

Stretchable composite monolayer electrodes for low voltage dielectric elastomer actuators

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ABSTRACT

In this work, a Multiwalled Carbon Nanotube/poly(alkylthiophene) (MWCNT/PT) composite is developed as the electrodes for dielectric elastomer actuators (DEAs) using the Langmuir-Schaefer (LS) method. These composites form stable monolayers at the air-water interface that can then be LS transferred onto a poly(dimethylsiloxane) (PDMS) elastomer membrane. The monolayer electrode remains conductive up to 100% uniaxial strain. We present a method to fabricate DEAs using the LS transferred electrodes. By using a mask during the transfer step, the electrodes can be patterned with better than 200 μm resolution on both sides of a 1.4 μm-thick pre-stretched PDMS membrane to produce an ultra-low voltage DEA. The DEA generates 4.0% linear strain at an actuation voltage of 100 V, an order of magnitude lower than the typical DEA operating voltage.

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1. Introduction

Soft actuators are required when one wishes to integrate active motion or deformation control in compliant or stretchable objects. Soft actuators are thus used in a broad range of fields where the system must be both soft yet capable of actively changing shape, such as soft robotics [1,2], tunable optics [3,4], and compliant grippers [5,6]. Dielectric elastomer actuators (DEAs) are a promising soft actuator technology due to their high energy density [7], large deformation strain [8], and fast response [3]. A DEA consists of a dielectric elastomer (DE) (usually silicone [9] or acrylic [7,10]), sandwiched between two compliant electrodes. When a potential difference is applied between such electrodes, the DE is squeezed in thickness and expands in plane [7]. For deformations of less than approximately 10% (depending on materials and pre-stretch), the in-plane strain S_x is given by [11]:

$$S_x = \varepsilon \frac{E^2}{2Y_m} = \frac{1}{2} \frac{\varepsilon}{Y_m t_m^2} V^2 \quad (1)$$

where ε is the dielectric permittivity of the DE membrane, Y_m is the Young's modulus of the DE membrane, E is the electric field

between the two electrodes, V is the applied voltage, and t_m is the DE membrane thickness.

The electrodes used for DEAs are generally assumed not to contribute to the stiffness of the devices. This has been the case for many DEAs fabricated using carbon grease electrodes on acrylic films of thickness several tens of μm. The electrode stiffness can only be ignored when the following inequality is respected [12]:

$$Y_e t_e \ll Y_m t_m, \quad (2)$$

where Y_e is the Young's modulus of the electrode, t_e is the electrode thickness, Y_m is the Young's modulus of the DE, and t_m is the DE membrane thickness.

If Eq. (2) is not satisfied (eg, for very thin elastomer membranes, or stiff metallic electrodes), Eq. (1) must be corrected to account for the stiffening impact of the electrodes. This highlights the role of the electrode mechanical properties on the performance of DEAs.

The maximum strain of a DEA is limited by the breakdown field of the DE (more correctly, the failure mode of DEAs is an electromechanical instability [13], but the breakdown field is the key limiting factor for small strain actuator configurations). For typical elastomer thicknesses of 10 μm to 100 μm, and working near typical elastomer breakdown fields of 100–150 V/μm, DEAs require from 1 kV to 15 kV to reach maximum strain. These high operating voltages limit some possible applications of DEAs, due to the cost, size, and efficiency of high voltage electronics. Therefore, significant

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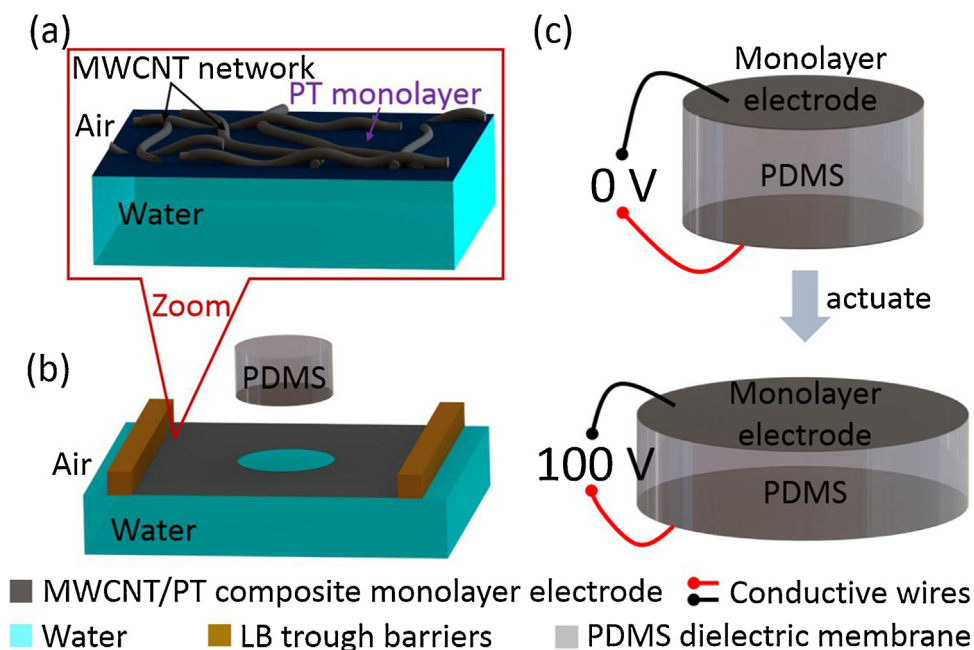


Fig. 1. Low-voltage DEAs made using Langmuir-Schaefer transferred monolayer electrodes (a) Monolayer composite electrode formed at the air-water interface: interconnected MWCNT network embedded inside an poly(alkylthiophene) (PT) monolayer. (b) Langmuir-Schaefer (LS) transfer of the composite monolayer from the air-water interface onto the PDMS dielectric membrane to make one electrode of the DEA. (c) The DEA consists of a 1.4 μm -thick silicone membrane sandwiched between two sub-100 nm thick composite monolayer electrodes.

research has been carried out to decrease the DEA operating voltage, while keeping the same actuation performance. As can be seen from Eq. (1), to maintain a given actuation strain while decreasing the voltage, either ε must be increased [9,14], or Y_m and t_m must be decreased [15,16]. The strain-to-voltage-squared ratio (S_x/V^2) metric has been used to compare the performance of DEAs with different operating voltages [16]. Decreasing the membrane thickness t_m has resulted in the highest previously reported S_x/V^2 value of 125%/kV², for a 3 μm -thick DEA generating 7.5% linear strain at 245 V [16]. Given that the electrodes are generally stiffer than the elastomer ($Y_e > Y_m$ for nearly all materials used in DEAs), when the membrane is made thinner, then the electrode thickness t_e or the electrodes stiffness Y_e must also be further decreased to maintain actuation strain, as summarized in Eq. (2).

Technologies for stretchable electrodes for DEAs, reviewed in references [12,17], include metal ion-implantation [18], transfer of SWCNT layers [19], ionogels and hydrogels [20,21], or silicones or silicone oils doped with carbon black applied by pad printing [3,16], spray-coating [10], blade casting [22] or screen-printing [23]. Those electrode fabrication methods are not suitable for DEAs with a membrane thickness of 1 μm , which would allow for DEAs working at 100 V, as the electrode thickness is either not negligible with respect to that of the DE membrane, or, for the ion-implanted method, with 50 nm thick electrodes, the electrode stiffness is much too high. A major breakthrough in low-voltage DEAs could be achieved by developing nanometer-thick and stretchable electrodes presenting a low $Y_e \cdot t_e$ value. This would allow the fabrication of DEAs with 1 μm -thick membrane with strain of over 10% at 100 V. To date, electrodes that enable DEAs with more than 1% linear actuation strain under 100 V have not been reported [16,19,22].

Langmuir technology is an appealing alternative to commonly used electrode fabrication methods as it allows the formation of nm-thick films. It is a powerful tool to transfer molecular monolayers from an air-water interface to a solid substrate. By first spreading and then compressing amphiphilic molecules at the air-water interface, one can fabricate monomolecular films, called

Langmuir monolayers, that are highly ordered over areas of several hundreds of cm^2 [24]. In addition to producing films one single molecule thick, this technique has the advantage of controlling the density of molecules in the monolayer. These Langmuir monolayers can then be transferred to a chosen substrate using the vertical Langmuir-Blodgett (LB) or horizontal Langmuir-Schaefer (LS) method [25]. Several devices including molecular sensors [26], photo-electrochemical devices [27], organic semi-conductor devices [28], and field effect transistors [29], have been fabricated using Langmuir technology. DEA electrodes based on stretchable monolayer conductors fabricated by the Langmuir technology have not yet been reported.

In this article, Langmuir technology is used to fabricate stretchable monolayer electrodes for DEAs (Fig. 1). Hydrophobic poly(alkylthiophene) (PT) and hydrophilic Multiwalled Carbon Nanotubes (MWCNT) are mixed in a solvent to form a stable amphiphilic composite dispersion. This dispersion can be spread on the water surface to form a composite electrode, in which the MWCNT network is embedded in a PT monolayer (Fig. 1a). PT, as conducting polymer, should contribute to the electronic conductivity and stabilize non-functionalized hydrophilic MWCNT at the air-water interface. Two types of PT with different linear alkyl side chains poly(3-hexylthiophene) (P3HT) and poly(3-decylthiophene) (P3DT) are studied, since it has been shown that the side chain length has a significant effect on the PT material properties. The longer this chain is (up to 12C), the smaller the Young's modulus and the electrical conductivity [30]. The MWCNT/PT composite monolayer is then transferred from the air-water interface to a poly(dimethylsiloxane) (PDMS) elastomer membrane using the LS method (Fig. 1b). The adhesion is provided by the hydrophobic affinity between the PDMS substrate and PT from the composite monolayer. The 1.4 μm -thick pre-stretched PDMS membrane is sandwiched between two LS transferred composite electrodes to make a 100 V operating DEA (Fig. 1c). The electrodes are evaluated based on their morphological, electrical and mechanical properties with regards to DEA application.

2. Experimental section

2.1. Chemicals

Regio-regular poly(3-hexylthiophene-2,5-diyl) (P3HT, CAS 156074-98-5 and purity of 99.995%), and regio-regular poly(3-decylthiophene-2,5-diyl) (P3DT, CAS 110851-65-5 and purity of 99.995%) were ordered from Sigma-Aldrich and used as received. Multiwalled Carbon Nanotubes (MWCNTs; external diameter 15–35 nm, length $\geq 10 \mu\text{m}$) were purchased from Nanothinx S.A. (Rio, Greece). Poly(acrylic acid) (PAA, 25% soln. in water, CAS 9003-01-4) was ordered from Chemie Brunschwig. Ethanol (99.9%) and chloroform (99.2%) were ordered from VWR Prolabo Chemicals. PDMS (Sylgard 186, MED-4086) and PDMS solvent (OS-2) were ordered from Dow Corning (Auburn, MI).

2.2. Fabrication of DEA electrodes using LS method

2.2.1. Polythiophene (PT) solutions

PT (P3DT or P3HT) solution (0.167 g/L) was prepared in chloroform-ethanol 9:1 v/v and then sonicated for 30 min

2.2.2. MWCNT/PT mixed solutions

PT was dissolved in a chloroform solution (0.167 g/L), then sonicated for 30 min. MWCNTs were dispersed in ethanol (20 g/L), then sonicated for 1 h. Both solutions were mixed in a volume fraction of 9 (chloroform)/1 (ethanol) and then sonicated for 5 h before being centrifuged for 15 min at 3000 rpm. The supernatant was collected and two additional centrifugations of 15 min each were performed. This process was optimized according to the optical microscopy images and the surface resistance value of the LS transferred composite MWCNT/PT monolayers as outlined in the Supplementary data (Section 1, Fig. S1 and Table S1).

2.2.3. Monolayer electrode fabrication

The monolayers were formed in a KIBRON Langmuir-Blodgett (LB) trough (MicroTroughX). An adequate solution volume was spread over an ultrapure water surface (18.2 M Ω cm Millipore Simplicity, Billerica, MA) using a micro syringe. After solvent evaporation, the monolayer was compressed at a barrier speed of 10 mm/min and the surface pressure recorded. In the following, the isotherms were presented as a function of the trough area instead of the area per monomer. The monolayer homogeneity at the air-water interface was verified in-situ by Brewster Angle Microscopy; more detail on this technique is given in the Supplementary data (Section 2) [31]. For the LS transfer, the monolayer was kept at a surface pressure of 15 mN/m and the PDMS substrate was horizontally moved towards the monolayer at 2 mm/min using a stepper motor from KIBRON. Once substrate/monolayer contact was established, the PDMS substrate was raised until the transfer was complete.

2.3. Atomic force microscopy (AFM)

100 μm -thick PDMS membranes were fabricated using the method reported by Rosset et al., [32] and used as substrates for the LS transfer of the monolayer electrode (Supplementary data, Section 3.1). The AFM images were performed using the Peak Force Tapping mode with a Dimension ICON microscope from Bruker. AFM imaging was carried out in air using ScanAsyst-air cantilevers (Bruker) with a spring constant of 0.4 Nm $^{-1}$. 10 μm \times 10 μm images were obtained with the height mode and a 256 \times 256 resolution, at a 0.5 Hz scan rate. Data processing was performed with NanoScope software version 1.40 (Bruker).

2.4. Surface resistance measurement

The monolayers LS transferred onto 100 μm -thick PDMS substrates were placed against two rectangular copper electrodes enclosing a 1 cm \times 1 cm square as active zone. The resistance was determined from the measured current with 10 V applied between the copper electrodes. A Gamry Instruments potentiostat (reference 600) was used for these measurements.

2.4.1. Surface resistance stability as a function of time

The effect of PT doping on the surface resistance stability was investigated. The transferred PT monolayers were immersed into 0.15 M FeCl $_3$ in acetonitrile for 5 min and then rinsed with acetonitrile [29]. For each type of monolayer, six individual samples were measured to obtain an average value and standard deviation.

2.4.2. Surface resistance as a function of strain

The surface resistance of monolayers LS transferred onto suspended 100 μm -thick PDMS substrates was measured for different stretching conditions. Two samples were used in each case and a speed of 1% lengthening/s was applied during stretching. The effect of sample cycling on the surface resistance was also investigated. For that, 10 stretch-release cycles (1%/s) per sample were used, with 30 s delay between each cycle.

2.5. Young's modulus measurement of monolayers

The Young's modulus of the monolayer electrode was measured by Pull test using a uniaxial tensile testing setup. By measuring the stiffening impact of the monolayer on a very soft 10 μm -thick PDMS substrate (Young's modulus of 40 kPa), the Young's modulus of the monolayer could be computed (more details on the PDMS preparation are given in Supplementary data, Section 3.2). Uniaxial cyclic stretching (20% strain) was applied to the PDMS membrane using a linear motor (UAL from Saia-Burgess) at a strain rate of 0.67%/s. The stretching direction was parallel to the 2 mm edge of the PDMS rectangle so that stretched PDMS membrane was in a pure shear stress state. During the measurement, the force and the sample elongation were simultaneously measured using a force sensor (Futek LSB200, capacity 100 mN) and the encoder of the stepper motor, thus enabling the representation of the stress-strain relationship. A LabVIEW code was written to control the motor and the force sensor for the whole experiment process.

After measuring the Young's modulus of bare PDMS membranes, the monolayer electrodes were LS transferred onto those PDMS membranes. The Young's modulus of the PDMS + electrode bilayer was determined using the same parameters as for the bare PDMS membrane. The PDMS + electrode bilayer was formed by two adherent layers with equal length and width, so the electrode Young's modulus was calculated using [33]:

$$Y_{\text{bilayer}}t_{\text{bilayer}} = Y_{\text{PDMS}}t_{\text{PDMS}} + Y_e t_e \quad (3)$$

where Y was the Young's modulus and t was the thickness.

2.6. DEAs fabrication

A 2.0 μm -thick PDMS membrane (Sylgard 186, Dow Corning) was prepared as the DE membrane of the DEA (details on the PDMS membrane fabrication are given in Supplementary data, Section 3.3). To handle and pre-stretch sub-micrometer suspended PDMS membranes, a stretchable holder was developed, made from acrylic adhesive (3 M, VHB 4905) covered with silicone transfer adhesive (Adhesive Research, ARclear 8932). Using the stretchable holder, a suspended 2.0 μm -thick PDMS membrane was released from the PET substrate, and pre-stretched equi-biaxially to 1.4 μm -thick with a linear ratio of 1.2 (Fig. 2a). The pre-stretched PDMS was fixed

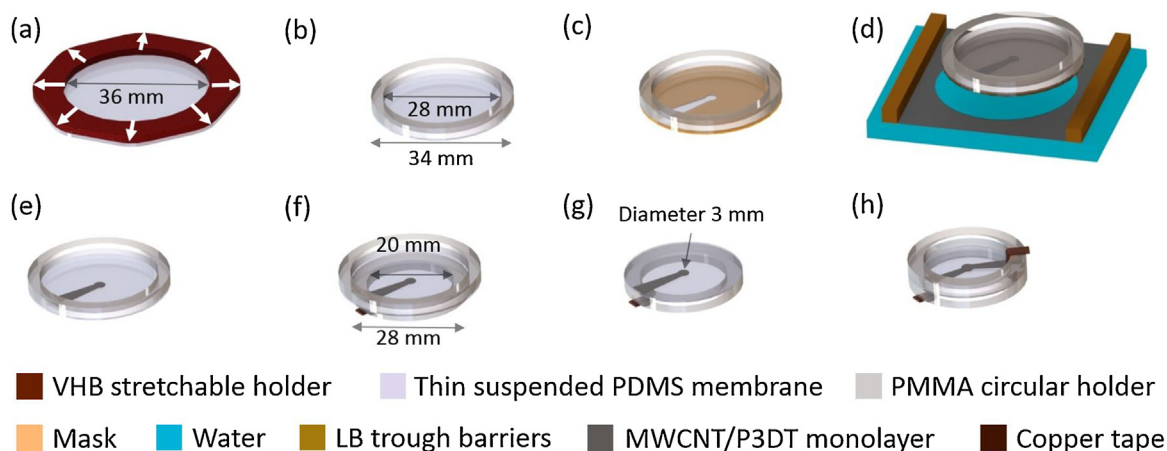


Fig. 2. Fabrication process of 1.4 μm -thick DEA by using LS technology. (a) Suspended PDMS (Sylgard 186) equi-biaxially pre-stretched (initial thickness: 2.0 μm , after stretch: 1.4 μm). (b) Suspended stretched 1.4 μm -thick PDMS membrane fixed onto a PMMA holder. (c) A mask is placed on the suspended membrane. (d) LS transfer of the monolayer electrode formed at the air-water interface onto the suspended PDMS membrane with mask. (e) Patterned monolayer electrode on the PDMS. (f) Transferring the PDMS membrane covered with the patterned monolayer electrode onto a smaller PMMA holder. (g) Patterned monolayer electrode on the lower side of PDMS with the electrode connected with copper tape, and the upper side of PDMS without electrode. (h) DEA made with LS electrode technology.

onto a poly(methylmethacrylate) (PMMA) holder (Fig. 2b) using silicone transfer adhesive. A mask (made from the backing film of the silicon adhesive, ARclear 8932) was placed on the suspended PDMS (Fig. 2c). The mask served to pattern the monolayer by LS transfer and to keep the suspended PDMS membrane flat (Fig. 2d). After the LS transfer of monolayer electrode, one drop of ethanol was deposited between the gap of the mask and the PDMS layer to help in peeling off the mask. The thin pre-stretched PDMS membrane with patterned monolayer electrode on one side was obtained (Fig. 2e). The PDMS membrane with one transferred electrode, was applied onto a smaller holder, with the PDMS bare surface facing up (Fig. 2f). On this smaller holder, the first patterned electrode was in contact with the copper connection (Fig. 2g), and the second electrode was LS transferred on the other side (Fig. 2c–e). Another smaller holding ring was bonded to the DEA using silicone transfer adhesive to provide the electrical contact for the second electrode (Fig. 2h). A small drop of conductive silver epoxy was used to ensure a good electrical connection between the monolayer electrode and the copper tape (See Supplementary data, Section 4, Fig. S3). The active zone of the DEA (3 mm diameter cycle) was located at the center of the pre-stretched 1.4 μm -thick PDMS membrane, where the two electrodes overlapped.

Voltages up to 130 V were applied between the two electrodes of the fabricated DEA. The diameter linear strain of the center active zone was measured as a function of the applied voltage. The linear strain was also measured as a function of frequency to characterize the speed of the DEA.

3. Results and discussion

3.1. Monolayer electrode properties

In the two following sections, electrodes based on MWCNT/P3HT and MWCNT/P3DT monolayers transferred onto PDMS substrates are characterized regarding structure, surface morphology, surface resistance and Young's modulus.

3.1.1. Characterization of the monolayer electrode

The MWCNT/PT monolayer properties are first investigated at the air-water interface. The monolayers are then transferred onto PDMS substrates and their morphology is characterized by AFM. Surface resistance is measured vs. time.

3.1.1.1. Monolayer structure at the air-water interface and onto PDMS substrate. Compression isotherms of the two MWCNT/P3DT and MWCNT/P3HT composite monolayers spread at the air-water interface are shown in Fig. 3a. The isotherms for both systems have similar shapes, characterized by a steep rise in surface pressure until collapse is detected at around 60 mN/m. This indicates the formation of condensed and stable monolayers at the air-water interface. It should be noted that in the absence of PT, MWCNTs do not form a Langmuir monolayer at the air-water interface. A Brewster Angle Microscopy (BAM) image of the MWCNT/P3DT monolayer compressed at 15 mN/m is shown as inset in Fig. 3a. By comparison with the pure PT monolayer (Supplementary data, Section 2, Fig. S2), MWCNTs embedded in the PT condensed phase can be observed as small brighter spots with a size of a few microns. Some slightly larger bright spots corresponding to MWCNT aggregates can also be observed. Similar behavior is observed for the MWCNT/P3HT monolayer. BAM images thus confirm that PTs are good dispersants for MWCNT [34]. To gain further insight in the structure of this monolayer, AFM images are taken of the monolayers transferred onto 100 μm -thick PDMS substrates at a surface pressure of 15 mN/m (Fig. 3b). As no significant effect of the PT side chain length has been detected, only the AFM image of the MWCNT/P3DT system is shown. AFM topography reveals a uniform and dense MWCNT carpet. MWCNTs are clearly interconnected forming a network which reflects the successful LS transfer of the composite monolayer from the water surface to the PDMS substrate.

The electrode thickness is obtained from AFM height profiles on a MWCNT/P3DT monolayer electrode transferred onto a smooth glass substrate. The MWCNT network presents an average thickness of about 30 nm, which corresponds to the expected diameter of the MWCNT. As the very thin P3DT continuous phase is not easily detected on these height profiles, its thickness of 2 nm is obtained from LS transferred pure P3DT monolayers onto glass substrate. The thickness of the composite monolayer electrode thus varies between 2 nm and 30 nm, according to the thickness of both components (Supplementary data, Section 5, Fig. S4).

3.1.1.2. Monolayer electrode surface resistance: stability over time. Because doping of electronically conducting polymers can strongly increase their electronic conductivity [29], the surface resistances of doped and undoped pure P3DT monolayers (see Section 2.4.1) have been compared. The role of MWCNTs within the

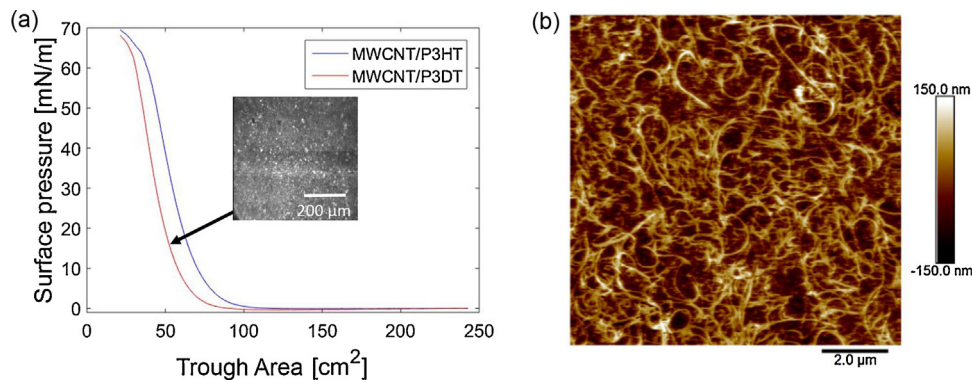


Fig. 3. (a) Surface pressure versus trough area isotherms for MWCNT/P3HT and MWCNT/P3DT monolayers with BAM image of MWCNT/P3DT monolayer at 15 mN/m. (b) AFM image of MWCNT/P3DT monolayer transferred at 15 mN/m onto PDMS substrate.

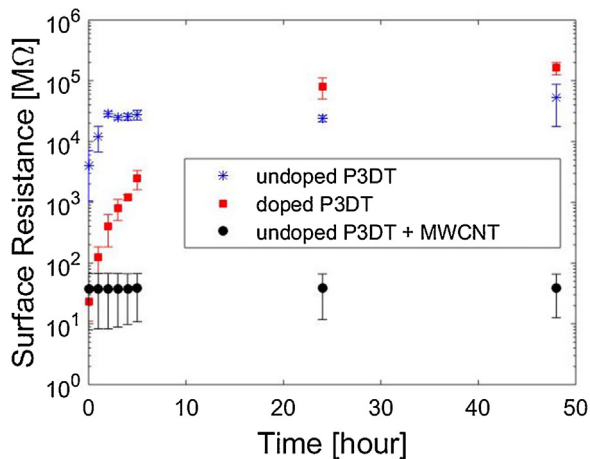


Fig. 4. Surface resistance of doped P3DT, undoped P3DT and undoped MWCNT/P3DT monolayer electrodes as a function of time.

MWCNT/P3DT composite monolayer is then highlighted by comparison with pure P3DT monolayer.

The change in surface resistance as a function of time is shown in Fig. 4 for undoped and doped P3DT monolayers (with no MWCNTs). The surface resistance of doped P3DT monolayer presents an acceptable value for DEAs of about $20 \text{ M}\Omega/\square$ immediately after doping. However, the resistance increases with time due to a progressive de-doping process, reaching a high and stable value of $80 \text{ G}\Omega/\square$ after 24 h. Since the electrode conductivity must remain stable for DEA applications, this electrode based on a doped P3DT monolayer cannot be used. The undoped P3DT monolayer has an initial surface resistance of order $\text{G}\Omega/\square$, increases by about one order of magnitude after a few hours, and finally reaches a stable high value ($\sim 50 \text{ G}\Omega/\square$) after 24 h. Thus, the undoped P3DT monolayer is not stable with time neither, and cannot be used as an electrode for DEAs.

For the composite monolayer consisting of undoped P3DT and MWCNTs, an initial surface resistance of about $20 \text{ M}\Omega/\square$ is measured, two order of magnitude lower than that of undoped P3DT. This value is close to the one measured for freshly doped P3DT, however the surface resistance stability is greatly improved by the presence of MWCNTs, remaining stable even after 48 h (Fig. 4). This result indicates that in the presence of undoped P3DT, the electronic properties of the composite monolayer are dominated by MWCNTs.

The surface resistance as a function of time for the undoped MWCNT/PT electrode is independent of the PT side chain length (Supplementary data, Section 6, Fig. S5). Electrodes with both PTs

present a stable surface resistance for 48 h, with almost similar values ($\sim 40 \text{ M}\Omega/\square$). While side chain length of PT usually has a significant effect on electronic properties of bulk material [30], no effect is observed here since the electronic properties of the composite monolayers are mainly governed by the MWCNT network.

The surface resistances of both MWCNT/PT composite monolayers have values that are acceptable for DEAs [17]. The DEA must be evaluated in terms of its charging time, i.e. RC time constant (see Section 3.2).

3.1.2. Influence of different stretching conditions

Because the surface resistance and topography are very similar for both MWCNT/P3HT and MWCNT/P3DT systems, the electrode characterizations performed under different stretching conditions are carried out only on MWCNT/P3DT monolayers. The morphology of the MWCNT/P3DT composite monolayer for different stretching conditions is investigated. The surface resistance as a function of strain is then characterized. Finally, the electrode Young's modulus is measured.

3.1.2.1. Morphology of MWCNT/P3DT electrode under different PDMS membrane stretching conditions.

As mentioned above, the electrode characterization is carried out on MWCNT/P3DT monolayers transferred onto $100 \mu\text{m}$ -thick PDMS substrate. To study the possible changes in surface topography upon stretching of the PDMS substrate covered by the MWCNT/P3DT electrode, AFM images are taken under different stretching conditions (Fig. 5 and Supplementary data, Section 7, Fig. S6).

From Fig. 5a, taken at 20% uniaxial strain applied to the PDMS substrate, one can see that the MWCNTs are slightly deformed along the stretching direction, but remain interconnected. For device at 0% strain, taken after 100% uniaxial strain or after 10 cycles with 60% uniaxial strain, AFM images show an interconnected MWCNT network, indicating that stretching up to 100% (Fig. 5b) or after 10 cycles with 60% uniaxial strain (Fig. 5c) does not break the network. For all stretching conditions, no significant morphology change is detected at this length scale once the sample is relaxed back to 0% strain, compared with the sample not submitted to any strain (Fig. 5d).

3.1.2.2. Influence of the applied strain on the electrode surface resistance.

The evolution of the surface resistance of the MWCNT/P3DT composite monolayer as a function of the applied strain is shown in Fig. 6, based on two samples (see Section 2.4). Fig. 6a shows the change of the surface resistance for a sample submitted to different successive cycles of increased maximum strain between 20% and 100%. Only the stretching up cycles are presented. During the first 20% strain, the resistance increases by

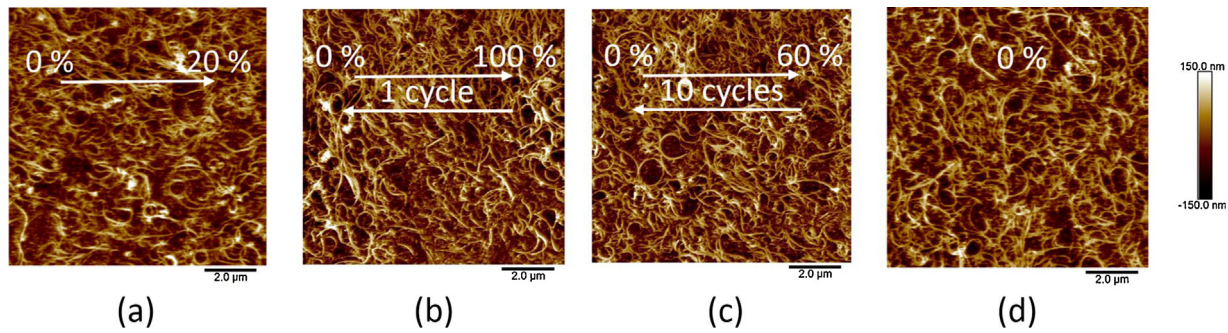


Fig. 5. AFM images of MWCNT/P3DT monolayer electrode. (a) At 20% uniaxial strain. (b) Returning to 0% strain after 100% uniaxial strain. (c) Returning to 0% strain after 10 cycles with 60% uniaxial strain. (d) At 0% uniaxial strain without applying any strain. The arrows indicate the stretch direction.

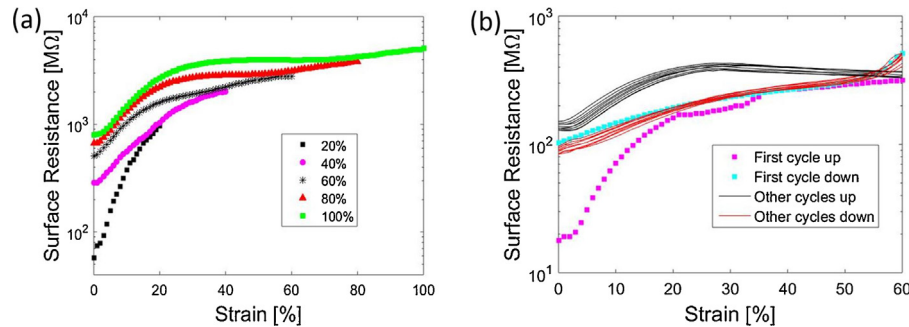


Fig. 6. Surface resistance vs. strain for MWCNT/P3DT monolayer transferred onto 100 μm -thick PDMS substrate (a) Starting with 20% strain up to 100% with 20% steps on the same sample and with a release to 0% after each stretch. (b) During 10 cycles with 60% uniaxial strain (30 s delay between each cycle).

about one order of magnitude, indicating a decrease in the interconnection ratio within the MWCNT network. When returning to 0% strain, the resistance does not reach its initial value, but increases by a factor of 6. This highlights an irreversible change in electrical properties due to mechanical deformation. This occurs on every cycle with increasing maximum applied strain. One can however observe that the increase in surface resistance after returning to 0% strain is less pronounced above 60% strain. It is noteworthy that the monolayer electrode remains conductive up to 100% uniaxial strain.

In order to understand whether this change in resistance is related to cycle number or to the maximum strain, another sample is stretched repeatedly to a constant maximum strain of 60%. The surface resistance variation through each of the 10 stretch cycles is shown in Fig. 6b. One should mention that the end points of both up and down cycles do not present exactly the same value, which is due to the 30 s delay during each measurement. Upon the first cycle, the surface resistance increases by about one order of magnitude reaching $\sim 317 \text{ M}\Omega/\square$ as the strain varies from 0% to 60%. One can observe that this variation is lower than the one obtained at 60% strain for the sample considered in Fig. 6a, due to the different history that both samples have experienced. One can also notice that the main evolution is observed during the first 40% strain. After returning to 0% strain, as previously evidenced, the surface resistance does not recover its value before stretching, meaning that the MWCNT network interconnection is changed irreversibly. For the 9 other following cycles to 60% linear strain, the surface resistance does not change drastically. Thus, even though monolayer electrical properties degradation occurs during the first stretch cycle, the sample can be submitted to many successive cycles at quite large strain without significant variation of electrode surface resistance. By comparing Fig. 6a and b, it can be concluded that the degradation of the monolayer electrode is mainly related to the maximum applied strain.

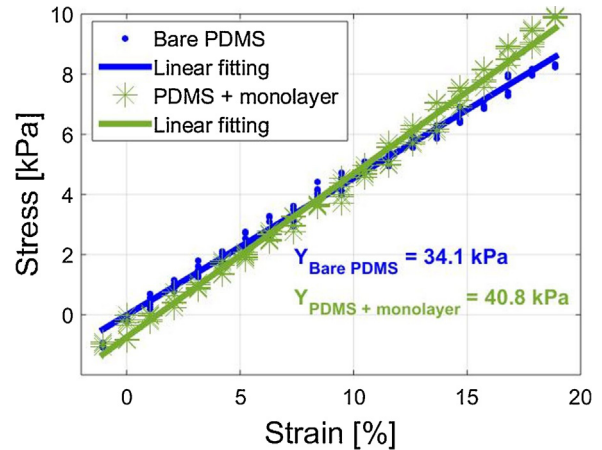


Fig. 7. Stress-strain curve of a bare PDMS substrate and of the same PDMS substrate covered with MWCNT/P3DT monolayer electrode, allowing the monolayer stiffness to be determined.

3.1.2.3. Electrode young's modulus. An example of stress-strain curves is shown in Fig. 7 for both the 10 μm -thick bare PDMS substrate and the bilayer consisting of the same PDMS substrate covered by the MWCNT/P3DT monolayer electrode. Young's moduli of 34.1 kPa and 40.8 kPa are extracted for the bare PDMS substrate and the PDMS/electrode bilayer respectively. A $Y_e \cdot t_e$ value of $0.08 \pm 0.03 \text{ N/m}$ is then deduced from Eq. (3). Since the composite monolayer consists of a 30 nm-thick interconnected MWCNT network embedded inside a 2 nm-thick P3DT monolayer (Section 3.1.1.1), the Young's modulus of the electrode $Y_{\text{electrode}}$ can then be computed as being between 3 ± 1 and $37 \pm 14 \text{ MPa}$, depending what electrode thickness is used.

The Young's modulus of pure P3DT monolayers (without MWCNT) is also measured for comparison. A $Y_{PT} \cdot t_{PT}$ value of

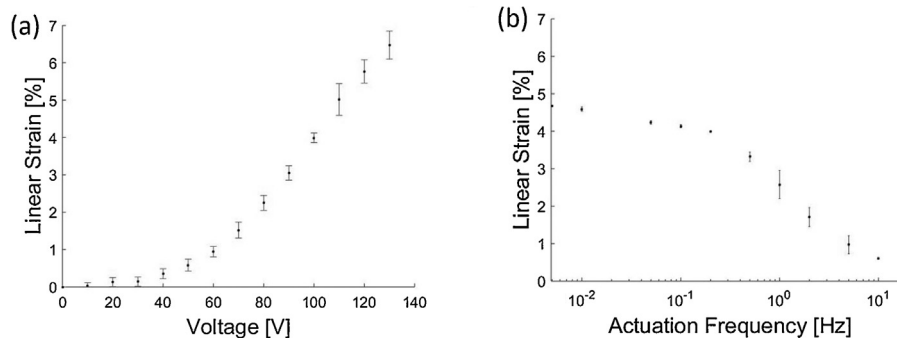


Fig. 8. Characterization of DEA consisting of a 1.4 μm -thick PDMS membrane with the monolayer electrodes. (a) Strain vs. voltage curve, showing about 4% linear strain at 100 V. (b) Strain vs. actuation frequency curve.

$0.07 \pm 0.03 \text{ N/m}$ is obtained, leading to a Y_{PT} value of $37 \pm 16 \text{ MPa}$ using 2 nm as electrode thickness. For both pure P3DT and MWCNT/P3DT monolayers, nearly the same Y^*t value is obtained. Therefore, it can be deduced that within the composite monolayer, the P3DT continuous phase plays the dominating role for the Young's modulus. The presence of the MWCNT network embedded inside the P3DT monolayer does not significantly increase the stiffness of the monolayer.

The composite MWCNT/P3DT monolayer electrodes have a surface resistance of about $20 \text{ M}\Omega/\square$, remain conductive at 100% linear strain, and show a small $Y_e^*t_e$ product (0.08 N/m) in comparison with the $Y_{PDMS}^*t_{PDMS}$ product of the 1.4 μm -thick PDMS membrane used in the ultrathin DEA ($1 \text{ MPa} \times 1.4 \cdot 10^{-6} \text{ m} = 1.4 \text{ N/m}$). All these properties lead to a promising electrode material to fabricate a low voltage operating DEA.

3.2. 100 V operating DEA with stretchable MWCNT/P3DT monolayer electrodes

A Dielectric Elastomer Actuator is fabricated by patterning the stretchable MWCNT/P3DT composite monolayer electrodes on both sides of a 1.4 μm -thick suspended pre-stretched PDMS membrane (see Section 2.6). Prior to our work, one important factor limiting strain in extremely thin DEAs is the stiffening impact of the electrodes [16]. The MWCNT/P3DT monolayer electrodes add very little stiffness to the DEA, allowing good strain at 100 V, but such thin electrodes have higher electronic resistivity, limiting device speed. We thus report here both strain and speed data for our DEAs.

The linear strain of the fabricated DEA active zone is plotted as a function of the applied voltage in Fig. 8a. This device is the thinnest DEA reported to date. For the first time, DEA actuation strains of well above 1% are obtained with driving voltages below 100 V. 4.0% linear strain is obtained for a 100 V driving voltage, which corresponds to a S_x/v^2 value of $400\%/kV^2$. This value is three times higher than the one reported by Poulin et al. [16]. The strain vs. true electric field is shown in Supplementary data (Section 8, Fig. S7). Despite the very thin elastomer, the curve matches well with our typical data for thicker Sylgard 186 membranes.

The actuation strain vs. actuation frequency curve is recorded, as shown in Fig. 8b. For frequencies below approximately 0.2 Hz, the strain is constant, and for higher frequencies the strain decreases. The electromechanical 3 dB point occurs at 1 Hz. Two main reasons can lead to this quite low response speed: electrical charging time, and visco-elastic losses.

The electrical charging time of a DEA can also be approximated as RC, where R is the total resistance of the electrodes (including feedlines) and C is the capacitance of the DEA. At 100 V (i.e., at 4% strain), the total resistance of the 2 electrodes is $860 \text{ M}\Omega$, and the capacitance of the DEA is calculated as $1.4 \times 10^{-10} \text{ F}$. The computed RC time constant is 120 ms.

The charging time constant of the DEA is determined experimentally by recording the current flowing to the DEA in response to a step in drive voltage. The classical current jump followed by an exponential decay is observed, from which an electrical charging time constant τ of 150 ms is extracted. In the highly simplified model of an RC circuit, the RC time constant corresponds to the time at which the voltage reaches 63.2% of its maximum value. Given the quadratic response of DEAs, 63% of the voltage corresponds to 40% of the maximum strain. Using 100 V as our drive voltage, one sees in Fig. 8a that the linear strain at 63 V is 1.5%. From the strain vs charging time plot at 100 V (see Supplementary data, Section 8, Fig. S8), 1.5% linear strain is reached between 125 ms and 250 ms, consistent with the electrical charging time.

The overall response speed can thus be mostly explained by the electrical charging time constant. The response time has also a small component due the visco-elastic response of the elastomer. We expect the later to be very small, given our prior experience with kHz DEAs using similar silicone elastomers [3].

4. Conclusions

The Langmuir-Schaefer method is used for DEAs electrode fabrication for the first time. Multiwalled Carbon Nanotube and poly(alkylthiophene) are combined to form stable monolayers at the air-water interface, which then can be transferred onto a PDMS membrane using the Langmuir-Schaefer technology. The monolayer electrode consists of an interconnected MWCNT network embedded in a PT monolayer, in which the PT imparts the mechanical properties while the MWCNTs ensure the electrical conductivity of the system. The composite monolayer is stretchable, and conductive up to 100% strain ($\sim 20 \text{ M}\Omega/\square$ at 0% strain, $\sim 5 \text{ G}\Omega/\square$ at 100% strain). Using the LS method to fabricate patterned ultrathin stretchable electrodes enables the fabrication of a thin DEA with a 1.4 μm -thick PDMS dielectric membrane. At only 100 V, this DEA reaches 4.0% linear strain. Compared to the kV driving voltage generally required for DEAs, this low operating voltage opens new applications for DEAs. The LS electrodes that we report here are a key building block towards DEAs generating full strain at less than 5 V: by using LS/LB techniques to make both the elastomer and the electrodes, it will be possible to make multilayer DEAs where all layers are one single molecule thick. This will be the ultimate physical limit in DEA technology.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.snb.2018.01.145>.

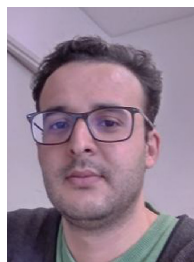
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Francesca Sorba received the B.S degree in physics engineering from the Politecnico di Torino, Italy, in 2013 and the M.S degree in microengineering from the Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, in 2015. She is now a PhD student at the Swiss Center for Electronics and Microtechnology (CSEM SA) and in the group of professor Herbert R. Shea at EPFL. Her current research activity involves the developing of an elastomer-based device to study mechanical properties for life science applications.



Samuel Rosset received the M.S. and Ph.D. degrees in microengineering from the Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland, in 2004 and 2009, respectively. From 2005 to 2008, he was a Research Assistant with the Soft Transducers Laboratory (LMTS) at EPFL. After a few years in industry developing tunable optics based on soft elastomers, he reintegrated the LMTS in 2011 as a Research Scientist, overseeing the activities on dielectric elastomer actuators. In 2017, he joined the Biomimetics group at the University of Auckland, New Zealand. His research interests include soft actuators, compliant electrodes, development of new fabrication processes for soft sensors and actuators, and reliability and

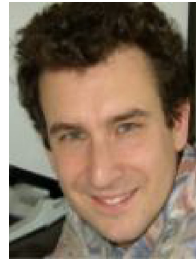
lifetime of these devices.



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