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Chemical Vapor Detection Using Parent Polythiophene Nanofibers

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Chemical vapor sensing using organic thin films as chemiresistors or ChemFETs is a promising research area because it is possible to incorporate many attractive design features like light weight, flexibility, low power consumption, etc., based on the application.[1] Thin films of conducting polymers deposited on rigid and flexible supports have been used to detect common organic solvent vapors,[2,3] nerve agent simulants,[4] and chemically aggressive vapors.[5,6] However, irreversible signal responses are observed when these films are used to detect highly oxidizing vapors like NO_2, Cl_2, SO_2, etc.,[7,8] consistent with strong chemisorption along the polymer backbone (chlorination, nitration, etc.). We recently demonstrated the bulk synthesis of parent polythiophene nanofibers (powder) using a variant of our nanofiber seeding method[9] and wanted to evaluate these nanofibers for chemical vapor detection. However, thin polythiophene films that spontaneously deposits on the surface of substrates (for sensor studies) during the polymerization by in situ adsorption polymerization do not have nanoscale morphology (unlike the polyaniline and polypyrrole systems). Importantly, the polythiophene film also spontaneously dedopes in air, rendering it unsuitable for sensor studies. In this study, we show how thin conducting nanofiber polythiophene films can be rapidly synthesized on plastic substrates directly from the polymerization (one-step) and how the spontaneous dedoping phenomenon mentioned above can be leveraged to fabricate a reversible and selective detector for NO_2, Cl_2, SO_2, etc. (selective to a class of highly oxidizing vapors).

To obtain nanofibrillar films of polythiophene on surfaces, we modified our previously published synthesis procedure by immersing a sheet of hydrophobic poly(ethylene terephthalate) (PET, Mylar) in the reaction. In brief, a rolled-up sheet of PET is placed inside a beaker containing 60 mL of a stirred dispersion of ~4 mg of freeze-dried V_2O_5 in 60 mL of acetonitrile (contents stirred for 45 min). Thiophene monomer (1 mL) is added, and stirring continued for an additional 20 min followed by addition of 1.9 g of solid anhydrous $FeCl_3$. After 3 h, the PET sheet containing a 8−10 μm thick film of in situ deposited doped polythiophene nanofibers is removed and left in air to dry. Unlike glass and other less hydrophobic surfaces, the hydrophobic PET surface promotes fibrillar growth, and the in situ deposited polythiophene film is composed entirely of a nonwoven mesh of micrometers long, 40−80 nm diameter nanofibers (Figure 1). Electrical connection was established by first sputtering four gold lines on top of the film and inserting sip sockets (Figure 1 inset). Freshly prepared in situ films of polythiophene have sheet resistance of 8 KΩ/sq with 85% optical transparency at 550 nm. The highly flexible sensors were mounted in a glass chamber equipped with a large magnetic stir bar. NO_2, Cl_2, and SO_2 vapors were introduced into the sensor chamber by using a standard Environics gas dilution system.

The dramatic role hydrophobic surfaces play in promoting nanofiber formation is consistent with our recently published study on the origins of fibrillar polymer growth in conducting polymers.[10] For example, hydrophobic surfaces act as nucleating sites for the deposition and subsequent accumulation of dimers and/or small molecular weight oligomers on the surface. These then spontaneously form oligomeric nanofibers by a double heterogeneous nucleation mechanism. We believe a similar mechanism is operating in our system; i.e., thiophene dimer could spontaneously oligomerize to tetra- or sexithiophene nanofibers on the PET surface which would act as seeds which transcribe its nanoscale morphology to the evolving bulk polymer.

Upon exposure to highly reactive and oxidizing vapors like NO_2, Cl_2, and SO_2, the conductivity increases sharply over a period of 5 min exposure cycle (Figures 2 and 3).[5] In contrast, the conductivity decreases by 5−15% when exposed to common organic solvent vapors like $CHCl_3$, hexane, ethanol, etc. (not shown). The conductivity decreases also in the case of other conducting polymers when exposed to NO_2, Cl_2, etc.,[7,8] consistent with over oxidation of the polymer backbone and/or ring substitution resulting in an irreversible resistance response. The increase in conductivity in polythiophene films suggests that the polymer is in a partially reduced state and is being chemically doped by these oxidizing vapors. Unlike other conducting polymers, there is a tendency for $[FeCl_4]^-$ doped polythiophene films to dedope in air evidenced by a change in color from gray to pink. Observed previously, this phenomenon has been attributed to a photodedoping phenomenon involving $[FeCl_4]^-$ ions.[11] This reaction is exacerbated in thin (100−400 nm) films, e.g., on glass, ITO, etc., making them unsuitable for sensor studies. Because the film obtained on PET is much thicker, the photodedoping reaction does not proceed to completion, and the film remains conducting and suitable for sensor studies.

Interestingly, this photodedoping mechanism can be leveraged to achieve signal reversibility; i.e., the resistance recovers to the original value when films are exposed to UV irradiation in the case of all three vapors tested (Figures 2 and 3). For example, the conductivity increases by ~20% when exposed to 100 ppm NO_2 vapor (Figure 2) but does not recover on its own, i.e., when removed from the sensor chamber or during a standard pump down cycle. When the sensor is removed from the chamber and exposed to 254 nm UV light, the signal reverses readily. There are no significant changes in the X-ray photoelectron spectroscopy, FT/IR (film on AgCl pellet), and nonaqueous electrochemistry before and after the vapor exposure/UV cycle, suggesting the polymer backbone is intact and no irreversible reaction is taking place. In the case of other conducting polyaniline films, however, the irreversible increase in resistance is also accompanied by spectroscopic changes consistent with polymer backbone functionalization. To confirm the role of the $[FeCl_4]^-$ dopant in signal reversibility, the film was first electrochemically dedoped in $Bu_4N^+BF_4^-/CH_3CN$ and redoped with I_2 vapor. Sensor testing showed that the resistance did not recover upon UV irradiation. A similar behavior is observed in films of poly(3-hexylthiophene)s drop-cast on PET, i.e., an $[FeCl_4]^-$ doped film is UV reversible whereas an I_2 doped film is not. It is to be noted that UV irradiation has been used previously in carbon nanotube based NO_2 sensors to reverse the signal, although this occurs by an entirely different mechanism.[12]

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