Electrospun conducting polymer nanofibers as the active material in sensors and diodes

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Abstract. Polyaniline doped with camphorsulfonic acid (PANI-HCSA) and poly(3,4-ethylenedioxythiophene) doped with polystyrene sulfonic acid (PEDOT-PSSA) were electrospun separately to obtain individual nanofibers which were captured on Si/SiO₂ substrates and electrically characterized. The fiber resistance was recorded as a function of time in the presence of vapours of aliphatic alcohols of varying sizes. Due to the large surface to volume ratio, uniform diameter and small quantity of active material used in the construction, these sensor responses are very quick. Sensors made from individual fibers also show true saturation upon exposure to and removal of the sensing gas. A Schottky diode was also fabricated using an n-doped Si/SiO₂ substrate and a single PANI-HCSA fiber and tested in vacuum and in ammonia gas. The diode response was instantaneous upon exposure to ammonia with nearly complete recovery of the current upon pumping out the ammonia, thereby making it a reusable sensor with rectifying behaviour i.e. multifunctional.

1. Introduction
The rapid detection of minute traces of toxic gases in an inadequately ventilated environment is crucial to effectively reduce any widespread loss to life and property. This requires sensors capable of detecting small quantities of gas, such as those fabricated using nanofibers that possess enhanced surface to volume ratio. Organic conducting polymers (CP’s) are especially suited for use as gas sensors for a variety of reasons. In particular, the oxidation/reduction states of these polymers can be reversibly tuned by exposure to basic/acidsic environments, resulting in several orders of magnitude change in the conductivity [1] with no polymer degradation and that would extend the lifetime of sensors based on these polymers. Furthermore, CP’s are cheap and easy to synthesize in bulk quantities, they are relatively stable under ambient conditions and can readily be processed as films or fibers.

Individual polyaniline (PANI-HCSA) and poly(3,4-ethylenedioxythiophene) (PEDOT-PSSA) nanofibers were electrospun and used separately to sense a variety of alcohols of increasing sizes with response times that are faster than sensors made from thin films of the same material [2,3]. The advantage of using a single nanofiber chemical sensor is its small size and potential for higher sensitivity. When comparing the two polymer nanofiber sensors, the PEDOT-PSSA sensors were relatively more robust and could be reused multiple times for sensing different gases. The sensors made from PANI-HCSA had reduced response after use in any gas and it was best to use a new sensor for multiple gas sensing. The ability to prepare long nanofibers of conducting polymers via
electrospinning that have a large aspect ratio and an even larger surface to volume ratio, makes this technique very attractive for use in the fabrication of cheap, low power consumption and rapid response gas sensors. Finally, we fabricated Schottky diodes based on these fibers and tested them in a gaseous environment with near complete recovery [4]. This leads to the possibility of fabricating multifunctional devices making them more versatile.

2. Experimental
The basic apparatus used for the electrospinning of polymer nanofibers is shown in Figure 1. It consists of a hypodermic syringe (½ cc tuberculin syringe), a high voltage power supply (Gamma Research), a grounded cathode (Al foil) and a syringe pump (Cole Parmer).

2.1. PANi-HCSA fibers. In the electrospinning process, 100 mg of emeraldine base polyaniline was mixed with 129 mg of HCSA (solid state doping) and dissolved in 10 ml CHCl₃ for a period of 4 hours. The resulting deep green solution (doped polyaniline) was filtered and 3.2 mg of polyethylene oxide (PEO) having molecular weight 2,000,000 was added to the solution and stirred for an additional 2 hours. PEO was added to assist in fiber formation by acting as a plasticizer and the solution was then filtered again using a 0.45 µm PTFE syringe filter. About 0.5 ml of the solution was placed in the hypodermic syringe and the needle connected to the power supply, with the cathode (Al foil) grounded and situated about 20 cm from the tip of the needle. The flow rate was controlled to approximately one drop per 10 s. As the voltage applied to the needle increased to about 10 kV, the electric force on the polymer droplet at the end of the needle overcomes the surface tension and a polymer jet exits toward the cathode in short bursts. As the solvent evaporates in air, thin fibers of PEDOT-PSSA of varying diameters and lengths covered the substrate. Individual fibers were captured on pre-patterned doped Si/SiO₂ wafers and had diameters in the range 20-150 nm.

2.2. PEDOT-PSSA fibers. PEDOT-PSSA was purchased from Bayer Corp. (Baytron P) and used as received[5]. A 1wt% of polyethylene oxide (PEO-plasticizer) in PEDOT-PSSA was prepared and the solution used to fabricate nanofibers via electrospinning. Using the same process indicated above, individual fibers of PEDOT-PSSA were electrospun and then captured on pre-patterned doped Si/SiO₂ wafers.

An optical microscope image and an AFM image of a PANi-HCSA and a PEDOT-PSSA nanofiber are shown in Figures 2. The PANi-HCSA nanofibers were relatively long and could be manipulated with a tweezer without damage after electrospinning. The PEDOT-PSSA fibers on the other hand could not be moved after formation and were ribbon-like due to the water based solutions from which they were electrospun.
As seen in Figure 2(Right), their surface morphology was rougher than the PANi-HCSA nanofibers leading to higher surface to volume ratio. The sensors were made from individual fibers of these polymers, where the current through the fiber was monitored as a function of time in the presence of the carrier and sensing gases.

![Figure 2: Left: Electrospun single PANi-HCSA nanofibers across electrodes. Right: Electrospun PEDOT-PSSA nanober showing rough surface morphology](image)

2.3. The Schottky diode was prepared by using an n-doped Si wafer ($<111>$, 0.1-1.0 W-cm) with a 200 nm thermally grown oxide layer and an isolated polyaniline (PANi-HCSA) nanofiber. After pre-patterning gold electrodes over the oxide via standard lithography and lift-off techniques the substrate is cleaved through the electrodes. The exposed cleaved surface has the edge of the gold electrode separated from the doped Si by the insulating oxide layer. Using the electrospinning technique reported earlier[6,7], individual, charged, dry and flexible PANi-HCSA nanofibers were deposited over the wafer edge making contacts to the gold and the doped Si and that are stable with no apparent degradation or oxidation. The resulting Schottky diode is formed along the vertical edge of the substrate at the nanofiber-doped Si interface. Such a vertical orientation may offer higher levels of integration in circuitry than that provided by in-plane horizontal structures. External electrical contacts were then made and the device current-voltage (I-V) characteristics measured via a Keithley 6517A electrometer in a vacuum of $\sim 2 \times 10^{-2}$ Torr. Figure 3 shows a schematic of the device and the external electrical circuit.

![Figure 3: Schematic diagram of the Schottky diode with external electrical contacts](image)

3. Results and Discussion
The electrospun fibers were used in aliphatic alcohol vapour sensing and also in the fabrication of a Schottky diode that was tested in the presence of ammonia vapour.
3.1 Alcohol gas sensors. Figure 4 shows the PANI-HCSA and PEDOT-PSSA nanofiber sensor response to various alcohol vapours of increasing molecule sizes.

![Graphs showing sensor response](image)

**Figure 4:** Time dependence of the normalized resistance of PANi-HCSA (left) and PEDOT-PSSA (right) nanofibers to vapours of methanol (a), ethanol (b) (e) and 2-propanol (c) (f)[2,3].

Figures 4 (a), (b) and (c) show the time dependence of the change in the normalized resistance for individual isolated electrospun PANi-HCSA doped polyaniline nanofibers as seen in Figure 2 upon exposure to vapours of methanol, ethanol and 2-propanol respectively, where $R_{N_2}$ is the resistance of the fiber under a flow of dry $N_2$ gas prior to the first exposure of alcohol vapour. In the case of methanol and ethanol vapours there is a rapid increase in the resistance followed by an equally rapid decrease that quickly stabilized to a relatively constant value. Such was not the case for 2-propanol as seen in Figure 4(c) where the initial increase in the resistance was slower and then the decrease was much more slower with little evidence of reaching a constant value after approximately 5 minutes. However, in all three figures we see that subsequent application of dry $N_2$ gas followed by the sensing alcohol vapour yield qualitatively similar results in the five complete cycles that followed viz. the flow of $N_2$ decreases the resistance while the flow of alcohol vapour increases the resistance. Figures 4(d) (e) and (f) show the time dependence of the change in the sensor resistance for individual isolated electrospun PEDOT-PSSA nanofibers (as seen in Figure 2) upon exposure to vapours of methanol, ethanol and 2-propanol respectively. Upon exposure to these alcohol vapours
there is a rapid increase in the resistance that quickly saturated, followed by a decrease with a longer recovery time. These measurements were made on the same sensor beginning with methanol and ending with 2-propanol after which the sensor was annealed. The response times are rapid with large response amplitudes. The small fiber diameter and rough surface morphology contribute to the extremely large surface to volume ratio of the sensor. In addition, the sensor contains a small quantity of active material, hence this result is consistent and the response time is slightly faster than previous results using PEDOT-PSSA as alcohol sensors [8-11]. The larger the alcohol molecule, the longer is the response time and smaller the amplitude response which could be related to the slower diffusion of larger molecules into the fiber. For conducting polymers where charge transport is dominated via hopping mechanisms, changes in the polymer resistance in the presence of a sensing gas occur mainly due to chemical (doping/dedoping) changes, conformational changes (tight coil vs. expanded coil) or polymer swelling (increase in inter-chain separation) [12]. When PEDOT-PSSA or PANi-HCSA is exposed to alcohol vapours, the increase in the resistance is attributed to polymer swelling [9,13] that would increase the inter-chain separation and subsequently reduce the hopping rate. This is consistent with the rapid decrease of the sensor resistance when exposed to the alcohol vapour and the slower recovery when the sensing gas is removed. Since the sensor is dried in the presence of N₂ gas prior to introducing the sensing gas, the response to the sensing gas is rapid with the alcohol vapour immediately penetrating the polymer chains causing swelling and moving them apart, then when the sensing gas is removed, the polymer chains relax more slowly to their original positions and the recovery time would depend on how effectively the sensing gas is removed. Increasing the size of the alcohol molecule increases the response time since a larger molecule would take a longer time to diffuse into the polymer. No drift in the response with time is observed which implies that the response does not affect the sensor baseline conductivity in the absence of the sensing gas and the response is therefore reversible. The sensing amplitude is also among the highest recorded for PEDOT-PSSA based alcohol sensors and must be correlated to the very large surface to volume ratio for these individual nano fibers and the high gas concentration used. Table 1 gives the response and recovery times of these sensors and the relative response amplitude changes.

| Sensing gas | PANi-HCSA nanofiber sensor | PEDOT-PSSA nanofiber sensor |
|-------------|---------------------------|----------------------------|
|             | Response time (s) | Recovery Time (s) | (ΔR/RₓN₂) x 100 | Response time (s) | Recovery time (s) | (ΔR/RₓN₂) x 100 |
| Methanol    | 32 | 20 | 94 | 8 | >100 | 40 |
| Ethanol     | 20 | 20 | 94 | 10 | >100 | 40 |
| 2-Propanol  | >110 | >50 | 97 | 20 | >100 | 30 |

3.2. Schottky diode and ammonia gas sensor. The diode prepared as mentioned in the experimental section was characterized in vacuum and in the presence of ammonia vapour. Figure 5 shows the results of this experiment in an as prepared device measured in vacuum. There is clear evidence that the curve is asymmetric and diode-like with a turn-on voltage in the range 0.4-0.6V and a rectification ratio of ~100. When ammonia gas in introduced into the chamber the current immediately gets smaller but the curve is still asymmetric. This means that the rectification ratio of the diode can be changed. Due to the large surface to volume ratio of the fiber, the change in the diode response was instantaneous upon exposure to ammonia with near complete recovery of the current upon pumping out the gas, thereby making it a reusable sensor. The recovery response can be improved by using a more efficient vacuum system. As seen from Figure 5, the diode turn on voltage is not affected by the sensing action, possibly due to the presence of surface states at the junction that control device operation. The freshly cleaved Si substrate is susceptible to containing several dangling Si bonds that
would interact with the fiber upon contact thereby pinning the Fermi levels. Such pinning would make the application of this device as a sensor more reliable due to a fixed turn on voltage even in the presence of harmful gases.

Figure 5: I-V characteristic curves for a Schottky nanodiode when used as a gas sensor: (○) -as prepared sample measured in vacuum; (□) – a few seconds after exposure to ammonia vapour: -after 5 hours of pumping out the ammonia vapour

4. Conclusions
We have successfully fabricated true conducting polymer nanofibers of PANi-HCSA and PEDOT-PSSA using the electrospinning technique and used them as sensors in the presence of various alcohol vapours and also tested a Schottky diode in vacuum and in ammonia vapour. Larger alcohol molecules have a slower response time. Nanofiber sensor responses are seen to be faster or comparable to thin film sensors and have the potential to be used in detecting small amount of gases. They can also be used in diodes that exhibit rectification and sensing capabilities and are reusable making them multifunctional.

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5. References
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