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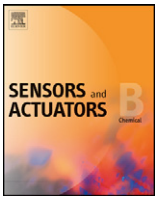

Short communication

Nitrogen dioxide vapor detection using poly-*o*-toluidine

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ABSTRACT

We describe a flexible, lightweight, reversible NO_2 vapor sensor based on resistance changes of a thin film of a doped conducting polymer, poly-*o*-toluidine, deposited on plastic substrates. Unlike the irreversible signals typically observed in organic films, signal reversibility in the concentration range 100–10 ppm is readily achieved using a short burst of UV irradiation at room temperature in ambient air without the aid of heating or pump down cycles. Interestingly, signal response is dependent on the organic solvent used to cast the polymer film with dipolar aprotic solvents yielding films showing a strong response. There are striking differences in electrical and electronic properties including morphology of films cast from different solvents. This phenomenon is traced to polymer chain conformation in solution that is preserved in the solid state (cast film) which opens a new structural vector to tailor sensor response and selectivity. This study also expands the use of conducting polymers for the detection of vapors that were previously believed to be chemically too aggressive.

1. Introduction

Although all-plastic detectors have attractive features like light weight, flexibility, and optical transparency, the organic sensor elements are vulnerable to chemical attack from aggressive vapors like NO_2, Cl_2, etc. Therefore, most chemiresistors used for detecting aggressive chemical vapors employ inorganic metal oxide films as the sensor element, often requiring high operating temperatures [1–4]. Conducting polymers have been used as chemiresistors or ChemFETs to detect a variety of common organic vapors [5–7], including electron donating vapors like ammonia, alkyl amines [8–11] and hydrazine [12]. Signal response is dependent on the film morphology with nanofibrillar films showing significantly enhanced response [13]. However, exposure to chemically aggressive electron withdrawing vapors like SO_2, Cl_2, NO_2, etc. [14–16], often times results in an irreversible resistance change [13–17] that is believed to be due to over-oxidation of the polymer backbone. This effect is expected to be exacerbated in nanofibrillar films due to its high surface area [17]. In this study, we overcome these issues by optimizing sensor film morphology using solvent-driven changes in chain conformation and demonstrate a polyaniline-based chemiresistor that is sensitive and selective to aggressive vapors like NO_2 under ambient conditions. We chose NO_2 as a prototype aggressive chemical vapor because of the importance of detecting NO_2 vapor in the environment (air quality) and also because of its known reactivity with aromatic organic films.

2. Experiments and methods

Poly-*o*-toluidine was used as a prototype system because of its ease of synthesis and low molecular weight that facilitates processing from a variety of organic solvents. The electrically conducting emeraldine salt form of poly-*o*-toluidine was synthesized using conventional oxidative polymerization of *o*-toluidine in dilute aqueous acids using peroxydisulfate oxidant (σ_{RT} ~10^{-2} S/cm, 4-probe, pressed pellet). The corresponding electrically insulating and solution processable emeraldine base form was obtained by dedoping the emeraldine salt form in dilute aqueous base and dissolving in a variety of solvents. Thin films of poly-*o*-toluidine base (1–2 μm thick) are solution cast on poly(ethylene terephthalate) (PET) having four gold sputtered lines as electrodes and re-doped by immersing in aqueous 1.0 M HCl for sensor measurements (see SI section for further details).

3. Results and discussion

When a film of poly-*o*-toluidine cast from 1-methyl-2-pyrrolidinone (NMP) is exposed to successively increasing concentrations of NO_2 vapor, the resistance increases sharply (Fig. 1) and does not recover when the vapor is turned off or pumped off. However, when exposed to UV irradiation for <2 min the signal completely recovers suggesting that NO_2 does not react irreversibly with the polymer in the timeframe of the experiment. In contrast, a film cast from $CHCl_3$ behaves very differently, i.e., the resistance change is irreversible even upon UV irradiation (Fig. 1, inset). Successive exposure to NO_2 vapor results in a progressive increase in resistance until the signal plateaus. This phenomenon of

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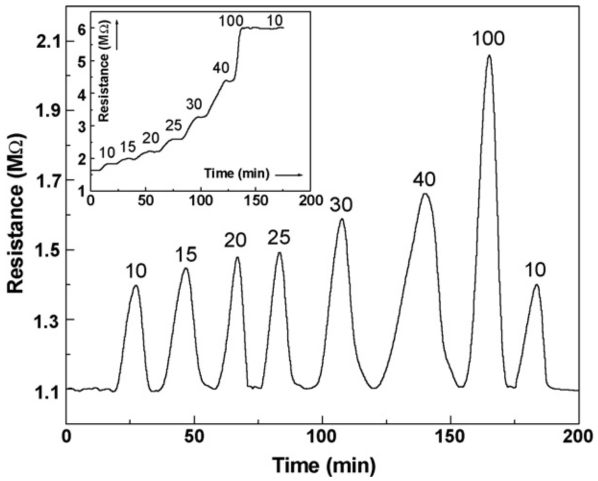

Fig. 1. Plot of resistance of poly-*o*-toluidine film on PET cast from NMP when exposed to NO_2 vapor at different concentrations (ppm values shown at peaks). Film is UV irradiated at peak for signal reversibility (vapor desorption). Inset: film cast from $CHCl_3$.

a conducting polymer showing two different reversible responses for a single vapor has not been previously observed. The irreversible signal response in $CHCl_3$-cast films is consistent with previously published results indicating oxidation of the polymer from emeraldine to insulating pernigraniline [13,15,17]. However, films cast from both solvents remain bright green during the entire experiment suggesting that the polymer remains in the emeraldine oxidation state. Importantly, this does not account for the signal reversibility upon UV irradiation in NMP-cast films.

Vapor concentration vs. resistance (ΔR/R%) plots show a pseudo-linear response for NMP-cast films (Fig. 2a) and a scattered, non-linear response for $CHCl_3$-cast films (Fig. 2a, bottom inset). It is important to note that the pseudo-linear response observed in NMP-cast films is based on data obtained in the 100–10 ppm concentration range and does not rule out a possible non-linear region at low vapor concentration. The NO_2 vapor exposure cycle was set to 2 min when the signal saturates. Longer exposure times were avoided to minimize any oxidative bleaching or damage to the poly-*o*-toluidine film or the PET substrate. The signal recovery cycle for NMP-cast films shown in Fig. 1 consists of 2 steps shown in Fig. 2 (top inset), (i) an NO_2 removal step when the sensor is removed from the chamber, and (ii) a NO_2 desorption step when the sample is UV irradiated. The NO_2 desorption step is carried out by placing a 254 nm UV lamp horizontally 1.0 cm away from the sensor (0.5 mW/cm^2) with the sip sockets still attached. Without UV irradiation the signal takes a long time to partially recover in ambient air, e.g., 45–90 min depending on film thickness.

Films of poly-*o*-toluidine are also selective to aggressive oxidizing vapors like NO_2 and unresponsive to a variety of common organic solvent vapors (unlike the parent polyaniline system). For example, films cast from both NMP and $CHCl_3$ show very little resistance change when exposed to hexane, toluene, CH_2Cl_2, and $CHCl_3$ under saturated vapor conditions (Fig. 2b). This is to be contrasted to the ~90% ΔR/R reversible response observed in the case of films cast from NMP and ~40% ΔR/R irreversible response observed in the case of films cast from $CHCl_3$ when exposed to 100 ppm NO_2 vapor. It is important to note that a strong response to NO_2 vapor is observed even in the presence of common organic vapors under saturated vapor conditions which could be useful in applications under complex, cluttered environments (urban air, battlespace). The selectivity profile observed so far is also promising in the design and development of an e-nose detector array using a combination of chemically different sensor nodes.

It is unclear why UV irradiation should facilitate NO_2 vapor desorption from the conducting polymer film, and that too only in NMP-cast films, although a qualitatively similar phenomenon has been reported in a carbon nanotube/NO_2 detector system [18]. Slow signal reversibility in this system has been attributed to a bimolecular reaction of NO_2 on the nanotube surface yielding NO which rapidly desorbs, and NO_3 which has a long residence time [19]. Evidence consistent with this rationale is obtained from the morphology of films cast from NMP and $CHCl_3$.

For example, the morphology of films cast from NMP and $CHCl_3$ are strikingly different, e.g., NMP-cast films are more textured, inhomogeneous and have large open pores whereas $CHCl_3$-cast films are compact and featureless (Fig. 3). Since both films were cast under very similar conditions (see SI section), the difference in film morphology is due to something other than simple effects, such as, solvent evaporation rate, polymer concentration, etc. Interestingly, the 4-probe, pressed pellet conductivity of the hydrochloride salt precipitated from NMP is higher ($\sigma \sim 10^{-1}$ S/cm) compared to $CHCl_3$ ($\sigma \sim 10^{-2}$ S/cm). Our working hypothesis is that the difference in film morphology is due, in part, to different chain conformations of poly-*o*-toluidine base in NMP vs. $CHCl_3$. Indeed, solutions in NMP are navy blue in color whereas solutions in $CHCl_3$ are deep purple (Fig. 2b, inset) displaying solvatochromism that has been attributed to different chain conformations, i.e., the higher excitonic transition energy in $CHCl_3$ (570 nm) is consistent with a coil-like, localized chain conformation compared to NMP (608 nm).

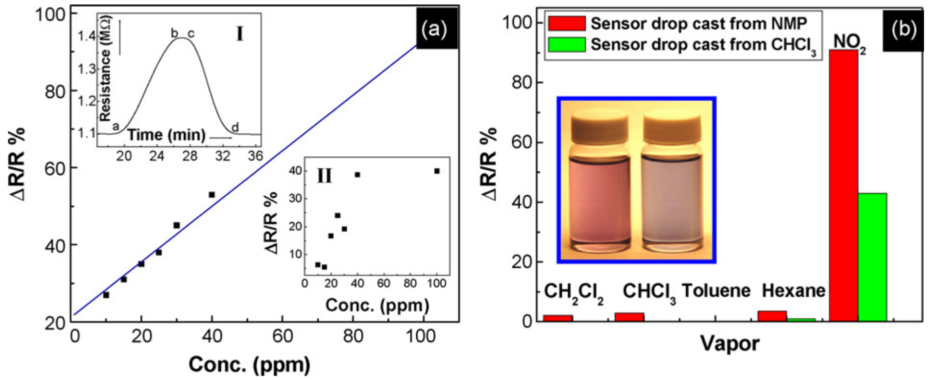

Fig. 2. (a) Plot of vapor concentration vs. percent change in resistance (ΔR/R%) of HCl doped poly-*o*-toluidine/PET sensor cast from NMP. Inset-I: resistance profile of a single vapor exposure cycle; NO_2 vapor introduced at point "a", signal saturates at point "b" when sample is removed from the chamber, UV irradiation started at "c", and stopped at "d" when sensor is placed back in the chamber for the next NO_2 exposure cycle. Inset-II: plot of vapor concentration vs. percent change in resistance (ΔR/R%) of HCl doped poly-*o*-toluidine/PET sensor cast from $CHCl_3$. (b) Plot of ΔR/R% of film cast from NMP (red) and $CHCl_3$ (green) when exposed to satd. organic vapors and NO_2 (100 ppm) in ambient air. Inset: digital image of solutions in (a) $CHCl_3$ (left) and (b) NMP (right). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

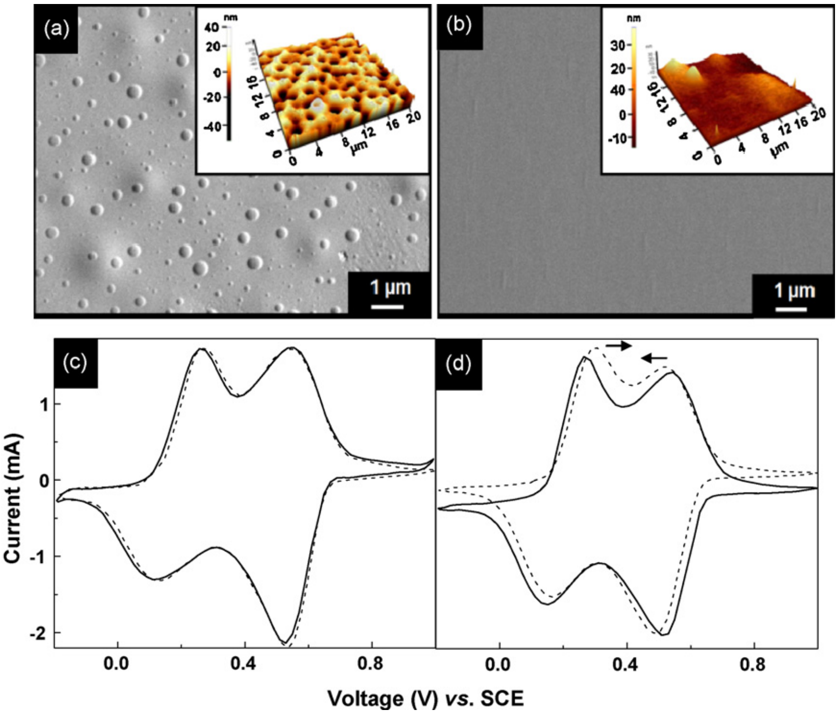

Fig. 3. SEM images of poly-*o*-toluidine film on PET: (a) cast from NMP, and (b) cast from $CHCl_3$. Inset: corresponding AFM images. Cyclic voltammograms of poly-*o*-toluidine deposited on Pt mesh from solutions in (c) NMP, and (d) $CHCl_3$ (aq. 1.0 M HCl electrolyte, SCE reference). Solid line: plot before exposure to NO_2 vapor. Dotted line: plot after seven NO_2 vapor exposure/UV irradiation cycles from Fig. 1.

We have obtained confirmatory evidence for the first time by measuring relative molecular weight in NMP and $CHCl_3$ using size exclusion chromatography. The M_w of poly-*o*-toluidine base in NMP/Li^+ (mobile phase) is ~15,000 g mol^{-1} whereas in $CHCl_3$ M_w is strikingly different, i.e., only ~800 g mol^{-1} [20]. Since molecular weight values obtained by size exclusion chromatography values are relative to internal polystyrene standards, this unusually large difference is consistent with different chain conformation in solution, i.e., rod-like in NMP vs. coil-like in $CHCl_3$ (solvatochromism) [21,22]. Absolute molecular weight measurements (light scattering) show that the molecular weight is ~4,000 g mol [20] suggesting that, the larger relative molecular weight value observed in NMP is consistent with a more extended and delocalized rod-like, open conformation in solution that is retained in the solid state when a film is cast from solution. These films are therefore more porous, displaying higher conductivity and faster vapor desorption. Conversely, films cast from $CHCl_3$ are more compact, displaying lower conductivity and slower vapor desorption kinetics.

We believe that the open, porous structure of NMP-cast films results in facile NO_2 desorption upon UV irradiation whereas in $CHCl_3$-cast films the residence time of physisorbed NO_2 vapor is higher which could attack the polymer backbone, or could disproportionate to NO and NO_3 which could both attack the polymer backbone. Aqueous electrochemistry provides additional clues, e.g., there is essentially no change in the half wave potentials ($E_{1/2}$) in NMP-cast films before and after exposure to NO_2 vapor (Fig. 3c). In contrast, in $CHCl_3$-cast films, there is a noticeable change in both the redox peaks upon exposure to NO_2 vapor consistent with chemical interaction with the polymer backbone (Fig. 3d). It is to be noted that UV irradiation alone does not significantly alter the properties of the poly-*o*-toluidine film since the overall redox features are retained in both cases.

There are other interesting solvent effects that could also significantly impact sensor performance. For example, the FT/IR spectrum of an NMP-cast film on AgCl pellet shows that the film is more oxidized than corresponding $CHCl_3$-cast films. This is consistent with a higher open circuit potential for NMP-cast films (E_o = 0.53 V) vs. $CHCl_3$-cast films (E_o = 0.41 V). These changes could be due to differences in polymer chain conformation in solution that are retained in the solid state when the film is cast from solution (see SI section).

The robust strong sensor response of 2-alkyl substituted polyanilines to NO_2 vapor does not translate to other derivatives, e.g., NMP-cast films of poly-*o*-ethoxyaniline, poly-*o*-methoxyaniline, and poly-2,5-dimethoxyaniline all show a strong response when exposed to NO_2 vapor but the signal is not reversible due (possibly) to strong chemisorption of the electron deficient NO_2 with the electron rich polymer backbone. Significant challenges remain in leveraging the above findings to develop a commercial vapor detector for highly oxidizing vapors. For example, when compared to traditional high-temperature inorganic materials based NO_2 detectors, conducting polymer detectors offer the potential for room temperature detection. However, the use of UV irradiation to affect signal recovery is cumbersome and could pose a significant challenge to commercialization. In addition, a more detailed study is needed to minimize noise and baseline drift frequently observed in organic thin film chemiresistors, although we have been able to calculate a theoretical value of signal resolution based on the signal/noise ratio. For example, even though the lowest measured concentration of NO_2 vapor used in this study was 10 ppm, the theoretical value for signal resolution is expected to be at least 2 orders of magnitude lower [18].

4. Conclusions

In summary, we demonstrate: (i) a conducting polymers based chemiresistor that can reversibly detect NO_2 vapor at room temperature under ambient conditions, (ii) the use of UV irradiation to induce vapor desorption and achieve signal reversibility, (iii) the use of polymer chain conformation in solution to optimize film morphology and improve sensor performance.

Supporting information

Poly-*o*-toluidine synthesis, sensor fabrication and sensor measurement procedure, spectroscopic characterizations, cyclic voltammogram.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.snb.2009.09.033.

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Sanjeev K. Manohar received his Ph.D. degree in 1992 from the University of Pennsylvania in organic chemistry (conducting polymers) under the mentorship of Professor Alan G. MacDiarmid, a co-recipient of the 2000 Nobel Prize in Chemistry. From 1992 to 1997 he worked at The Procter and Gamble Company in Cincinnati, Ohio, USA in technology/product development on surfactant and polymer technologies for P&G's flagship detergent brands. From 2001 to 2006 worked at The University of Texas at Dallas as Research Associate Professor to lead Professor Alan G. MacDiarmid's research effort in soft electronic organic nanomaterials. In 2006 he joined the University of Massachusetts Lowell as Associate Professor in the Chemical Engineering department where he is currently Director of the Green Technology Laboratory and leads a research group to explore areas where nanotechnology and green chemistry overlap.