Flexible thin films based on nanostructured polymeric composites as ultra sensitive piezoresistive materials and their applications

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ABSTRACT

In nanostructured polymeric composite thin films it is possible to translate elastic elongations of the film into reversible nanoscale deformations of the soft organic-crystal components, leading to films with extreme sensitivity to strain changes with durable, fast, and completely reversible responses. A first generation of prototypes, demonstrate that these sensors are highly promising for a wide range of applications.

Keywords: nanostructured composite materials, flexible electronics, organic electronics, piezoresistive materials, thin films

The development of intelligent materials that can respond to the application of an external stimulus is of major interest for the fabrication of artificial sensing devices able to sense and transmit information about the physical, chemical and/or biological changes produced in our environment [1, 2]. In addition, if these materials can be deposited or integrated on flexible and transparent substrates and processed employing low-cost techniques their appeal is greatly increased [3, 4]. In this context, organic materials, which have already shown a huge potential in a wide range of (opto)electronic applications, can play a crucial role [5–7]. Here, we show that by using bilayer (BL) films, composed of a polymeric matrix with a toplayer formed by a crystalline network of a conducting molecular charge-transfer salt, it is possible to translate micrometer-scale elastic elongations of the film into reversible deformations of the soft organic charge-transfer salt crystals at the nanometer scale. These multiple-length-scale movements are responsible for the ultrasensitive piezoresistive properties of the BL films that are extremely sensitive to strain changes with durable, fast, and completely reversible responses [8]. Such BL films have a sensitivity that is one order of magnitude larger than the most commonly used electromechanical sensors [9]. In addition, a few proof-of-concept experiments with simple prototypes are also reported demonstrating that these flexible, low-weight, transparent and soft composites are very attractive as a new generation of durable and low-cost all-organic strain sensors, being highly promising for a wide range of applications in areas such as biomedicine, human health care, smart textiles, robotics, and in the industry of automotive, aeronautic, and space components.

Much effort has recently been devoted to fabricating conducting polymeric films and devices, in which electrotransport properties remain unchanged when the devices are bent [10, 11]. However, the preparation of light and flexible organic materials that respond rapidly and reversibly after being submitted to small stresses also promises great opportunities in the field of strain sensors. It is well known that single crystals of molecular conductors, consisting of ion-radical salts (IRSs), typically based on tetrathiafulvalene (TTF) derivatives, exhibit striking conducting properties and that such properties are affected under applied pressure. This fact is due to the softness of such crystalline materials that permits the large modification of intermolecular distances by moderate pressures and, as a consequence, the control of their electronic band structures. In order to exploit the conducting properties of TTF-based IRS in a technological feasible way, composite BL films based on polycarbonate (PC) with a conducting surface layer of crystalline halide salts of TTF derivatives, like bis-(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) or bis-(ethylenethio)tetrathiafulvalene (BET-TTF), have been developed [12, 13]. These BL films combine the transport properties of single crystals benefiting from the processability, transparency, and flexibility of classical polymers. These results prompted us to investigate the response of such BL films to strain changes in order to use them as intelligent materials for all-organic sensing devices. BL films based on a poly-(bisphenol-A-carbonate) (polycarbonate, PC) matrix containing a conducting toplayer of microcrystals of α-(BEDT-TTF)$_2$I$_3$ (**F1**), β-(BEDT-TTF)$_2$I$_3$ (**F2**) and β-(BET-TTF)$_2$I$_3$ (**F3**), were prepared as previously reported [12, 13].

All the BL films were fully characterized by electronic paramagnetic resonance (EPR) and UV-vis-NIR (NIRnear IR) spectroscopy, scanning electron microscopy (SEM), and X-ray diffraction (XRD) analysis [14]. Such characterizations unambiguously revealed the phases of the IRSs in the **F1**-**F3** films, which differ in the packing motif of the TTF molecules modifying the electronic band structures of the IRSs and, thereby, influencing the resulting transport properties. SEM images of the conducting microcrystalline top-layers of **F1**-**F3** films show
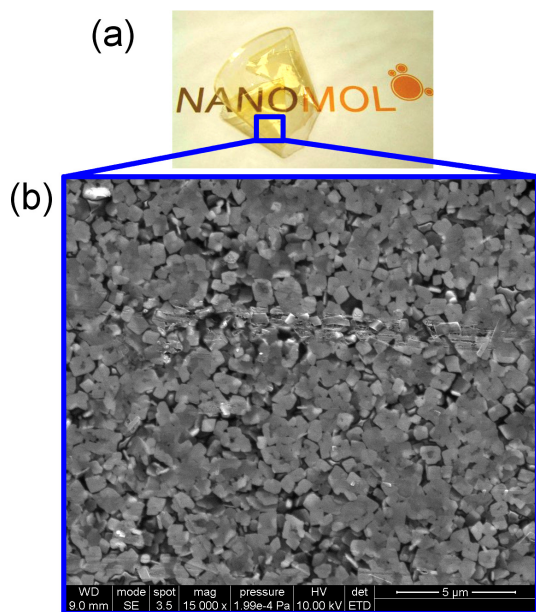
Figure 1: Nanostructured polymeric composite. (a) Photograph of **F2** showing its transparency and flexibility. (b) SEM image of the covering layer of **F2** exibiting the crystalline network of the topmost layer of BL-films.

the presence of well-connected rod-like crystals that are randomly oriented with their longer dimensions parallel to the film surface. The X-ray analysis indicates in all three cases the presence of only (00l) reflections, demonstrating that the crystals of the TTF salts are randomly oriented with the c-axis (nearly parallel to c*) being mainly perpendicular to the film surface and, consequently, the molecular conducting layers of the crystals are parallel to the surface. Such crystal orientations, together with the high-quality contacts between the crystals and the film-coverage density, explain the similarity of their conducting properties to those of the corresponding single crystals. The optical-transmission spectra of the films **F3** shows a transmission above 30% between 380 and 600 nm, while in films **F1** and **F2** the transmission increases from 15-20% to 50% in the range 500-600 nm. In the rest of the visible range the transmission reaches values of up to 85% for **F1**, 70% for **F2**, and 50% for **F3**. The transparency of **F1-F2** films in the 600-800nm region compares well with that of commonly used transparent conducting oxides (i.e., indium-tinoxide (ITO)).

All films were examined by four probe direct current (dc) resistance measurements, exhibiting conductivity values at room-temperature between 0.5 - 5.0 S/cm. Representative averaged values for freshly obtained films were 1.4 ± 0.1, 3.3 ± 0.1, and 0.7 ± 0.1 S/cm for **F1**, **F2** and **F3**, respectively. Such averaged conductivity values remained constant for periods of several years for **F1** and **F2** films when stored at ambient conditions, revealing

their exceptionally high stability. The stability of the **F3** film is somewhat lower, since its resistance values remained constant only for a period of a few months.

The effect of monoaxial strain on the resistance of the films was studied subjecting a small piece of the film with a gauge area of ca. 4.0mm x 2.5mm to multicyclic monoaxial deformations; as it is schematically represented in Fig. 2(a). In this configuration, the strain is applied parallel to the conducting crystallographic ab-planes of the randomly oriented microcrystals of the top layer of the composite films. Fig. 2(b) shows the resistance dependence of **F2** upon application of four cycles of monoaxial elongations up to a maximum elongation of 20 μm This corresponds to a relative strain (ϵ) value of 0.005 (i.e., 0.5%); where $\epsilon = (L-L_0)/L_0$ with L_0 and L the lengths of the films without and under elongation, respectively. This plot reveals that the film resistance differences ($\Delta R/R_0$) linearly increases with the film deformations ($\Delta L/L_0$). Here R_0 is the sample resistance at room temperature without applying any strain and R is the resistance of the strained sample. The influence of the maximum applied strain as well as of the strain rates on the conductivity responses were also investigated for all films concluding that their response is fully reversible at relative strain values lower than 1%. Fig. 2(c) clearly shows the linear dependency of the resistance on the elongation for all studied **F1**-**F3** films in the applied range of deformation. For comparison purposes, we have also plotted in this graph a typical electrical response of a conventional foil-strain gauge based on a CuNi alloy,[9] illustrating that the BL-films are much more sensitive than conventional strain gauges. The gauge factors (k), calculated as the ratio between the relative resistance change and the relative strain value, $k=(\Delta R/R_0)/(\Delta L/L_0) = (\Delta R/R_0)/\epsilon$, were found to be as high as 10 ± 2, 18 ± 2, and 12 ± 2 for **F1**, **F2**, and **F3** films, respectively [14]. Another indicative figure that shows up the extremely high sensitivity of such films to uniaxial deformations is given by the minimum value of $10^{-3}\%$ of the relative strain that they are able to sense, which is well below those of many conventional strain gauges but also of recently shown strain gauges based on Pt-coated polymer nanofibres [15].

An important advantage of BL-films compared to metal-alloy based strain gauges arises due to the fact that such films are produced employing a soft and flexible polymeric matrix as substrate and a topmost conducting network of crystals which makes cutting of custom shapes and sizes suitable. Moreover, it has been shown that custom pattern with a resolution of about 10 μm in BL-films can be obtained by directly writing on the organic conducting surface using a local heat source such as a laser beam [16].

In order to test practical applications with the reported BL film, a series of prototype devices were de-
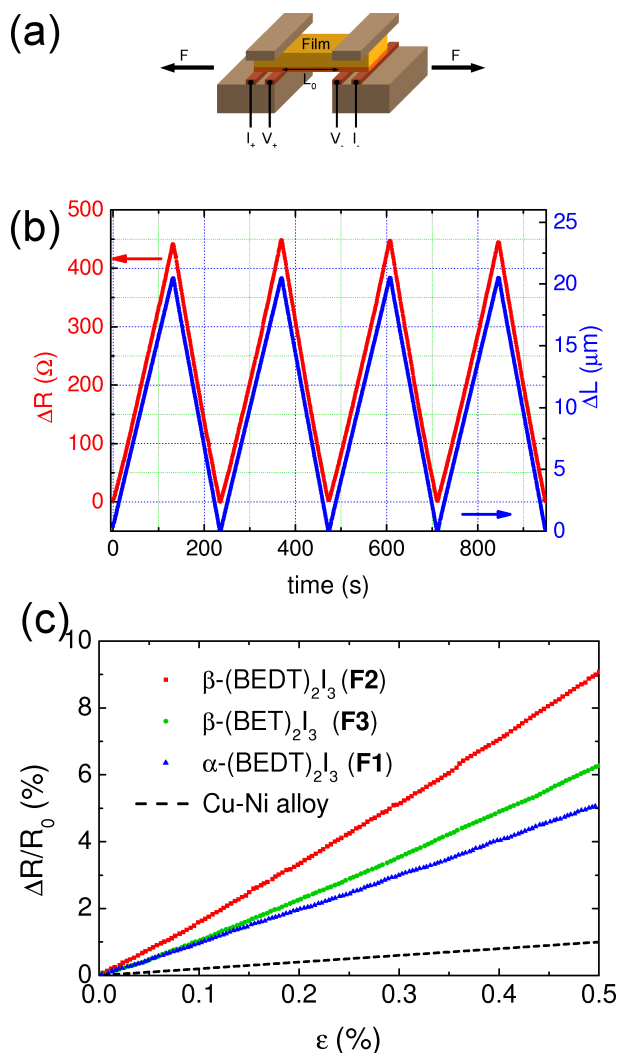
Figure 2: Studies on the changes in the electrical resistance for **F2** upon application of monoaxial stress. (a) Schematic representation of the setup employed to study of the influence of monoaxial strain on the resistance of the films. (b) Resistance change as a function of time for **F2** with $R_0 = 4.8$ kΩ upon application of 4 cycles of 20-μm monoaxial elongations. (c) Linear dependence of the relative resistance change of films with respect to relative strain ϵ applied. Extracted gauge factors k = 10, 18 and 12, for **F1**, **F2** and **F3**, respectively. A resistance-strain curve for a Cu-Ni alloy based strain gauge is shown for comparison (Figures adapted from [14])

veloped at (http://www.icmab.es/nanomol/technology-offer/plastic-electronic-sensors). A first example in this respect is a device to monitor the persons breathing rhythm. As shown in Fig. 3, the breathing movement of a person resulted in an oscillating resistance curve that can be easily recorded and analyzed. BL-film strain sensors can also be employed to detect very small pressure changes by placing the BL film in a diaphragm configuration glued onto a hole of a spherical container and exposing it to small changes of pressure through an air injection inside the container. Due to the flexibility and high sensitivity of the film, it is possible to detect very small pressure changes of the order of just a few mbar with a very large resistance response. The resistance of the BL film in the range 0-100 mbar linearly increases with a rate of 45% bar^{-1}. This range of pressure sensitivity makes these devices very promising for biomedical applications such as the detection of tissue movements. As a proof-of-concept experiment a prototype, composed of two rigid rings with a disc of an **F3** film in between a diaphragm configuration was designed to register the blood-pressure pulses of a person. The film resistance, which is influenced by the blood pressure, is plotted versus time and, thus, the pulse frequency as well as its profile can be extracted and analyzed. Recently, also the integration of polycarbonate films metalized with the highly strain sensitive β-(BEDT-TTF)$_2$I$_3$ in a polyester textile was reported, demonstrating that the strain sensing properties of this unique organic molecular metal can be completely transferred to the fabric exhibiting the same gauge factor for both directions, warp and weft, measured in this smart textile [17]. A highly promising approach of a contact lens sensor (CLS) based on BL-films for monitoring the intraocular pressure (IOP) variations in a non-invasive way has been developed. The designed CLSs are biocompatible permitting to transmit the changes in cornea curvature induced by the IOP variations, directly to the flexible conducting polymeric sensor embedded in the CL. The electrical response of the CLS to pressure changes reveals a high linearity as well as a good reproducibility having the proper sensitivity to perform continuous monitoring of IOP [18]. This development is expected to have a strong impact on human health care making an early diagnosis of the Glaucoma disease by the CLS possible. For this new sensor generation aiming at biomedical applications and human health care hard wire setups are a strong limitation and not convenient, a series of portable prototypes of strain sensors including wireless data transmission was therefore developed [19].
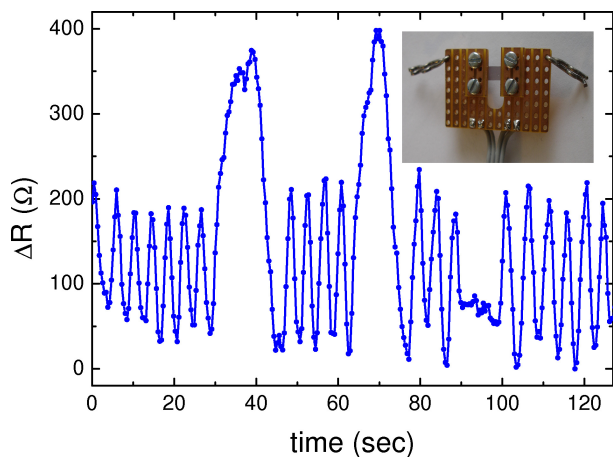
Figure 3: First generation prototype developed to monitor the change of resistance with time obtained for a device designed to measure a persons breathing rhythm. The two larger increasing resistance values and the relatively long time flat period between the oscillations correspond to periods of forced inspirations and of holding breath, respectively. (inset) Photo of the device fabricated by fixing a piece of **F3** on a springy plastic u-shaped plate (Figure adapted from [14]).

In conclusion, BL films make the fusion of the striking piezoresistive properties of organic molecular conductors with the flexibility and process-ability of classical polymers feasible leading to a ultrasensitive piezoresistive composite able to detect multiple-length-scale movements. These BL films offer great promises as strain sensors for a wide range of applications due to their fast responses, high sensitivity and stability, and large durability. Moreover, such flexible, transparent, and lightweight soft composite materials benefit from the fact that they can be produced at low cost and that their conducting properties can be chemically tuned. Thus, BL-film sensors are very attractive as a new generation of low-cost all-organic piezoresistive materials and are expected to have a strong impact in areas such as biomedicine, human health care, smart textiles, robotics, and in the industry of automotive, aeronautic, and space components.

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