which it had been designed) with a sensitivity of 59.3% (within a concentration window 0.005 ppm to 0.5 ppm of NH₃). The Au nanoparticle decorated sensor, on the other hand, showed a lower detection limit of 0.005 ppm for CO (the analyte for which it had been designed) with a sensitivity of 54.8% (within a concentration window 0.005 ppm to 0.5 ppm of CO). Linearity characteristics of the devices were also commendable.

A comparative sensing performance of the fabricated devices has been tabulated below. Best sensing platform has been highlighted -
### Table

<table>
<thead>
<tr>
<th>DEVICE</th>
<th>ANALYTE</th>
<th>DETECTION RANGE</th>
<th>LINEARITY</th>
<th>SENSITIVITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>3µC P(NMP) functionalized SWNTs/Fe</td>
<td>NH₃</td>
<td>0.005-0.5 ppm</td>
<td>$R^2 = 0.963$</td>
<td>59.3%</td>
</tr>
<tr>
<td>3µC P(NMP) functionalized SWNTs/Au</td>
<td>CO</td>
<td>0.005-0.5 ppm</td>
<td>$R^2 = 0.957$</td>
<td>54.8%</td>
</tr>
</tbody>
</table>

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