Introduction

Sensors and actuators with gas-detecting capability have recently gained considerable attention due to their critical applications in industry, agriculture, electronics, and medicine. Some of these applications include detection of disease by breath analysis, detecting and monitoring flammable and hazardous gases in environment, and air-quality monitoring. So far, several technologies for monitoring and detecting gases namely propanol, ethanol, and acetone have been developed. One type of these technologies is based on semiconductor materials such as silicon,1 metal oxides,2–7 and metal nitrides.8 Another type is based on conducting polymers among which polyaniline has attracted considerable attention because of its ease of fabrication by chemical and electrochemical process. Conducting polymers typically have five transduction modes, including Conductometric mode (changes in electrical conductivity), potentiometric mode (changes in the chemical potential without current flow), amperometric mode (measurement of the current generated by the redox reaction of an analyte at a sensing electrode), colorimetric mode (changes in optical absorption), and gravimetric mode (change in the polymer weight, as a result of analyte–polymer interaction),9,12 and several sensors have been developed based on one of these transduction modes.13–16

Conducting polymers are perfect candidates for actuators as well, as they respond to electrical and chemical stimuli in their surrounding environment by movement. In conducting polymer-based electromechanical actuators, an electrical stimulus triggers volume change and thus movement is induced during the electrochemical doping-de-doping process.17,18 More importantly, changes in the conducting polymers’ chemical environment can prompt motion or mechanical work in them. Therefore, the latter are called ‘chemomechanical

Abstract

This study addresses the role of PANI–CA composites in the detection of acetone vapors with high sensitivity and selectivity in the presence of alcohols. The PANI–CA composites were fabricated by the solution-casting method and were cut to 4 cm x 3 mm rectangular strips of about 20-μm thickness. The composite strips behave as gas sensors/chemoactuators and respond to gaseous species by converting their relative concentration to a corresponding mechanical motion (bending). The bending-recovery responses of PANI/CA sensor was examined thoroughly by exposing it to varying headspace concentrations of acetone and alcohols, and by removing the analyte once the sensor reached its maximum bending angle. Sensitivity was determined by comparing the bending response of the composite strips to different headspace concentrations of acetone. Selectivity was determined through analysis of the angle change in 50/50 ml solutions of four different (potentially interfering) chemicals. The results indicate that the sensor highly discriminates between acetone and alcohols making it a potential wearable acetone skin sensor for indirect measurement of glucose in the blood for diabetics.

Keywords

Polymer, Composite, Acetone, Actuator

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polymers\textsuperscript{19–21} and are unique in that they can function simultaneously as chemical sensor and an actuator.	extsuperscript{22} However, for most conducting polymers studied to date, the focus has been on their electromechanical activity rather than an unassisted chemomechanical activity and there have been few reports discussing chemomechanical actuators.

Earlier work by our group has demonstrated that a polyaniline–cellulose acetate chemomechanical thin-film actuator bends in response to acetone during a reversible process.	extsuperscript{23} In this study, the focus is on developing a polyaniline-based actuator for acetone detection and monitoring. For this purpose, a composite of polyaniline and cellulose acetate (CA) was synthesized by solution casting. CA is an insulating polymer with high degree of crystallinity and very high melting point. It also has the important advantages of low cost, good film-forming abilities, and good mechanical properties.	extsuperscript{24} CA is a good candidate matrix for polyaniline, as it can overcome some of its drawbacks including poor mechanical properties and low processability. Polyaniline–cellulose acetate composite also shows enhanced structural and electrical stability.	extsuperscript{25–27} As a result, PANI–CA composite is an ideal model for studying chemomechanical actuation. This work aims to lead the way toward the development of wearable skin sensor for monitoring skin acetone emissions with the aim of indirect measurement of blood glucose level in diabetes.	extsuperscript{28,29} For the PANI/CA actuator to be an effective blood glucose monitor and alert a patient for insulin intake, it must be both selective and highly sensitive to acetone. These properties have not been studied before for the PANI–CA system.

**Experimental method**

**Materials**

For this study, polyaniline (leucoemeraldine base), CA, and hydrochloric acid were used to synthesize the composite thin films. The chemicals were purchased from Sigma-Aldrich. Acetone and ethanol were purchased from Pharmco-AAPER, 1-butanol and 2-propanol were purchased from J. T. Baker.

**Headspace calculation**

Equation 1 was used to calculate the headspace concentration

\[
\text{Headspace Concentration} = \frac{\text{Concentration of solution}}{\text{Phase Ratio} + \text{Water – Air Partition Ratio}} \quad (1)
\]

\[
\text{Phase Ratio} = \frac{\text{Volume of Headspace}}{\text{Volume of Sample}} \quad (2)
\]

\[
\text{Concentration of solution} = \frac{\text{Original Weight of Chemical}}{\text{Volume of Sample}} \quad (3)
\]

A water–air partition ratio of 300 was used for acetone calculations;\textsuperscript{30–32} 1300 was used for ethanol;\textsuperscript{33} 2600 and 3100 were used for calculations for 1-butanol, and 2-propanol, respectively.\textsuperscript{33} Because there are no widely agreed upon values for partition ratios of these chemicals, these values were an approximate average from several sources.

**Actuator formation**

Three steps are required to synthesize a PANI/CA actuator: (1) solution preparation, (2) casting, (3) strip cutting. In the solution preparation step, 0.1 g of LEB-PANI powder was doped with 10 ml of hydrochloric acid. Following the acid doping process, the solution was centrifuged and the acid on the top was removed. This process was repeated with water for several times and each time the precipitate was taken. Then, the acid-treated PANI was dried in air at room temperature. To the acid-treated PANI, 12 ml of acetone were then added and the mixture was ultrasonicated for 1 h to let PANI distribute in the acetone evenly. After that, 0.5 g of CA was added to the solution and dissolved in it properly by ultrasonicing the solution for extra time. Then in the casting step, PANI/CA solution was poured onto the glass slide to form the thin film and the film was flattened using a glass slide. Figure 1 shows a solution casted on a glass slide. After sufficient amount of time the thin film dried, and it was cut into approximately 4 cm by 3 mm strips. Figure 2 shows actuators formed by this method.

**Characterization**

Scanning electron microscopy analysis was conducted on the as-cast actuators to observe their morphology. A LEO 1550 Schottky field emission SEM was used to analyze the gold-coated film surfaces. Fourier transform infrared spectroscopy and Raman spectroscopy were conducted on the actuator for determining molecular structure of the sample. A Nicolet Model Magna 760 FTIR spectrometer with a Thermo Spectra-Tech Infinity Reflchromat 32X lens, and a Nicolet Almega dispersive Raman spectrometer with a 785-nm laser source were used for analysis.

**Actuator testing**

**Acetone sensitivity testing**

100 ml of solutions were prepared in a 400 ml beaker covered with parafilm with the acetone to water ratio of 10/90,
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between the straight line connecting the fixed end and the original position of the free end of the strip, and the line connecting the fixed end and the final position of the free end of the strip.

**Results and discussion**

The headspace concentrations of acetone and alcohols in 400-ml beaker obtained from Equation 1 are shown in Tables 1 and 2. The concentration increases linearly with increased volume of acetone.

**Chemomechanical behavior of PANI–CA in acetone**

Figure 4 shows the time lapse of bending-recovery movement of the PANI–CA strip in acetone headspace in a 400-ml beaker containing 100 ml of acetone. As the strip is inserted into the headspace, it starts bending until it reaches the maximum bending angle in about 55 s. Then, the strip is removed from the headspace and is put in the air. The strip starts unbending until it reaches its initial state in about 50 s.

**Sensitivity test result**

Figure 5 shows the result of the sensitivity test of the PANI/CA strips to acetone. As the diagram shows, the actuator has strong sensitivity to acetone and the sensitivity trend shows almost a linear correlation between headspace concentration and maximum bending angle. The relative sensor sensitivities are represented by the slopes of the linear regression fit to the actuator response which is about 0.021 degree/ppm. This diagram shows that the PANI–CA actuator could be good sensor of the acetone as it has different sensitivity to different amount of the acetone.

**Selectivity test result**

Figure 6 shows the result of the selectivity test of the PANI/CA composite to acetone among ethanol, 1-butanol, and 2-propanol. As this figure shows, PANI–CA actuator has different maximum bending angle in different organic vapors. The PANI–CA actuator showed the highest sensitivity to acetone. Besides, it has a slight response to ethanol and almost negligible sensitivity to 1-butanol and 2-propanol.

**Table 1** Headspace concentration for varying volumes of acetone samples

| Liquid acetone in 100-ml solution (ml) | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |
|--------------------------------------|----|----|----|----|----|----|----|----|----|----|
| Headspace concentration of acetone (ppm) | 261 | 522 | 783 | 1044 | 1305 | 1566 | 1827 | 2088 | 2349 | 2610 |

**Table 2** Headspace concentration for the same volumes of acetone, ethanol, 1-Butanol, and 2-propanol

| Chemical compound | Liquid volume in 100-ml solution (ml) | Headspace concentration of chemical compound (ppm) |
|-------------------|--------------------------------------|-----------------------------------------------|
| Acetone           | 50                                   | 1305                                          |
| Ethanol           | 50                                   | 300                                           |
| 1-butanol         | 50                                   | 160                                           |
| 2-propanol        | 50                                   | 130                                           |
Characterization result

Figure 4 Sensing response (bending-recovery movement time lapse) for PANI–CA composite in headspace of the 400-ml beaker containing 100 ml of acetone

Figure 5 Maximum bending angle of actuator vs. headspace concentration of acetone

Figure 6 Relative selectivity of the PANI–CA actuator to different gases

The main feature observed is the distribution and size of asperities on the actuators’ top surface that is about 20 μm (top figure). The back side of the strips (bottom figure) is more flat, presumably because it was resting on the glass slide when forming.
are indicating PANI and CA are interconnecting and formed the composite. Comparing the results of the FTIR analysis of the sample when it is exposed to acetone versus when it’s not exposed, an increase in baseline is noticed when the films are introduced to acetone. Also a peak shift toward higher wave-numbers is noticed when the films are subjected to acetone. The shift can be attributed to surface strains present due to bending of the sample in the presence of acetone. No changes in the chemistry of the composite films were noticed.

**Mechanism**

There have been two major studies on chemomechanical behavior of conducting polymers. The prevalent mechanism for chemomechanical activity of polymers stems from the study of polypyrrole films. In that work, one side of the film/strip was exposed to vapors from a tissue containing an adsorbate in a distance of about 2 mm, and the film bended. The mechanism for this bending motion is based on a reversible van der Waals adsorption of vapors onto the film. As a result of the adsorption of the vapor onto one surface of the actuator, the surface expands and thus bends.

Another study has been conducted on chemomechanical behavior of polyaniline asymmetric membranes. In that study, the films were exposed to acetone vapor and the response was monitored using Raman and FTIR spectroscopy. The results showed a peak shift towards higher wave-numbers when the films were exposed to acetone, which is attributed to surface strains due to bending of the sample. No changes in the chemistry of the composite films were noticed.
study, polyaniline actuator was exposed to organic vapor from both sides, but the PANI structure was not symmetric. One side of the PANI was more porous and the other side was denser. As a result, after absorption of organic vapor, the dense side had a larger volume expansion than the more porous side and this difference caused a bending toward the porous side that is recovered by desorption of organic vapor in the air. However, these mechanisms could not explain the bending-recovery movement of PANI–CA actuator in our experiment.

In our work, the PANI–CA composites fabricated by solution-casting method have symmetric structure in terms of porosity; moreover, the actuator is exposed to organic vapors from both sides. So, there is no morphological asymmetry that would force the actuator to bend to one side. Once the sample is introduced to acetone, it bends reversibly and reproducibly. This is likely the result of strong polar interactions between acetone and C–N+ bond. As the bond stretches, it results in bending of the composite films. The relative gas sensitivity has to do with the dipole moment of the gas. Acetone having almost double the dipole moment of that for alcohols, results in stronger interactions and more pronounced bending of PANI.

Conclusion
We have developed a new chemomechanical actuator based on PANI–CA composite which was prepared by solution-casting method. This composite undergoes bending/unbending movement as a result of sorption and desorption of organic vapors such as acetone and alcohols, and this movement is completely dependent on the type of organic vapor used. PANI–CA was tested for its sensitivity to acetone by exposing it to different headspace concentration of acetone and the results show that the maximum bending angle of actuator is different for different concentration of acetone. Its selectivity was examined by comparing the maximum bending angle of the actuator in the headspace of the 50 ml/50 ml solution of the four chemical compounds, and the result showed that this actuator has a lot more sensitivity to acetone than alcohols. The mechanism for this bending-recovery movement is based on stretching of C–N+ bond which is due to the strong polar interactions between acetone and C–N+. As this bond stretches, it results in bending of the films. This actuator has the potential to be used for a new non-invasive glucose monitoring technology based on PANI–CA wearable skin acetone sensors. Further experiments need to be conducted to determine the cytotoxicity and other properties of this actuator before it can be used for this reason.

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