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Fabrication of Silver-Nanowire/PVDF Self-Supporting Thin Flexible Electrode Membranes

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Abstract. Flexible electrodes play an increasing role for medical applications, such as ECG (electrocardiography) or TENS (Transcutaneous electrical nerve stimulation) due to comfort in use and thus their suitability for health monitoring under movement and during sport.

Polymers, such as polyvinylidene fluoride (PVDF), are promising for the development of fabrication methods and materials for such application cases, as stable flexible thin polymer membranes can be produced at large scale. We have compared different up-scalable fabrication techniques of thin electrode membranes based on PVDF as a function of silver nanowire concentration, using electrospinning, spincoating, and drop-casting techniques. The produced membranes and thin films were investigated by electrical four-point probing, optical microscopy, atomic force microscopy, as well as by stability tests under bending, and water exposure.

We show, that a combination of electrospinning and spin-coating presents a reliable method for the fabrication of AgNW-PVDF based flexible nanofiber membrane electrodes (NMEs). Our nanofiber membrane electrodes (NMEs) exhibit a 10 times lower sheet resistance than AgNW-PVDF thin film electrodes (TFEs) produced for comparisons by a combination of spincoating and drop-casting using the same amounts of AgNWs. Upon immersion in water for up to 48 hours, we do not detect any nanowire release or decomposition of the fabricated electrodes, which is promising in view of application of the AgNW-PVDF composite electrodes in humid environment.

Introduction

The application fields for flexible electrodes are strongly increasing due to the today's trends of increasing electrical signal monitoring [1,2]. In the biomedical sector, flexible electrodes can e.g. be used for ECG (electrocardiography) or TENS (Transcutaneous electrical nerve stimulation) [3,4]. The increased comfort in use, makes flexible electrodes of particular interest for long-term biosignal monitoring [5,6], as well as for health monitoring applications under movement and during sport. The development of fabrication methods and materials for flexible electrodes is further driven by the emerging field of flexible robotics [7]. Polymer nanocomposite materials are particularly promising for those fields, as they offer a broad range of mechanical properties, fabrication and formulation techniques to implement desired properties such as electrical conductivity, mechanical flexibility and stretchability, and water resistance or water repellence. Polymers, such as polyvinylidene fluoride (PVDF), are in particular promising for the development of fabrication methods and materials for such application cases, as stable flexible thin membranes can be produced at large scale. AgNWs represent a highly promising materials to form conductive filler networks in polymer nanocomposite electrodes [3]. However, AgNW/PVDF nanocomposites were found to exhibit high dielectric constants [8]. Thus, the generally low conductivity of AgNW/PVDF bulk nanocomposites, which can

be related to enrobing and insulation of AgNWs by PVDF, needs to be circumvented by dedicated design and fabrication methods in order to produce conducting AgNW/PVDF membranes for applications as flexible electrodes.

In this paper, we thus study dedicated fabrication methods for the manufacturing of silver-nanowire/PVFD self-supporting thin flexible electrode membranes using combined electrospinning, spin-coating and drop-casting techniques. The obtained sheet resistance values, as well as results from bending and water immersion show that our developed nanofiber membrane electrodes are promising for applications as AgNW/PVDF flexible electrodes.

Experimental

Flexible Electrode Preparation. Two types of flexible electrodes were prepared using AgNW dispersions (ACS materials, AgNWs in ethanol, nominal diameter 40 nm, nominal length 20-30 µm) at various concentrations (between 0.4 mg/ml and 3.0 mg/ml silver content) and PVDF (Sigma Aldrich: pellets). PVDF is dissolved in either (N,N-dimethylfomamide (DMF) or N,N-dimethylactetamide/Aceton (DMAc/Ac) 1:1.

Thin Film Electrode (TFE) Fabrication. Glass micro slides (cut to samples of 25 mm x 25 mm, thickness (1.00±0.04) mm, Sigma Aldrich (Corning)) are used as substrates. AgNW dispersions are spincoated on glass (300 µl of AgNW suspension, at 500 rpm during 30 s) and subsequently dried on a hot plate at 130°C for 10 minutes for evaporation of ethanol, and then let cooling down to room temperature. PVDF solutions (30 wt%, 333g/l) for deposition of homogeneous transparent films were prepared dissolving 1.7g PVDF in DMF, stirred during 30 min at 130°C.

For each thin film electrode 800 µl of the PVDF solution were deposited by drop casting such that the entire surface of the glass substrates is covered. After deposition, the films were immediately annealed on a hotplate (130°C, 10 minutes), and let cooling down to room temperature. The resulting transparent homogeneous thin film electrodes are then easily peeled-off from the glass substrates.

Nanofiber Membrane Electrode (NME) Fabrication. Electrospinning of PVDF nanofiber membranes followed by spincoating of AgNWs suspensions (300 µl of AgNW suspension, at 500 rpm, 30 s), has been used for the fabrication of NMEs. PVDF solutions (40.3 wt%) were prepared dissolving 2g PVDF in DMAc/Ac 1:1 v/v and stirred during 30 min at 130°C on a hot plate.

For each nanofiber membrane, 50 µl of PVDF solution were deposited with an electrospinning flux of 10 µl/min. The electrospinning was performed using flat ended needles (inner needle diameter 0.4 mm). The needle-collector voltage was set to 16 kV at a needle-collector distance of 6 cm. Electrospinning was performed at ambient conditions. (25°C ±4°C). Rotating brass discs (diameter 2.5 cm) were used as collector electrode with the rotation axis adjusted parallel and slightly off-axis with respect to the needle axes. The obtained homogeneous nanofiber membranes were used for subsequent spincoating of AgNWs.

Electrical Characterization. Electrical characterizations of the electrodes were made by 4-point probing for the measurement of the sheet resistance. A four-point probe sensor with osmium alloy tips and a Keithley 2400 Source meter were used. Current-voltage sweeps were typically acquired in the range of -0.4V to 0.4V for which an essentially linear behavior of the current-voltage characteristics is observed. The sheet resistance of the electrodes was deduced by linear regression of the measured current-voltage characteristics, and by applying the correction factor ($\pi/\ln 2$) for collinear probes [9,10]. In order to evaluate the effect of bending, we have measured the resistance of some of the electrodes using manual 2-point probing with a multimeter, while placing the flexible electrodes around glass tubes of different diameters. Further demonstration of conductivity was performed using the flexible electrodes in electric circuits for the illumination of LEDs.

Optical and Microscopy Analysis. Atomic Force Microscopy (AFM Park XE7) data were acquired in tapping mode. An optical microscopy (LEICA Leica DMILM) was used for evaluation of the overall homogeneity of the composite electrodes. A Scanning Electron Microscope (ZEISS Evo) equipped for EDX analysis was used to corroborate the presence of Ag at the surface of a nanofiber membrane electrode. Optical absorbance spectroscopy (UV-vis-NIR flame, oceanoptics) was used for the evaluation of water resistance of the AgNW/PVDF thin films and membranes.

Results and Discussion

Development of AgNW/PVDF nanocomposites and dedicated electrode fabrication techniques. Direct use of AgNW/PVDF blends (not shown here) leads to poor electrical conductivity, both in drop casting and in electrospinning for concentrations ranging from 0.3% to 3.0 %wt AgNW/PVDF. For drop casting, e.g. with an AgNW load of 3 wt%, a conductivity of only 10^{-9} S/cm was obtained, which is very far below the order of 10^2 S/m, which we had obtained recently for 3 wt% AgNW-biopolymer composite electrodes using poly(3-hydroxybutyrate) (PHB) as matrix material [3]. Tests of direct electrospinning of AgNW/PVDF blends (not shown here) also lead to very high sheet resistance of nanofiber membranes (we found e.g. $7.22 \cdot 10^7 \pm 0.73 \cdot 10^7$ Ω/sq for an electrospun membrane using a blend with 3 wt% AgNW/PVDF). This compare well with results of Han et al. [11] who have recently shown direct electrospinning of a AgNW/PVDF slurry as a method to produce electrically isolated core-shell nanocables with application potentials as antibacterial, ultrathin cables or in optoelectronic devices.

In order to circumvent AgNW embedding in PVFD in the perspective of the manufacturing of flexible electrodes, we have thus applied and compared alternative fabrication strategies which allow to form a conductive AgNW network exposed at the surface using PVDF as flexible support material. We thus fabricate, analyse, and compare flexible electrodes of two types: (i) **thin film electrodes (TFEs)** which are fabricated by AgNW network formation by spincoating on glass, followed by drop casting of PVDF and subsequent peel-off (which leads to thin film electrodes with AgNW network formation at the bottom side) and (ii) **nanofiber membrane electrodes (NMEs)** which are fabricated by electrospinning of PVDF membranes followed by spincoating of AgNW (for AgNW network formation on top of a membrane).

Electrical properties. Figure 1 shows the obtained sheet resistance values as a function of the used AgNW concentration in comparison for AgNW networks deposited on glass, as well as for the two types of flexible AgNW-PVDF electrodes (TFEs and NMEs) at various AgNW load concentrations.

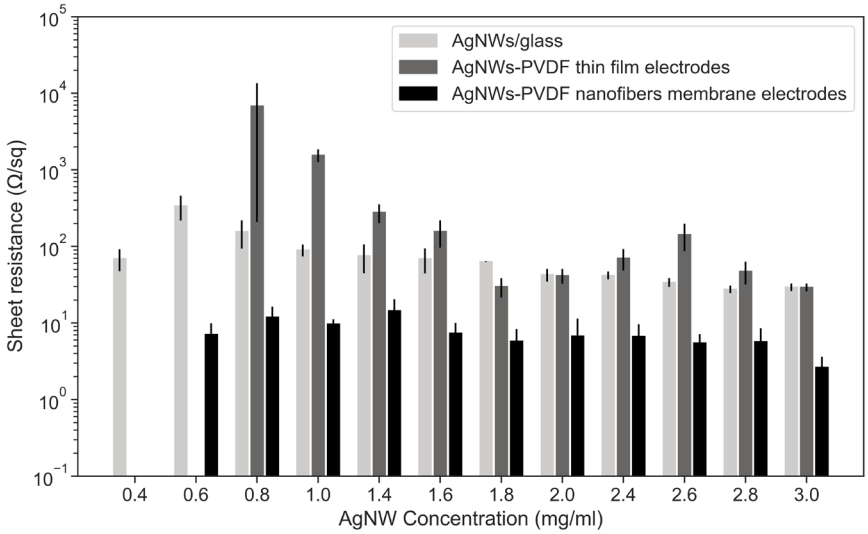

Fig. 1: Comparison of sheet resistance values measured on samples produced from various AgNW concentrations by three fabrication methods: (i) AgNW network on glass produced by spincoating on glass, (ii) thin film electrodes (TFE) produced by peel-off of the AgNW network using PVDF spincoating, (iii) nanofiber membrane electrodes (NME) produced by AgNW spincoating on a PVDF electrospun membrane.

The results from electrical characterizations (Fig1.) show that peel-off of AgNW networks using dropcasting of PVDF successfully leads to conducting thin film electrodes. For AgNW concentrations in the range of 1.6 mg/ml to 3 mg/ml, the obtained sheet resistance varies between (160±60) Ω/sq and (29±3) Ω/sq, which is comparable to the values of AgNW networks on glass (Fig. 1). This confirms that peel-off is a successful method for the fabrication of AgNW/PVDF electrodes in agreement with recent observations of Zhang et al. [12], who have demonstrated the peel-off of

AgNWs using PVDF drop casting. Compared to the study of Zhang et al. [12], differences in the resulting AgNW densities within the AgNW networks, and in the resulting final sheet resistances might be related to different AgNW dimensions, as well as to AgNW losses during spincoating. We note that our spin coating parameters could be optimized in order to reduce AgNW losses during the spin coating process.

For our nanofiber membrane electrodes, the obtained sheets resistance values range from (12 ± 4) Ω/sq for an AgNW concentration of 0.8 mg/ml to (2.6 ± 1.0) Ω/sq at 3 mg/ml (Fig. 1). This represents a decrease of the sheet resistance by one order of magnitude compared to AgNWs on glass. This decrease is consistent with a higher surface roughness on PVFD nanofiber membranes compared to the flat glass substrate, which may influence the result of the spin-coating process, as well as with the smaller surface area of the circular membranes compared to the square shaped glass substrates.

Silver-nanowire surface distribution and attachment to the PVDF films and membranes.

In order to elucidate and compare the AgNW distribution at the conductive electrode surfaces of TFEs and NMEs, we have performed atomic force microscopy analysis and acquired topography images as well as phase contrast images. Figure 2 and figure 3 show representative AFM images of TFEs and NMEs, respectively.

Fig. 2 shows representative examples of AFM images of AgNW distributions at the surface of TFEs. In topography images, some AgNWs are only partially well distinguished, i.e. not along their full length. Comparing various topography images, as e.g. shown in figure 2a) and 2b), we find that the AgNWs do not necessarily appear with their full length in topography images. This can be attributed to partial embedding in PVDF along the nanowires. Fig 2b,c) show examples of partially embedded AgNWs for which a portion along the wire is on top of the PVDF. This is convincingly supported by comparing the corresponding phase contrast images (Fig 2 bottom) showing sample regions with sub-surface AgNWs. The observed partial embedding in PVDF along AgNWs is consistent with observations in SEM by Zhang et al. [12]. Our TFEs are thus promising to provide a long term adherence of AgNWs at the surface of the electrodes.

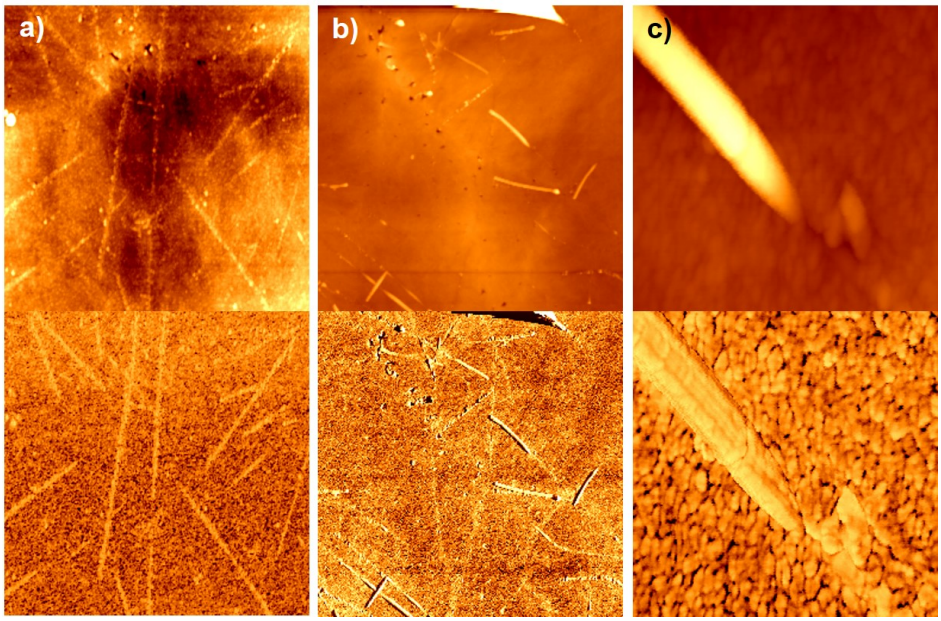

Fig. 2: Representative AFM data of PVDF/AgNW thin film electrodes measured upon peel- off. Topography images (a-c) with their corresponding phase contrast images (d-f). Concentration of AgNW suspensions as used for spincoating a) 2.52 mg/ml AgNWs, b),c) 3mg/ml AgNWs. Scan sizes: a), b) 10 µm x 10 µm; c) 800 nm x 800 nm (zoom of b).

Figure 3 shows in comparison AFM data of representative networks of AgNW-wires and PVDF fibers for a nanofiber membrane electrode. AgNW network formation and partial alignment of

AgNWs along the polymer nanofibers, and also across, can best be distinguished in the phase contrast images at AFM scan sizes of 10 µm x 10 µm and below.

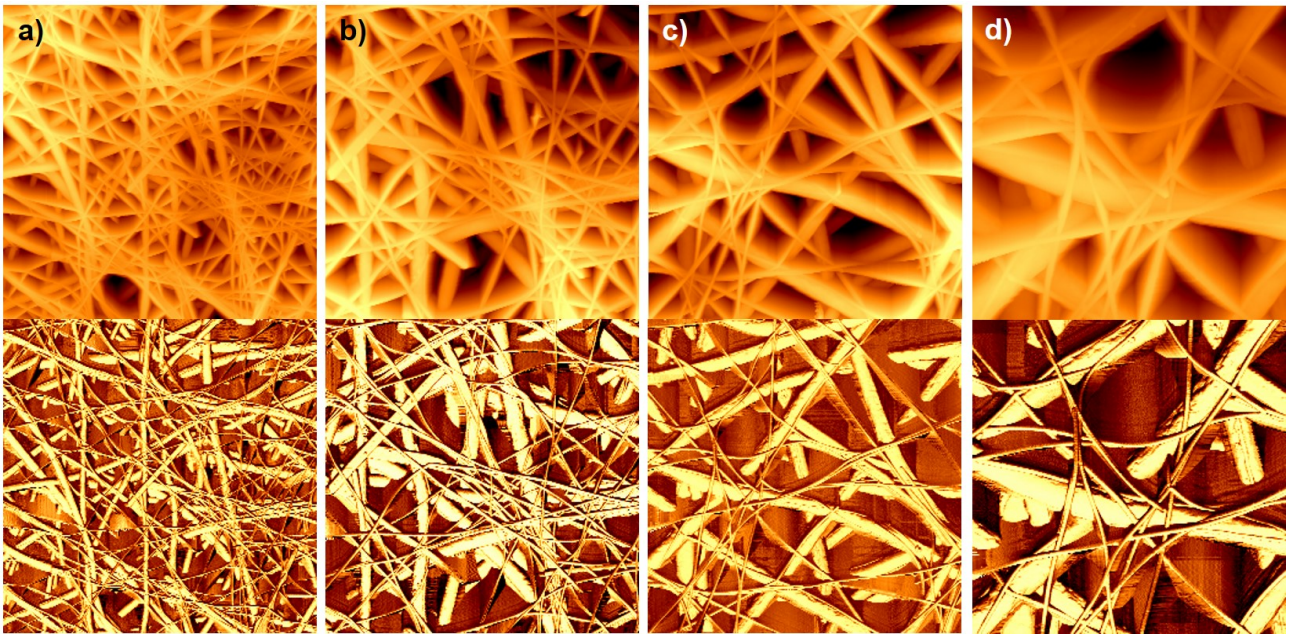

Fig. 3: Representative AFM data of AgNW networks on a PVDF nanofiber membrane: topography (top) and phase contrast images (bottom); scan size a) 20 µm x 20 µm, b) 10 µm x 10 µm (zoom of a)), c) 10 µm x 10 µm, d) 5 µm x 5 µm (zoom of c)). Concentration of AgNW suspensions as used for spincoating 3mg/ml.

Comparative SEM analysis (Fig. 4) performed on the same sample as shown in Fig. 3, shows a homogeneous membrane surface also at lager scales. In order to confirm the presence of silver on the membrane surface, we have performed EDX analysis (Fig. 4c). From EDX analysis, the surface silver content can be estimated to a normalized mass percentage of 19.6%, while in an area with a small topographical defect on the film a normalized mass percentage of 5% silver was detected at the surface. The presence of AgNWs at the surface is thus well confirmed.

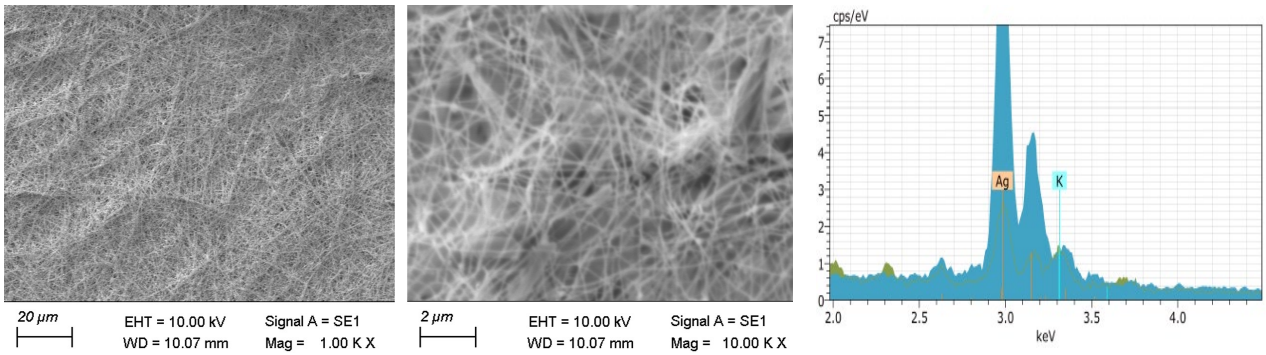

Fig. 4: Scanning electron microscopy images and EDX data confirming homogeneous nanofiber membrane formation with presence of silver at the NME surface. High voltage was set to 20.0 kV.

From our AFM data we find, for the same initially deposited amount of AgNWs (here 800 µl at a concentration of 3 mg/ml), that the apparent AgNW density at the electrode surface is higher in case of the nanofiber membrane electrode (Fig.3) than for the thin film electrode (Fig 2). This is consistent with the above discussed differences of sheet resistance (Fig. 1). In order to also compare and confirm the attachment of AgNWs for both type of electrodes, we test their resistance to water exposure and bending.

Water resistance and bending tests. In the perspective of long term usage of flexible electrodes exposed to humid conditions or to bending, we evaluate, as a first estimate, the attachment (or release)

of AgNWs under exposure to water and we measure the electrical resistance of the electrodes under bending at various radii, and after bending.

In order to estimate a possible AgNW release under humid conditions, a nanofiber membrane electrode (NME) and a thin film electrode (TFE) were each immersed in 5ml of distilled water over several hours up to about 5 days. Absorbance spectra of the water measured after immersion of the TFE or NME (Fig. 5b), c)) show very low absorbance values, with only some absorption in the UV (<up to 48 hours). For immersion during 5 days (120h, 132h respectively) increasing absorption change in the visible is observed for both samples, possibly to be associated to PVDF or solvent residues. For comparison Fig. 5a) shows absorbance spectra of diluted AgNW suspensions in ethanol at various AgNW concentrations ranging from 0.05 mg/ml down to 0.937 µg/ml. The spectra show absorbance peaks at 290 nm and at 380 nm, which can be attributed to plasmon resonances of the nanowires [13, 14]. While the peak at 380 nm is not distinguished anymore for the lowest measured concentration, the one at 290 nm is still well detected with an absorbance > 0.6. The spectra from the immersed electrodes do not show any signatures at these wavelengths. This indicates that AgNWs do not easily detach from the AgNW-PVDF electrodes when immersed in water (we note the different absorbance scales in Fig 5b),c) in comparison to Fig. 5a)). This result is thus promising in view of long term use of the electrodes when exposed to humidity. Further experiments, e.g. including also methods for the detection of Ag-ions in water and further liquids, as well as electrical measurements on the membranes upon immersion are needed to quantify a possible detachment of AgNWs or Ag release from the electrodes.

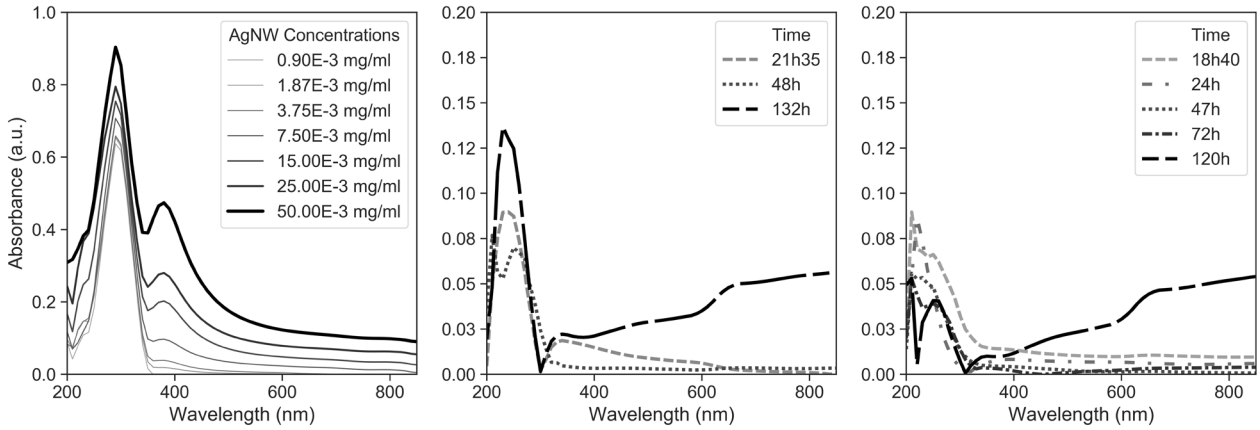

Fig. 5: a) UV-vis-NIR absorbance spectra of AgNWs, concentrations (in 10^{-3} mg/ml) from highest to lowest: 50.00; 25.00; 15.00; 7.50; 3.75; 1.87; 0.90. b),c) UV-vis NIR absorbance spectra from water resistance tests b) TFE and c) NME.

Figure 6 shows results of manually performed mechanical bending tests. The electrical resistance of TFEs and NMEs was measured before bending, under bending at four different radii of curvature, and again in flat geometry after the bending experiments.

The relative resistance increase under bending, for each type of electrodes and as a function of the bending radius, is summarized in Table 1; averages were calculated over the entire concentration range from 0.8 mg/ml to 3.0 mg/ml for the 10 concentrations shown in Fig.6, with one sample each). R_0 is the initial resistance (flat electrode) and R_r the resistance measured under bending at a radius of curvature r. As a general trend, our NME membranes show a slightly higher increase in resistivity than the TFEs for all tested radii of curvature (table1, Fig. 6).

Table 1: Average resistance increase under bending as measured for TFEs and NMEs.

Bending radius r [cm]	R_r/R_0 (TFE)	R_r/R_0 (NME)
0.77	3.1	4.5
1.50	2.1	2.6
2.11	1.4	2.4
2.76	1.5	1.6

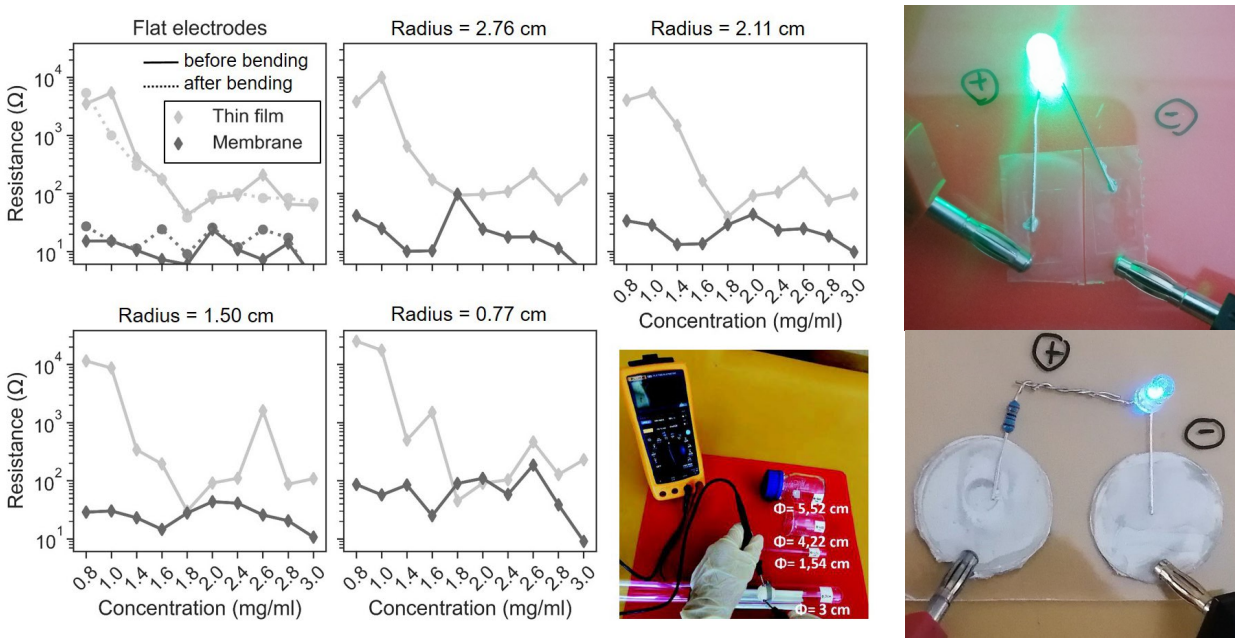

Fig. 6 Left: Bending tests data of AgNW electrodes for nanofiber membrane electrodes and thin film electrodes produced from AgNW suspensions of different concentration. Results before bending, for a bending under different radii of curvature and after the bending test are shown, as well as a photo of the manual measurement set-up used for the bending tests. Right: TFEs (top) and NMEs (bottom) used within an electrical circuit to illuminate an LED.

Figure 6 shows recovery of resistance values after the bending cycle for the NME membranes. The measured values on flat electrodes after and before bending are lower than those measured e.g. under bending at a radius of curvature of 0.77 cm. Both types of our membranes can successfully be integrated in electrical circuits, as illustrated by the illumination of an LED connected via our developed electrodes (Fig. 6).

Summary

We have compared the fabrication of flexible AgNW-PVDF composite electrodes using different methods which lead to exposure of an AgNW network at one of their surface sides.

In summary, our study shows, that a combination of PVDF electrospinning and AgNW spin-coating presents a reliable method for the fabrication of AgNW-PVDF based flexible thin electrode membranes. The nanofiber membrane electrodes (NMEs) exhibit a 10 times lower sheet resistance than AgNW-PVDF thin film electrodes (TFEs) produced for comparisons by a combination of spincaoting and drop-casting using the same amounts of AgNWs. Upon immersion in water for up to 48 hours, both electrode types stay stable and we do not detect any nanowire release from the fabricated electrodes, which is highly promising in view of application of the AgNW-PVDF composite electrodes even in humid environment.

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References

[1] P.J. Soh, G.A.E. Vandenbosch, M. Mercuri, and D. Schreurs, Wearable wireless health monitoring: current developments, challenges and future trends, IEEEMicrowave Mag. 16 (2015) 55-70.

[2] G. Acar, O. Ozturk, A.J. Golparvar, T.A. Elboshra, K. Böhringer, and M.K. Yapici, Wearable and Flexible Textile Electrodes for Biopotential Signal Monitoring: A review, Electronics 8 (2019), 479.

[3] C. Tematio, M. Bassas-Galia, N. Fosso, V. Gaillard, M. Mathieu, M. Zinn, E. Staderini, and S. Schintke, Design and characterization of conductive biopolymer nanocomposite electrodes for medical applications, Materials Science Forum 879 (2017) 1921-1926.

[4] B. Liu, H. Tang, Z. Luo, W. Zhang, Q. Tu, and X. Jin, Wearable carbon nanotubes-based polymer electrodes for ambulatory electrocardiographic measurements, Sensors and Actuators A 265 (2017) 79–85.

[5] P. F. Shahandashti, H. Pourkheyrollah, A. Jahanshahi, and H Ghafoorifard, Highly conformable stretchable dry electrodes based on inexpensive flex substrate for long-term biopotential (EMG/ECG) monitoring, Sensors and Actuators A 295 (2019) 678-686.

[6] M. Chi, J. Zhao, Y. Dong, and X. Wang, Flexible Carbon Nanotube-Based Polymer Electrode for Long-Term Electrocardiographic Recording, Materials 12 (2019) 971.

[7] N. Yogeswaran, W. Dang, W.T. Navaraj, D. Shakthivel, S. Khan, E.O. Polat, S. Gupta, H. Heidari, M. Kaboli, L. Lorenzelli, G. Cheng and R. Dahiya, New materials and advances in making electronic skin for interactive robots, Advanced Robotics, 29 (2015), 1359–1373.

[8] W. Zheng, X. Lu, W. Wang, M. Song, Y. Wang, and C. Wang, Fabrication of novel Ag nanowires/poly(vinylidene fluoride) nanocomposite film with high dielectric constant, Phys. status solidi 207 (2010) 1870–1873.

[9] A. Uhlir Jr., The Potentials of Infinite Systems of Sources and Numerical Solutions of Problems in Semiconductor Engineering, The Bell System Technical Journal 34 (1955) 105-128.

[10] F. M. Smith, Measurement the of Sheet Resistivities with the Four-Point Probe, The Bell System Technical Journal, 37 (1958), 711-718.

[11] M.-C. Han, H.-W. He, B. Zhang, X.-X. Wang, J. Zhang, M.-H. You, S.-Y. Yan, and Y.-Z. Long, Fabrication of Ag nanowire/polymer composite nanocables via direct electrospinning. Mater. Res. Express 4 (2017) 075043.

[12] L. Zhang, Y. Wang, J. Gui, X. Wang, R. Li, W: Liu, C. Sun, X.Zhao, and S. Guo, Efficient Welding of Silver Nanowires embedded in a Poly(vinylidene fluoride) Film for Robust Wearable Electronics. Adv. Mater. Technol. 4 (2019) 1800438.

[13] Q.N. Luu, J.M. Doorn, M. T. Berry, C. Jiang, C. Lin, and P.S. May, Preparation and optical properties of silver nanowires and silver-nanowire thin films, J. of Colloid and Interface Science 356 (2011) 151-158.

[14] J.P. Kottmann, and O.J.F. Martin, Plasmon resonances of silver nanowires with nonregular cross section, Phys. Rev. B 64 (2001) 235402.

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