Low-temperature solution processable electrodes for piezoelectric sensors applications

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Abstract

Piezoelectric thin-film sensors are suitable for a wide range of applications from physiological measurements to industrial monitoring systems. The use of flexible materials in combination with high-throughput printing technologies enables cost-effective manufacturing of custom-designed, highly integratable piezoelectric sensors. This type of sensor can, for instance, improve industrial process control or enable the embedding of ubiquitous sensors in our living environment to improve quality of life. Here, we discuss the benefits, challenges and potential applications of piezoelectric thin-film sensors. The piezoelectric sensor elements are fabricated by printing electrodes on both sides of unmetallized polyvinylidene fluoride film.

We show that materials which are solution processable in low temperatures, biocompatible and environmental friendly are suitable for use as electrode materials in piezoelectric sensors.

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1. Introduction

Printing methods have shown their applicability for low-cost manufacturing of flexible, light-weight and large-area electronic products1). A wide selection of solution processable materials has become available and they can be used for a variety of applications, such as flexible displays, RFID antennas, batteries and solar cells2). Use of printing technologies in combination with low-temperature processable, biocompatible and environmentally friendly materials, such as conducting polymers or carbon-based nanomaterials, makes the fabrication process safer and less energy-consuming than conventional manufacturing and the components potentially disposable. This all brings us closer to the dream about green electronics3).

Flexible piezoelectric thin-film sensors can be used in a wide range of applications, such as physiological measurements, medical applications or industrial monitoring systems. For example in healthcare applications, vital signals such as heart and respiration rate can be detected4). This type of sensor can be integrated into clothing5) or into the legs of a chair or a bed6). Also, a PVDF sensor matrix enables the measuring of normal and shear stresses, which can be used to detect the pressure distribution between the foot and the shoe in order to prevent the development of pressure ulcers7). A second application field is industrial process control8-10), where flexible and transparent sensors could be integrated for locally monitoring the steps of an industrial process. This type of sensor is also suitable for automotive and traffic management applications. A third area would be embedded piezo-elements for smart environments, e.g. floor sensor, which would suit as well for healthcare purposes than other monitoring/supervising purposes. Thus, there is a need for custom-made, application-specific piezoelectric sensors, which are suitable for cost-effective, large-scale manufacturing and where the electrode materials and their fabrication processes are compatible with the functional substrate material. Further, the flexibility and transparency would be beneficial for the sensor.

Conventional piezoelectric materials are mostly ceramics, but polymeric piezoelectric materials have also been introduced. Fully metallized polarized piezoelectric films are commercially available8), but for application usage, there is a need for electrode patterning. This reduces production speed and requires significant resources to cope with harsh chemicals used in the subtractive patterning process. Printing, as a simple, cost-effective, mass production compatible, purely additive manufacturing method, where material and energy losses are minimized, can be a competitive approach. Using printing techniques, a sensor design and geometry can be tailored by customer needs, e.g. from miniaturized to large area sensors and matrices. Printing processes can be done at low temperatures using materials which do not require high temperature treatments. With a right selection of materials the manufactured devices are environmentally friendly and/or disposable.

In our approach, we use a transparent, thin and flexible piezoelectric polymer film as both the sensing material and the substrate on which the electrodes are printed. Solution processable materials such as carbon-based nanomaterials and conducting polymers or their composites are used as electrodes in the sensors. The fabrication of piezoelectric sensors by using printed electrodes on a polyvinylidene fluoride (PVDF) film sensor and their use in physiological heart rate and respiration measurements were recently demonstrated by the authors4).

2. Materials and Methods

Polyvinylidene fluoride (PVDF) in its polarized β-crystalline form is a piezoelectric plastic material that generates an electric charge when mechanically deformed8, 11). Low-temperature curable electrodes were printed on both sides of unmetallized 28-μm-thick PVDF film (purchased from Measurement Specialities Inc.), which was used as a functional substrate for the sensors. The printing of the electrodes was done using a laboratory scale flexographic press (RK Flexiproof 100) and a bar coater (CX202 motorized bar coater).

Various solution processable materials, for instance, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), and a composite of carbon nanotubes (CNT) and carboxymethyl cellulose (CMC) were used.

The CNT:CMC composite ink was fabricated by mixing the CNT and the CMC by ultrasonication, which leads to wrapping of cellulose molecules along the nanotubes. The molecular structures are shown in Fig. 1. This method enables the fabrication of highly viscous printable inks. The viscosity of the CNT:CMC ink used in this study is ca. 0.07 Pa·s, which makes it suitable for e.g. gravure and flexographic printing.

The PEDOT:PSS conducting polymer ink formulations based on commercial product

(Clevios™ from H.C. Starck) were prepared in-house. The PEDOT:PSS ink was formulated by adding a certain amount of PVP to increase the solution viscosity to a suitable range4). The molecular structures are shown in Fig. 2.

For comparison, resistive carbon ink (purchased from Creative Materials) and silver flake ink (Electrodag PM-460A purchased from Henkel) were used as printed reference materials for sensors. Also metallized PVDF films were used as reference sensors.

The sheet resistance of printed electrodes were measured using a four-probe measurement setup made in-house and a multimeter (Keithley 2425 100 W SourceMeter). The sensitivity of the piezoelectric sensor was measured using a setup described elsewhere in more detail7). The schematic view of the setup is presented in Fig. 3. Briefly, a sinusoidal excitation is applied to the shaker and the normal force sensitivity is determined from the data obtained from a dynamic force sensor and a charge amplifier. Materials and fabrication methods are reported in more detail in Ref. 4.

3. Results and Discussion

3.1 Measurements with the piezoelectric sensors

DC sheet resistances of the printed electrodes and sensitivities of the sensor elements were measured. Sheet resistance vs. sensor sensitivity are shown in the Fig. 4. One can notice that the sheet resistance varied from 10^{-1} to 10^{6} Ω/□ while the sensitivity varied only from 23 to 29 pC/N. The variance in sensitivity is most likely due to poor electrical contact with the electrodes in the measurements. The sheet resistance is important only if piezoelectric resonance measurements are used.4)

It was observed that the sheet resistance of the CNT:CMC electrodes was in the order of 10 kΩ/□ even if it has been shown that an individual CNT can carry currents as high as a few mA12). This can be understood, since the contact resistances between crossing tubes are relatively high, which limits the conductivity of randomly oriented CNT networks13) and also because 50 % of the solid material content of the CNT:CMC composite is cellulose, which is an insulator.

Evaporated metal electrodes as well as commercially available sensor elements were used as reference sensors. Printed sensors show sensitivities comparable to commercial reference sensors. The sensing capability of printed sensors was quite insensitive to the sheet resistance of the electrodes.[4)]

3.2 Improvement of printability

There are several aspects which should be considered when thinking about replacing conventional electronics manufacturing methods by printing. One has to understand how the printing affects materials, interfaces and the device or circuit performance. Different aspects which have to be studied are (1) the printability of electronic ink formulations, (2) materials compatibility and interfacial properties and (3) the fabrication and characterization of printed materials and devices.

Initially, the printability of the water-based CNT:CMC ink was poor due to bad spreading onto the substrate. The spreading was improved by adding isopropanol to the CNT:CMC ink (final ratio IPA:H_2O was ~1:3), which lowered the surface tension of the ink. Printability was further improved by treating a polyethylene terephthalate (PET) substrate with UV/ozone for 5 min prior to printing (see Fig. 5). PET films were used instead of PVDF for initial printability testing when some changes to the ink formulations are made since the PVDF film is quite expensive.

3.3 Vital signal measurements

In medical applications, the vital signals such as the heart and respiration rate can be measured with various ways. We have recently demonstrated that these measurements can be done using our printed sensors. During the measurement, a patient was lying on a sofa while the sensor was placed between the pillows (see Fig. 6). Sensors were wired and placed to the plastic folder and a pillow was placed between the patient and the sensors. Data was amplified with a charge amplifier circuit and collected to the measurement computer. Cardiac (heart rate) and respiration signals recorded with the printed sensors showed the same results as the reference sensors (i.e. ECG and thermistor). Using this kind of measurement setup, the physiological signals were easily detected with all measured sensors containing different electrode materials (for physiological measurements results see Ref. 4). The measurement setup could be further improved by using a sensor matrix integrated into a sheet or mattress.

3.4 Other applications for piezoelectric elements

There are plenty of other potential application areas for flexible, transparent piezoelectric elements. One novel application area for the PVDF sensor elements would be the use as a keyboard: a piezoelectric sensor matrix could work as a flexible, transparent keyboard which could be embedded e.g. into a window.

PVDF has been found to be a biocompatible material14). This makes the use of printed PVDF sensors favourable for interesting fields of application i.e. biomedical and physiological applications. Instead of being used as a sensor where the mechanical force is measured, they can act as an actuator by applying an electric signal to the electrodes. For instance, PVDF has been used to promote neurite growth in rat spinal cord neurons15).

4. Conclusions

We demonstrated that alternative, printable electrode materials are compatible with temperature-sensitive functional substrates. We have fabricated flexible piezoelectric sensor elements using printing methods. Electrodes were printed on a temperature sensitive piezoelectric PVDF film. Solution processable materials, e.g. CNT-cellulose and PEDOT:PSS were used. Measured sensor sensitivities were comparable to commercial sensors. Heart and respiration rate measurements were demonstrated. All fabricated sensors were able to detect physiological signals from a patient. There are several application areas where this type of sensor can be applied. Embedding of ubiquitous sensors in our living environment has potential for improving the common welfare of humans.

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Figure captions

Figure 1. Molecular structures of (a) the multi-walled carbon nanotubes and (b) the carboxymethyl cellulose, which were mixed to formulate the printable CNT:CMC composite ink.

Figure 2. Molecular structures of (a) the PEDOT:PSS and (b) the PVP which are used in the conducting polymer ink formulation.

Figure 3. The schematic view of the measurement setup used for the determination of sensitivity of the PVDF sensors.

Figure 4. The measured sensitivities of the sensor elements versus sheet resistances of the electrodes. Closed (•) and open (o) symbols on the same sensitivity value describe the sheet resistances from the different sides of the PVDF film. In the legend, first and second symbols refer to sensors with CNT:CMC ink electrodes printed using bar coating and flexographic press, respectively. Third and fourth symbols refer to sensors printed using flexographic press with PEDOT:PSS and carbon ink electrodes, respectively. The fifth symbol refers to metallized sensors, which are either supplied by the manufacturer or metallized in-house by e-beam evaporation. The last symbol refers to silver-flake ink sensor where the electrodes are bar-coated. Data from the Supplementary Material of Ref. 4.

Figure 5. Examples of (a) poor and (b) good printability case when using the CNT:CMC ink.

Figure 6. The setup used for physiological heart and respiration rate measurements.

Figure 1

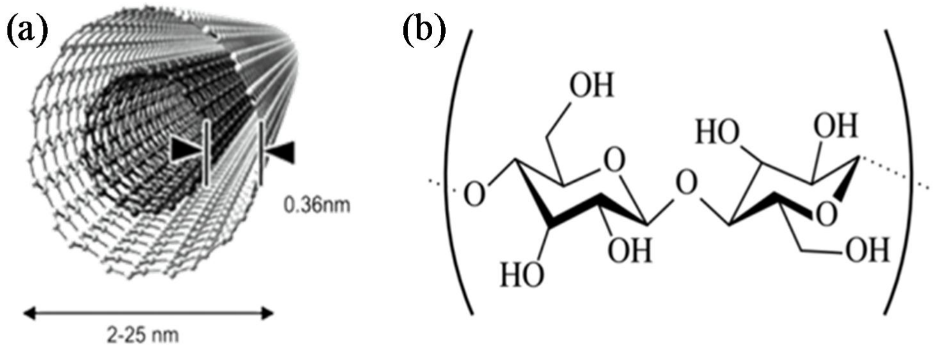


Figure 2

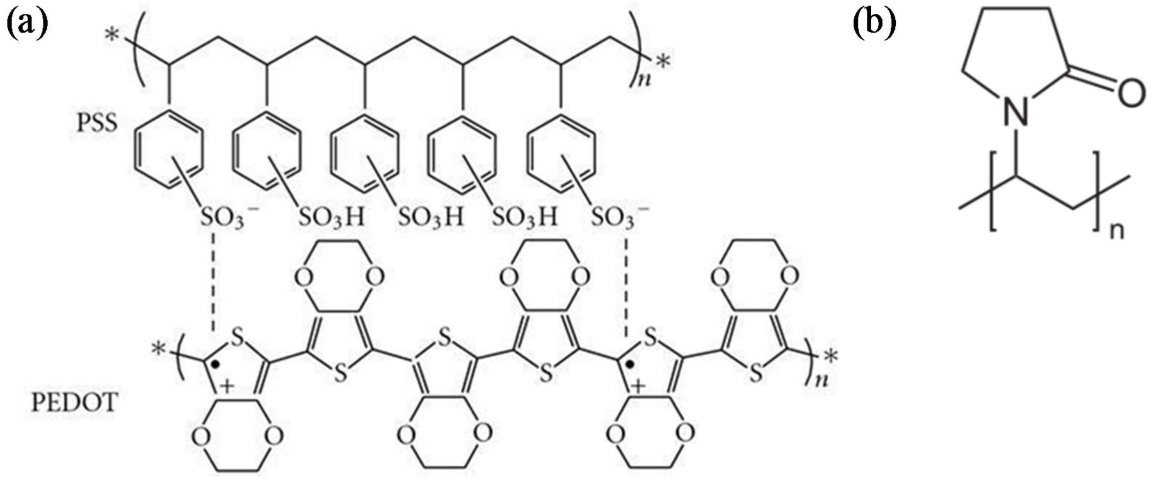
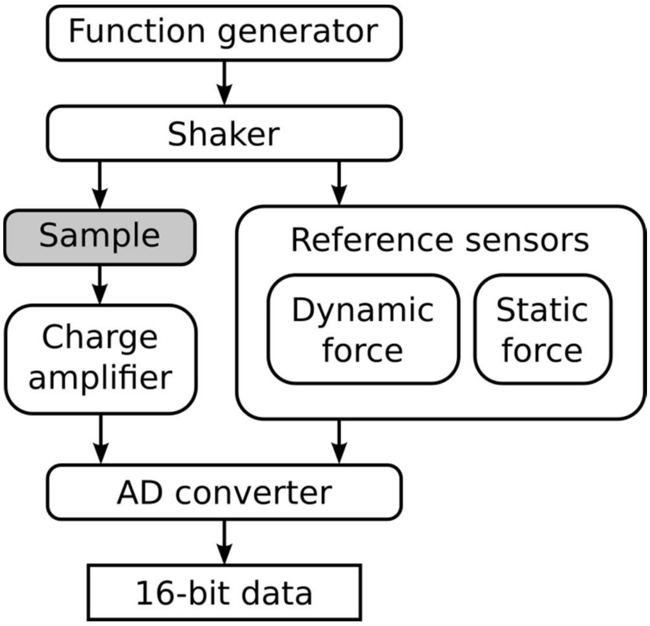


Figure 3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Shaker
Sample
Reference sensors
Dynamic force
Static force
Charge amplifier
AD converter
16-bit data

Figure 4

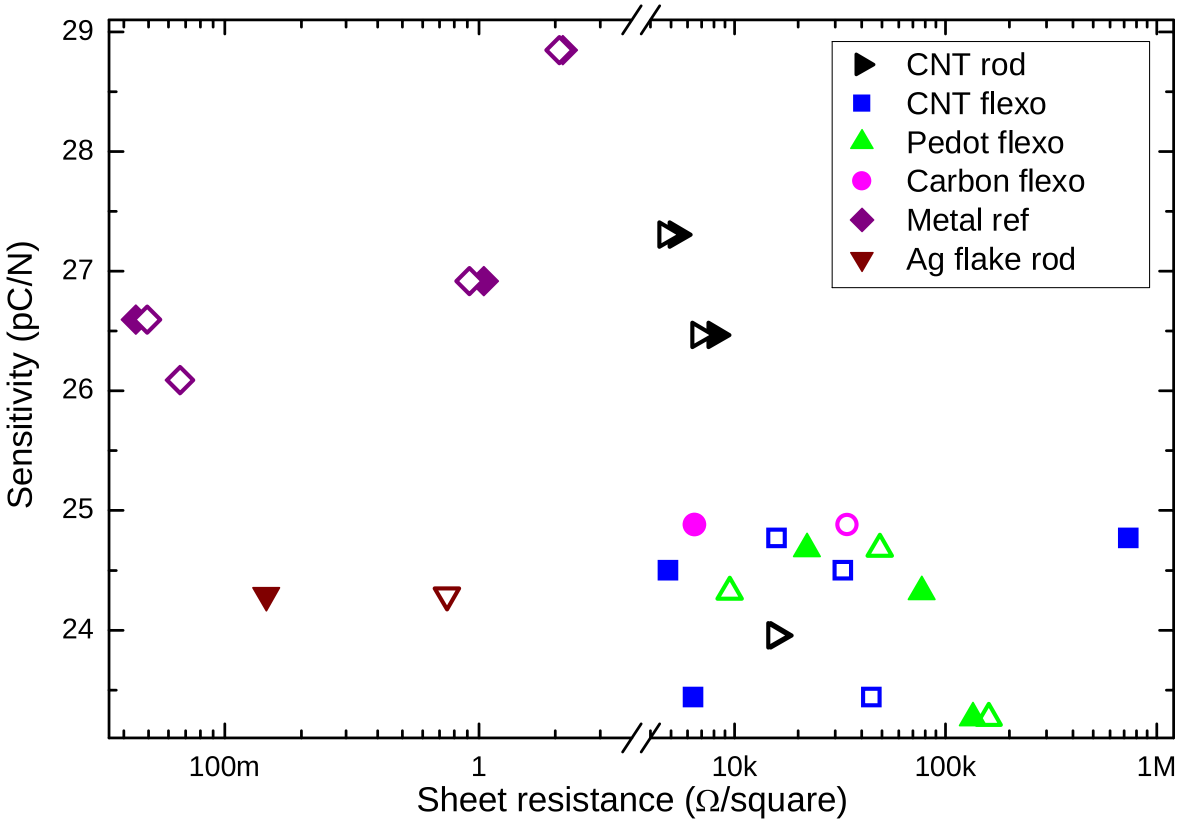
Sensitivity (pC/N)
29
28
27
26
25
24
Sheet resistance (Ω/square)
100m
1
10k
100k
1M
CNT rod
CNT flexo
Pedot flexo
Carbon flexo
Metal ref
Ag flake rod

Figure 5

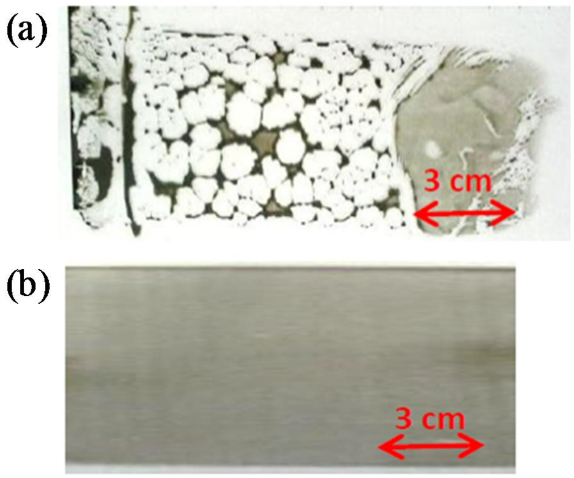

Figure 6