Vapor phase sensing of ammonia at the sub-ppm level using a perylene diimide thin film device†

Anamika Kalita, a Sameer Hussain, b Akhtar Hussain Malik, b Nimmakayala V. V. Subbarao a and Parameswar K. Iyer* abc

The fabrication of a two terminal sensor device based on a histidine substituted perylene diimide (PDI-HIS) thin film for the sensitive detection and quantification of ammonia (NH₃) vapors by monitoring the changes in its current intensity is reported at room temperature under ambient conditions. The thin film morphological variations of the drop cast PDI-HIS films before and after exposure to NH₃ vapors are characterized by FESEM and TEM confirming the diffusion/adsorption of the NH₃ vapors. The solution cast PDI-HIS thin film gas sensor device exhibited rapid, highly sensitive and selective vapor phase response towards NH₃ with a detection limit as low as 0.56 ppm which is much lower than the maximum permissible limit set for NH₃ (25 ppm) for prolonged exposure. Furthermore, control sensing experiments performed using alkyl substituted PDI (PDI-n-octyl) demonstrated that the presence of histidine groups at the imide position of PDI-HIS drastically affects the solid-state aggregation mode as well as redox potential that ultimately enhances the sensing response of the device. The key performance parameters of the device such as sensitivity, response/recovery time, selectivity, recyclability, stability and detection limit demonstrated the protocol as simple, reliable, cost-effective and most efficient in performing NH₃ detection under very realistic conditions.

Introduction

Electrical sensors have received incredible attention owing to their ease in the detection or analysis of information of various analytes through electrical signals. Moreover, the development of a semiconductor device is simple, since the signal does not necessitate intricate detection tools. Among electrical sensors, three-terminal transistors and two-terminal resistors are the most promising candidates for the advancement of low-cost, portable, low power, ultrasensitive and selective applications in chemical, biological and physical monitoring. Such ultrasensitive sensors can be utilized in detecting traces of various toxic gases and volatile organic compounds (VOCs) even at remote locations.

Ammonia (NH₃) detection has received immense attention among various volatile species owing to its severe effect on the environment as well as human health. NH₃ is highly toxic and corrosive that can be easily spread into the environment due to its widespread applications in fertilizers, refrigeration systems, manufacturing of dyes, drugs, synthetic fibers, plastics, etc. Moreover, ammonium nitrate (NH₄NO₃) found in many explosives gradually decomposes to release trace amounts of NH₃ which are essential to be monitored in order to prevent the lethal accidents. Ammonia, in its flammability range of 15% to 28% by volume can easily explode or catch fire. Although, it finds applications in various sectors, its exposure in high concentrations is a major threat to the human health. The lower limit of human NH₃ perception by smell is around 50 ppm. However, even below this limit, it is irritating to the respiratory system, skin as well as eyes. The long term (8 h) permissible concentration of NH₃ for workers is 25 ppm. Therefore, it is highly desirable to design and fabricate a long-term-reliable, highly-sensitive, miniaturized, room-temperature-efficient and low power consuming NH₃ gas sensor, which can detect and monitor NH₃ concentration surrounding the environment in real time.

In the past decade, there have been numerous reports on NH₃ detection based on nanostructured metal oxides, plasmaphores, conducting polymers, carbon nanotubes and nanostructured graphenes. However, a very few small molecule based sensors with improved properties such as lower operating temperature, high stability, fast response/recovery time, high selectivity and low detection limit have been reported. Among small molecules, perylene diimide derivatives (PDIs) are an important class of materials for the
fabrication of devices due to their numerous features such as high absorption coefficient, good chemical and thermal stability, better electronic properties and excellent photostability. Owing to their unique features, these materials have found versatile applications in organic field-effect transistors (OTFTs), organic solar cells and sensor devices. Recently, various types of PDIs composed of self-assembled aggregates, nanorods, nanobelts, nanofibres etc. have been developed for detecting volatile species such as amines, explosives, etc. Molecular modification has a vital role in improving the performance of such PDI-based organic semiconductor devices. In this context, modifications of PDIs have been achieved by either substituting electron withdrawing groups at the core position or introducing solubilizing groups at the imide position. Amino acids have achieved much attention as active groups to tune the structure of PDIs at the imide position, since they can deliver a range of supramolecular structures with variable degrees of arrangement due to the site-specific hydrogen bonding. Though, most of the efficient sensor devices reported for NH₃ detection are based on the functionalization of perylenes at the core position and the imide position has been modulated mainly for providing solubility to the system. Hence, meagre attention has been paid in designing perylene derivatives with suitable receptors at the imide position that can be utilized as tools to fabricate devices with a specific aim of sensing gases such as NH₃ with high sensitivity and selectivity.

Herein, we report the fabrication of a low cost two terminal sensor device using a PDI-HIS (Scheme 1a) thin film as an active layer and systematically investigated its sensing response towards NH₃ vapors by measuring the variation of current intensity. The sensor displayed notable features (i) solution processibility, (ii) fast signal response/recovery time (28 s/40 s), (iii) lower limit of detection at sub-ppm levels (0.56 ppm), (iv) high selectivity over other volatile species, and (v) operational ability at room temperature under ambient conditions. A control sensing experiment was also performed using simple alkyl substituted PDI i.e. PDI-n-octyl (Scheme 1b) to confirm the effect of amino acid attached onto the imide position of PDI on sensing behavior. Finally, we have demonstrated that the variation of substituent groups at the imide position of perylene dyes remarkably affects the solid-state aggregation modes as well as redox potential that cause the significant impact on the gas responses.

Experimental section

Materials and characterization

Perylene-3,4,9,10-tetracarboxylic dihydridre, octylamine, and zinc acetate were purchased from Sigma-Aldrich and were used as received without any further purification. Histidine and imidazole were purchased from Himedia Leading BioSciences Company and Alfa Aesar, respectively. Spectroscopic grade solvents were used for all the experiments. The ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker 600 MHz NMR spectrometer. The high resolution mass spectra (HRMS) were recorded on a Micromass Q-TOF ESI-MS instrument (model HAB273). Field emission scanning electron microscope (FESEM) images were recorded on a Sigma Carl ZEISS scanning electron microscope. Transmission electron microscopic (TEM) studies were done using a Tecnai G2 F20 S-twin JEOL 2100 transmission electron microscope. The UV-Vis absorption spectra were recorded on a Perkin Elmer Lambda-35 spectrometer. FT-IR was recorded on a Perkin Elmer spectrometer with samples prepared using KBr pellets. Electrochemical measurements were carried out using a CH instruments Model 700D series. The thickness of the deposited films was optimized using a profilometer (Dektat-150). An electrochemical workstation consisted of a three electrode system viz. Ag/AgNO₃ as the reference electrode, a platinum wire as the counter electrode and glassy carbon as the working electrode. A 0.1 M tetra n-butyl ammonium hexafluorophosphate (TBAPF₆) in acetonitrile (CH₃CN) and ferrocene was used as a supporting electrolyte and an internal reference, respectively at a scan rate of 50 mV s⁻¹ in an inert atmosphere.

Synthesis of PDI-HIS and PDI-n-octyl

PDI-HIS and PDI-n-octyl were synthesized using a modified reported procedure. A mixture of perylene-3,4,9,10-tetracarboxylic dihydridre (300 mg, 0.76 mmol), histidine (260 mg, 1.67 mmol) and/or octyl amine (216 mg, 1.67 mmol), zinc acetate (catalytic amount) and 5.0 g of imidazole was heated at 140 °C for 8 h under continuous stirring. The reaction mixture was then allowed to cool and poured into water. To the mixture, 2.0 M HCl was added under continuous stirring to obtain a precipitate. This was then centrifuged and washed several times with water followed by drying under vacuum to get the red colored solid product. PDI-n-octyl was further purified by column chromatography using hexane–chlorofom as an eluent.

PDI-HIS: yield = 460 mg, 90%. ¹H-NMR (DMSO, 600 MHz, δ ppm): 9.06 (s, 2H), 8.96 (s, 2H), 8.53 (t, 2H), 8.34 (b, 4H), 5.86 (t, 2H). ¹³C-NMR (DMSO, 150 MHz, δ ppm): 169.89, 162.50, 134.32, 134.19, 133.96, 131.59, 130.03, 124.15, 119.41, 117.15, 52.82, 28.49. ESI-MS: m/z [M + H]⁺ calculated for C₃₆H₂₂N₆O₈ 667.1551, found 667.1499.
PDI-n-octyl: yield = 291 mg, 62%. ¹H-NMR (CDCl₃, 600 MHz, δ ppm): 8.67 (d, 4H), 8.60 (d, 4H), 4.18 (t, 4H), 1.74 (m, 4H), 1.55–1.24 (m, 20H), 0.85 (t, 6H).

The detailed synthetic scheme and the characterization spectra are presented in Schemes S1, S2 and Fig. S1–S4 of the ESI†.

Device fabrication and characterization
For the fabrication of a two terminal sensor device, low cost microscopic glass slides (1 cm × 2 cm) were used as substrates. The glass substrates were cleaned in piranha solution (3 : 1/ H₂SO₄ : H₂O₂) for 1 h and washed several times with deionized water followed by sonication. The cleaned substrates were then dried under vacuum at 100 °C. A channel of 30 μm length (L) and 2000 μm width (W) was obtained by depositing 150 nm thick aluminum (Al) electrodes on to cleaned glass substrates by thermal evaporation under high vacuum <10⁻⁶ mbar. From the stock solution of PDI-HIS (10⁻³ M) in DMSO, a volume of 15 μL was drop-cast over the channel between the electrodes. The solvent was fully dried by heating on a hot plate for 30 min at 80 °C to form a thin film (thickness 60 nm) across the fabricated Al electrodes. All the electrical characterizations of the devices were carried out under ambient conditions using a Keithley 4200-SCS semiconductor parameter analyzer at room temperature.

Vapor phase detection
For the vapor sensing experiment, the fabricated device was kept in a chamber of approximately 0.06 L in volume. A certain volume of the analyte was injected into the test chamber by using a micropipette. The concentration of vapors was calculated using the following eqn (1):⁴⁹

\[ C_{\text{ppm}} = \frac{V_{\text{μL}} D_{\text{g mL}^{-1}}}{M_{\text{g mol}^{-1}} V_{\text{ml}}} \times 2.24 \times 10^7 \]  

where, \( C_{\text{ppm}} \) is the required vapor concentration, \( V_{\text{μL}} \) is the volume of the liquid analyte, \( D_{\text{g mL}^{-1}} \) is the density of the liquid, \( V_{\text{ml}} \) is the volume of the test chamber and \( M_{\text{g mol}^{-1}} \) is the molecular weight of the liquid analyte. All the subscripts are the corresponding units. Sensing studies using various commercially available common analytes were carried out by injecting the sample in a vial placed inside the chamber adjacent to the device at room temperature and under ambient conditions.

Results and discussion
Sensing studies
Sensing experiments were carried out using both PDI-HIS and PDI-n-octyl fabricated two terminal sensor devices with simple architecture as shown in Fig. 1a. The devices were kept in a chamber and connected to a Keithley 4200 SCS semiconductor parameter analyzer to perform electrical characterization. For I–V measurements, the devices were tested in a vacuum first and then under ambient conditions by sweeping the voltage from −10 V to +10 V to check their stability in the real environment. The I–V curve obtained for a PDI-HIS fabricated thin film demonstrated a good conducting behavior (Fig. 1b) compared to a PDI-n-octyl fabricated device (Fig. S5 in the ESI†).

To investigate the sensing response of a PDI-HIS film-based device towards NH₃, the concentrations of NH₃ were systematically varied from 100 ppm to 2 ppm and changes in the current intensity were observed. As shown in Fig. 2a, a significant increase in current was observed after exposing 100 ppm NH₃ vapors to the chamber that was seen enhancing continuously with very short response time. Upon turning off the NH₃ source, current intensity recovered quickly to its initial level. Thus, it can be concluded that the device exhibits excellent response and recovery time for the NH₃ detection. To perform the quantification by this device, the chamber was exposed to 50, 30, 20, 10, 5 and 2 ppm NH₃ vapors to obtain similar responses with lower current intensity that varied according to the concentrations. The corresponding sensitivity (S) was calculated using the formula \( S = \Delta I/I_0 \), where \( \Delta I \) is the change in current intensity upon NH₃ vapor exposure and \( I_0 \) is the initial current in absence of NH₃ vapors. The sensitivity of the device was then plotted as a function of different NH₃ concentrations. The curve showed a linear response with increase in the concentration of ammonia as shown in Fig. 2b.

The response and recovery times are considered as important parameters for any gas-sensing devices. The response time is the time needed for a sensing device to reach 90% of total current change after the supply of analyte vapors, whereas the recovery time is the 90% of current change to return to its original position after the analyte vapor source is turned off. The response
time of the device to 100 ppm of \( \text{NH}_3 \) was calculated to be very low as 28 s, whereas the recovery time was found to be 40 s (Fig. 3a). To the best of our knowledge, such low cost high stability devices have not been reported yet with such a remarkable response/recovery time for \( \text{NH}_3 \) detection and high sensitivity making the current protocol highly reliable and useful for the rapid detection of \( \text{NH}_3 \) vapors. To further verify the viability of this system for practical applications, the recyclability of the device was checked by exposing certain concentration of \( \text{NH}_3 \) vapors repeatedly after certain interval of time into the test chamber. Almost similar increment in current intensity (Fig. 3b) was observed after each exposure confirming the feasibility of the sensor device for realistic use.

The stability of the sensor device is another crucial and most vital criterion for practical applications. After leaving the device under ambient conditions for ~4 weeks, the sensor device was again tested with different \( \text{NH}_3 \) concentrations (Fig. 4a). It was observed that the change in current intensity in the devices showed excellent reversibility and stability under continuous operation and storage conditions with negligible to no loss in activity even after prolonged testing or storing under ambient conditions.

The limit of detection (LOD) is another vital parameter to be determined for a sensor device. To calculate the LOD, a calibration curve was constructed by plotting the maximum current intensity against the concentration of \( \text{NH}_3 \) (Fig. 4b). The curve demonstrates a good linear relationship with the correlation coefficient \( (R^2) \) value of 0.9994. The limit of detection (LOD) was calculated using the formula LOD = \( 3.3 \sigma / S \), where, ‘\( \sigma \)’ is the relative standard deviation of the current response of the device in the absence of \( \text{NH}_3 \) and ‘\( S \)’ is the slope of the calibration curve. The LOD was found to be 0.56 ppm which is compatible with the minimum permissible limit set for \( \text{NH}_3 \) in the working environment \( i.e. \) 25 ppm for long exposure upto 8 h.

**Effect of humidity and film thickness on sensing**

All the sensing experiments were carried out in the laboratory atmosphere (relative humidity-RH \( \geq 60\% \)) that provides an environment closer to the ultimate condition of the sensor devices. To further study the effect of humidity on the \( \text{NH}_3 \) response, sensing experiments were carried out by exposing 50 ppm \( \text{NH}_3 \) on three different devices at humidity levels RH 0%, 60% and 90%, respectively (Fig. S6 of ESI†). In a vacuum (RH 0%), the sensor device gave highest response for \( \text{NH}_3 \) and decreases by \( \sim 18\% \) on increasing the RH upto 60%. However, on further increasing the humidity levels from 60% to 90%, the response of the device towards \( \text{NH}_3 \) decreases by only \( \sim 8\% \). Low sensitivity of the device at higher humidity is consistent with the weak adsorption/diffusion of ammonia vapors on the surface of the film. It is believed that under higher humidity conditions, there is a probability of a strong competition between water and ammonia molecules to get adsorbed/diffused at the receptor sites (histidine units) of the PDI-HIS film. Thus, it can be concluded that the sensor device is functional over a wide range of humidity levels and can be used for sensing \( \text{NH}_3 \) under real environmental conditions.

To monitor the effect of film thickness on sensitivity, three devices with variable thicknesses (30, 60 and 100 nm) were optimized and investigated for their sensing response towards 100 ppm \( \text{NH}_3 \) (Fig. 5 and Fig. S7 of ESI†). It was found that the sensitivity of the devices rises by \( \sim 3.3 \) times on increasing the thickness from 30 nm to 60 nm with slight increment (1 s/4 s) in the response/recovery time. However, on further increasing the thickness from 60 nm to 100 nm, the sensitivity increases by only \( \sim 1.3 \) times with much larger increment (26 s/16 s) in response/recovery time. The high response time in a thicker film may be attributed to the diffusion of a large number of \( \text{NH}_3 \) molecules into the film which thereby takes a much longer time to get recovered. These studies helped in concluding that the thickness of a film affects the sensor response and a device with film thickness of \( \sim 60 \) nm is generally appropriate for \( \text{NH}_3 \) detection considering the response/recovery time and better sensitivity observed here.
Selectivity studies

To validate the selectivity of the device, similar sensing experiments were also performed with eight common volatile organic solvents (chloroform, acetone, methanol, isopropanol, ethanol, ethyl acetate, THF and hexane) by exposing five times higher concentration than NH₃ (Fig. 6a). Interestingly, the device responses to even 1000 ppm of common organic analytes were negligible in comparison to 200 ppm of NH₃. To date, such outstanding selectivity and reusability of NH₃ sensors with remarkably low detection limits has marked this sensor device as a rare example available in literature. To further explore the selectivity of this system, the device was also exposed to various other common organic amines such as cyclohexyl amine, triethyl amine, diisopropyl amine, pyridine and diethyl amine, since all these vapors have biological or environmental consequences. From Fig. 6b, it can be concluded safely that the response of a sensor device towards various other amines was insignificant compared to NH₃ even at much higher concentrations.

Sensing mechanism

Generally, the mechanism of organic semiconductor based conductometric gas sensors involves the adsorption of analytes onto the surface via dissociation and/or diffusion followed by the formation of a possible charge transfer complex that eventually leads to the variation of majority charge carriers than in the current.45,50 Depending upon the chemical nature of both the species, the binding can be weak or strong via some chemical interactions such as hydrogen bonding, dipole–dipole interactions etc. The molecular self-assembly due to π–π interactions in such semiconductors also provides efficient pathways for charge migration or transport. Change in redox potential is another major factor associated with the mobility of charge carriers.1,10,32,42,51,52

To understand the sensing mechanism, the surface morphology of the PDI-HIS fabricated film was initially studied before and after exposure to NH₃ vapors via FESEM and TEM, respectively. The PDI-HIS film showed an amorphous self-assembled nano-structured network throughout the surface (Fig. 7a and c) which indicates the huge surface area available for the adsorption and/or diffusion of gas molecules (Fig. 7b and d) that subsequently leads to the remarkable change in the current and response time. On introducing NH₃ vapors onto the PDI-HIS fabricated film, the current intensity displayed significant increment by several orders of magnitude with an excellent response time. This can be explained by donor–acceptor like complexation53 between n-type organic semiconductor materials i.e. PDI-HIS (electron acceptor) and NH₃ (electron donor) molecules. Since, each PDI-HIS molecule consists of two –COOH units at the imide positions that have the tendency to bind with NH₃ through an acid–base interaction, numerous ion pairs are expected to form in the film that can drastically increase the ionic conductivity and consequently the current. In addition, the presence of histidine groups will further boost up the sensitivity of the device due to the favorable hydrogen bonding interactions with NH₃. The aggregation of PDI-HIS molecules due to π–π interactions is another possible factor responsible for such a high sensitivity, since it can provide efficient charge transport into the material.

Furthermore, to validate the proposed sensing mechanism, we have monitored the changes in the IR spectrum of PDI-HIS before and after exposing it to NH₃ vapors (Fig. S8 of ESI†). The band observed at 3418 cm⁻¹ corresponds to the stretching vibrations of carboxylic –OH and/or histidine –NH, which showed a significant shift (3347 cm⁻¹) immediately after exposing it to NH₃ vapors confirming the adsorption/diffusion of ammonia vapors onto the surface of the film via hydrogen bonding interactions/acid–base interactions that subsequently leads to the increment in ionic conductivity and current.

In order to elucidate the effect of the amino acid anchoring groups on PDI-HIS, sensing studies were also performed using a fabricated device of a model compound PDI-n-octyl that does not consists of any active groups (e.g. COOH) at the imide position except long alkyl chains. Interestingly, no significant enhancement in the current (0.20 times) was observed after introducing NH₃ vapors to the PDI-n-octyl fabricated film even at much higher concentrations (Fig. S9, ESI†). These results confirm that the solubilizing/anchoring group attached onto the imide position of PDI-HIS played a vital role in the signalling process. The active –COOH groups on either side of PDI-HIS are
Table 1 Frontier molecular orbital energies as estimated from cyclic voltammetry and optical absorption

<table>
<thead>
<tr>
<th>Organic semiconductors</th>
<th>$E_{\text{red onset}}$ (eV)</th>
<th>HOMO (eV)</th>
<th>$\lambda_{\text{abs onset}}$ (nm)</th>
<th>$E_g$ (eV)</th>
<th>$\Delta E_{\text{LUMO}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDI-HIS</td>
<td>-0.65</td>
<td>-4.07</td>
<td>-6.32</td>
<td>549</td>
<td>2.25</td>
</tr>
<tr>
<td>PDI-(n)-octyl</td>
<td>-1.12</td>
<td>-3.60</td>
<td>-5.89</td>
<td>542</td>
<td>2.29</td>
</tr>
</tbody>
</table>

\[ \begin{align*}
{E_{\text{red onset}}} & = -4.8 + 4.8 \\
{E_{\text{HOMO}}} & = -{E_{\text{LUMO}}} - 4.8 \\
{E_{\text{g}}^d} & = 1240/{\lambda_{\text{abs onset}}} \\
{E_{\text{g}}^c} & = {E_{\text{LUMO}}} - {E_{\text{HOMO}}} \\
\end{align*} \]

Table 2 A comparative study of the PDI-HIS sensor with different reported materials

<table>
<thead>
<tr>
<th>Sensing material used</th>
<th>Response/recovery time</th>
<th>LOD</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perylene diimide thin film</td>
<td>28 s/40 s</td>
<td>0.56 ppm</td>
<td>Present manuscript</td>
</tr>
<tr>
<td>WO(_3)–SnO(_2) nanostructures</td>
<td>N/A</td>
<td>520 ppm</td>
<td>3</td>
</tr>
<tr>
<td>Diallyl tetra-thiapentacene derivative</td>
<td>36 s/10 s</td>
<td>10 ppm</td>
<td>2</td>
</tr>
<tr>
<td>Naphthalene diimide derivative</td>
<td>5 s/20 s</td>
<td>10 ppm</td>
<td>34</td>
</tr>
<tr>
<td>Pentacene thin film</td>
<td>N/A</td>
<td>0.5 ppm</td>
<td>35</td>
</tr>
<tr>
<td>Monolayer pentacene thin film</td>
<td>N/A</td>
<td>10 ppm</td>
<td>33</td>
</tr>
<tr>
<td>Fe(_2)O(_3)/MWCNT PhCOOH hybrid composite</td>
<td>200 s/&gt;200 s</td>
<td>250 ppm</td>
<td>14</td>
</tr>
<tr>
<td>Polymer PGMA-AN &amp; PGMA-S</td>
<td>N/A</td>
<td>13.9 ppm &amp; 16 ppm</td>
<td>53</td>
</tr>
<tr>
<td>ZnO nanostructures</td>
<td>20 s/25 s</td>
<td>25 ppm</td>
<td>15</td>
</tr>
<tr>
<td>Graphene network</td>
<td>N/A</td>
<td>20 ppm</td>
<td>29</td>
</tr>
<tr>
<td>SnO(_2) nanoparticle</td>
<td>75 s/67 s</td>
<td>50 ppm</td>
<td>16</td>
</tr>
</tbody>
</table>

Conclusion

In conclusion, a new and efficient platform for the vapor phase detection of NH\(_3\) using a two terminal sensor device based on...
PDI-HIS nanostructures fabricated on a simple glass substrate by the drop-casting method has been developed. The sensing parameters viz. sensitivity, selectivity, recyclability, response/recovery time and stability were studied that revealed the excellent performance of the device with a very low detection limit of 0.56 ppm for NH₃. We have also demonstrated that the molecular assemblies of PDI-HIS nanostructures, redox potential and ionic groups at the imide position are key aspects for the remarkable response of the device towards NH₃. Thus, the ability of the as-fabricated sensor device to detect NH₃ vapors at room temperature and under ambient conditions with high sensitivity, selectivity and low fabrication cost makes the protocol economical and feasible for potential applications under chemical, biomedical and competitive environmental conditions.

Acknowledgements

Financial assistance from Department of Science and Technology (DST), New Delhi, (No. SB/S1/PC-020/2014/000034), DST-Max Planck Society, Germany (IGSTC/MPG/PG(PKII)/2011A/48), and Department of Electronics & Information Technology, (DeitY) No. 5(9)/2012-NANO (Vol. II), is gratefully acknowledged. The authors acknowledge valuable discussions with M. Adil Afroz. The Central Instruments Facility, IIT Guwahati is acknowledged for instrument facilities.

Notes and references