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Metal-Free and Carbon-Free Flexible Self-Supporting Thin Film Electrodes

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Abstract. Conductive polymers are promising for application in the medical and sport sectors, e.g. for thin wearable health monitoring systems. While many today's electrodes contain either carbon or metals as electrically conductive filler materials, product design manufacturing has an increasing interest in the development of metal free and carbon free, purely polymer based electrode materials. While conducting polymers have generally rather low electrical conductivities compared to metals or carbon, they offer broad options for industrial processing, as well as for dedicated adjustments of final product properties and design aspect, such as colour, water repellence, or mechanical flexibility in addition to their electrical properties. The development of electrically conducting polymer blends, based on conductive polymers is thus timely and of high importance for the design of new attractive flexible electrodes.

We have developed material formulation and processing techniques for the fabrication of self-supporting thin film electrodes based on polyaniline (PANI) and polyvinylidene fluoride (PVDF) blends. Electrical four-point probing was used to evaluate the electrode conductivity for different processing and fabrication techniques. Optical microscopy and atomic force microscopy measurements corroborate the observed electrical conductivity obtained even at low PANI concentrations revealing the nanoscale material distribution within the blends. Our self-supporting thin film electrodes are flexible, smooth, and water repellent and were furthermore successfully tested under bending and upon storage over a period of several months. This opens new perspectives for the design of metal free and carbon free flexible electrodes for medical, health, and sports applications.

Introduction

Conductive polymers are of interest for flexible and stretchable electrodes for application in the medical and sport sectors, e.g. for thin wearable health and bio-potential monitoring systems [1], as well as for printed electronics and flexible robotics [2]. The demand and potential of conductive polymers is broad for biomedical applications [3], as well as for smart textile applications [4].

While significant progress has been made in the design of conductive polymer nanocomposite electrodes for electrode applications, many today's electrodes used in the medical and sports sector contain either carbon or metals as electrically conductive filler materials [5-9].

Most of these metal-polymer and carbon-polymer composite materials do not exploit the conductivity of intrinsically conducting polymers (ICPs), such as polyaniline (PANI). Product design and manufacturing have an increasing interest in the development of metal free and carbon free, purely polymer based electrode materials. Although conducting polymers have generally rather low electrical conductivities compared to metals or carbon, they offer broad options for industrial processing, as well as for dedicated adjustments of final product properties including design aspect,

such as colour, water repellence, and mechanical flexibility in addition to their electrical properties. The development of flexible electrically conducting polymer blends, based on conductive polymers is thus timely and of high importance for the design of new attractive flexible electrodes.

PANI shows electrical conductivity in particular in its form as emeraldine salt (PANI-ES) [10]. The material itself is brittle and has poor mechanical properties with respect to stretching or flexibility [11]. In order to use PANI for flexible films and membranes, blending with another polymer is needed Polyvinylidene fluoride (PVDF) is a promising candidate for producing conductive flexible PANI-PVDF blends due the mechanical flexibility of PVDF combined with a large variety of possible processing methods [12]. Several techniques have recently been investigated to obtain PANI/PVDF blends, using e.g. solvent mixtures or in situ oxidative polymerization of aniline [12-14].

PANI-PVDF blends are however difficult to obtain, due to poor solubility of PANI in most organic solvents which are compatible with PVDF which in turn is known as an inherent hydrophobic material [15]. Furthermore, the electrical conductivity of PANI strongly depends on morphology, crystallinity, oxidation state and dopants, as well as interchain reactions [16].

In this paper, we demonstrate the successful fabrication of PANI-PVDF blends by electrospinning and by solvent casting using emeraldine PANI with PVDF. The presented processing protocols include as strategies heating to facilitate PANI recrystallization and the use of PEG to favour a homogeneous distribution of PANI in the PVDF matrix. A processing protocol for electrospinning is presented, as well as a processing protocol for the manufacturing of self-supporting conductive flexible PANI-PVDF films by solvent-casting. We present AFM data, which in phase contrast show percolation network formation for the conducting thin films.

Experimental

Blend Formulation for Thin Film Preparation by solvent casting. Blends of polyaniline emeraldine salt (PANI-ES) powder (Sigma Aldrich) and polyvinylidene (PVDF) pellets (Sigma Aldrich) were prepared.

The protocol for solvent casting is the following: 1) the PANI-ES is dissolved in dimethylformamide (DMF) by ultrasonication during 15 min at 25°C; 2) the solution is filtered through a membrane (5 µm pores); 3) polyethylene glycol 400g/mol (PEG-400, Sigma Aldrich) is added to the solution in order to favour homogeneous dispersion of PANI-ES particles that might crystallize from the solution; 4) PVDF pellets are then added to the PANI-PEG solution followed by magnetically stirring for 1h at 130°C; 5) The solution is then directly employed at 130°C for deposition by solvent casting, using 1 ml of solution per sample.

The employed mass percentages are: PANI 1.0 wt%, PEG 0.9 wt%, PVDF 7.8 wt%, DMF 90.3 wt%. Glass micro slides (75 mm x 25 mm, thickness (1.00±0.04) mm, Sigma Aldrich (Corning)) are used as substrates and were pre-heated and kept on a hot plate at 130°C during 5-10 minutes for drying in ambient air. Deposition without heating and annealing leads to brittle films. Films without PEG and without heating, were prepared for comparison by dissolving PANI-ES in a solvent mixture of DMF/acetone (85:15, v/v).

Taking into account that the solvent evaporates, the mass percentages of the resulting polymer films presented here are: 10.3 wt% PANI + 9.3 wt% PEG + 80.4 wt% PVDF for PANI-PEG-PVDF films and 9.5% PANI + 90.5% PVDF for PANI-PVDF films without PEG, i.e. the PANI amount is approximately 10% in either case.

Blend Formulation for PVDF/PANI membranes by electrospinning. PVDF nanofiber membranes were fabricated by electrospinning. This process was conducted at ambient conditions (25°C ±4°C). A flat ended needle (inner needle diameter of 0.4 mm) was used, with a needle-collector distance of 6 cm. 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 protocol for membranes formulation is the following: 1) PVDF solutions (40.3 wt%) are prepared dissolving 2g PVDF in DMAc/Ac 1:1 v/v and stirred during 30 min at 130°C on a hot plate; 2) Per membrane, 50 µl of PVDF solution were deposited with an electrospinning using a flux of 10

µl/min. The needle-collector voltage was set to 16 kV; 3) the homogeneous PVDF membranes were immerged for 24h in an acid solution of PANI and then rinsed with distilled water in order to remove excess PANI from the surface.

Two formulation routes were compared, one using PANI- ES and one using PANI-EB (polyaniline emeraldine base). Acid solutions of PANI-EB (Sigma Aldrich, powder) were obtained by adding a few droplets of 0.1M HCl aqueous solution into a PANI-EB/DMAc solution (1.5g PANI-EB + 30 ml DMAc) until a pH value below 2 was reached. Doping of PANI-EB with HCl was inspired by [13] and adapted for the here developed formulation protocol. PANI dissolves well in acids, contrary to PVDF which dissolves in organic solvents such as DMAc and DMF when stirred at elevated temperature. The use of an acid PANI-EB/DMAc solution is here twofold: the HCl provides the needed ions for protonation (doping) of PANI-EB in order to make it conductive and the DMAc contributes to wetting of the hydrophobic PVDF membranes when they are immerged into the acid solution. The acid DMAc solution does not dissolve PVDF at ambient temperature, as verified by immersion of PVDF membranes for 24h.

For comparison, also the use of acid solutions of PANI-ES was tested, e.g. 0.1g PANI-ES + 1 ml DMF + 10 ml HCl 0.1 M, ultrasound 15 min, nanofiber membrane immersion during 24h, followed by membrane drying in air.

Electrical Characterizations, Optical and Atomic Force Microscopy Analysis. The free standing electrode films and membranes were analysed by optical microscopy, AFM and electrical four-point probing.

For analysis of the homogeneity of samples, visual inspection and optical microscopy (LEICA Leica DMILM) were used. Nano- and microstructures of the films and membranes were investigated by Atomic Force Microscopy (AFM Park XE7), recording data at the top side of the films prior to peel-off (topography, amplitude signal and phase contrast) in soft tapping mode.

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 a linear behaviour 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 (π/ln2) for collinear probes [17, 18].

Results and Discussion

Free-standing PANI-PEG-PVDF thin films. Figure 1 shows a typical flexible conducting film of PANI-PEG-PVDF blend upon peel-off from the front (top) and from the back side; the latter was in contact with the glass substrate used for solvent casting.

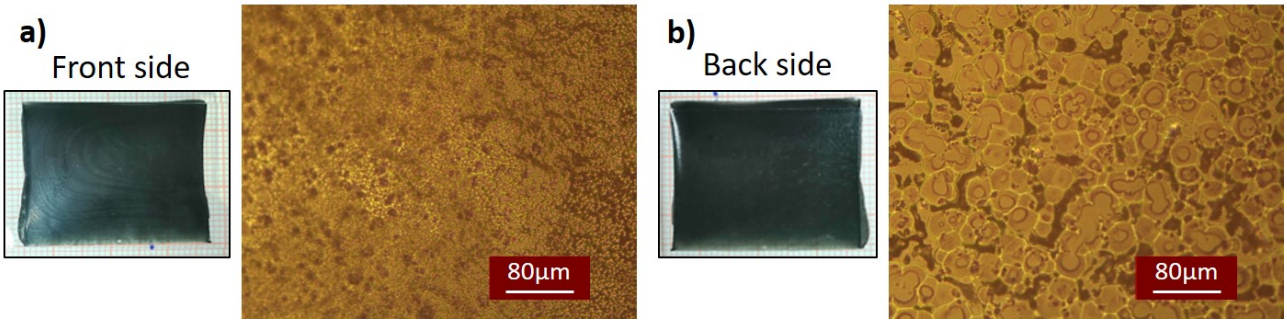

Fig. 1 Photographs and microscopy images of a PANI-PEG-PVDF film (10.3 wt% PANI/ 9.3 wt% PEG-400, PVDF 80.4%) upon peel-off, top(front)-side and bottom(back)-side are shown. The bottom side was in contact with the glass substrate during solvent casting.

The PANI-PEG-PVFD films are electrically conducting. Obtained average sheet resistance values range between $1.8 \cdot 10^5$ Ω/sq and $5.3 \cdot 10^5$ Ω/sq. The sample thickness was measured in side view by positioning the sample with the glass substrate in vertical position on the optical microscope. The thickest sample was 84.3 µm. Taking this value for a conservative estimate when calculating the

electrical conductivity σ, we obtain for our PANI-PEG-PVDF films conductivity values between $2.3 \cdot 10^{-4}$ Scm^{-1} and $6.4 \cdot 10^{-4}$ Scm^{-1}. Our best sample showed a conductivity of $1.44 \cdot 10^{-3}$ Scm^{-1} (based on an average sheet resistance value from four different zones and calculated with the measured layer thickness of 37.6 µm).

For comparison, solvent casting of PANI-PVDF blends with 10 wt% and 15 wt% PANI load with respect to the PVDF matrix (i.e. 9.1 wt% and 13 wt%, respectively, with respect to the total polymer) were reported with electrical conductivities of $4.6 \cdot 10^{-4}$ Scm^{-1} and $1.9 \cdot 10^{-4}$ Scm^{-1}, respectively [19 supporting material]; the authors used heating to 50°C during 6h and a hydraulic press in order to obtain PANI-PVDF wafers for electrical measurements; they furthermore report that the conductivity of the PANI-PVDF blends increases with increasing PANI load up to a load of 17.5% (i.e.14.9 wt% with respect to the total polymer weight) for which they report $3.1 \cdot 10^{-3}$ Scm^{-1}.

For our films, we did not use any press, but we observe that sheet resistance values measured at the front (top) side are about one order of magnitude higher than at the back side. In fact, the back side was in direct contact with the heated glass substrate during deposition and drying and shows a smoother surface with larger grains. Consistently, it shows a lower sheet resistance than the top surface. Further investigation is needed, to conclude to which extend PEG and the different heating process lead to the observed enhancement of the conductivity for our PANI-PEG-PVDF compared to pressed PANI-PVDF wafers.

In order to elucidate the nano- and microstructure of the conducting material, we have investigated the polymer blend surface by AFM, and in particular by phase contrast imaging. Fig. 2a shows AFM data of the conducting PANI-PEG-PVDF film (topography, amplitude and phase signals) measured on the top side of the sample shown in Fig. 1. Fig 2b shows for comparison AFM data of a non-conducting PANI-PVDF film. Taking into account that solvent evaporates, the mass percentages of the resulting polymer films are: 10.3 wt% PANI + 9.3 wt% PEG + 80.4 wt% PVDF (Fig. 2a) and 9.5% PANI + 90.5% PVDF (Fig. 2b), i.e. the PANI amount is approximately 10% in both cases.

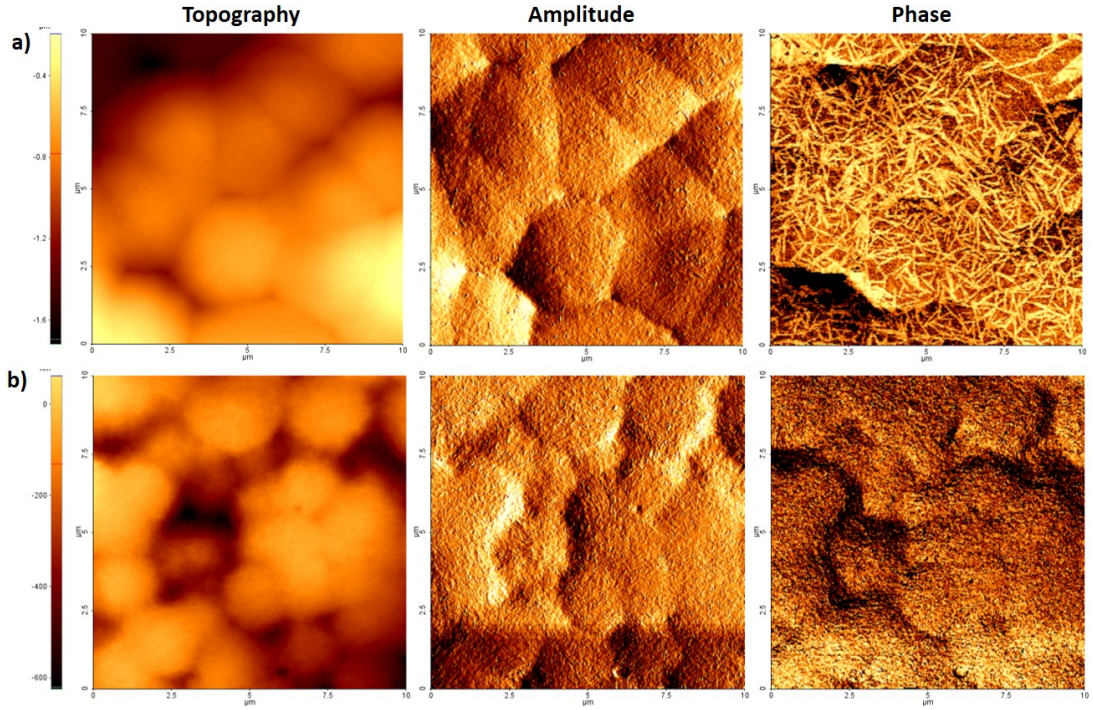

Fig. 2 AFM data (topography, amplitude and phase signals, scan size 10 µm x 10 µm) of PANI-PVDF solvent casted films. a) PANI-PEG-PVDF conducting film (blending ratios 10.3 wt% PANI, 9.3 wt% PEG, 80.4 wt% PVDF, substrate heated to 130 °C for deposition, kept at 130°C for about 5 min for drying), b) PANI-PVDF non conducting film (blending ratios 9.5 wt% PANI, 90.5% PVDF, substrate not heated for deposition).

Figure 3 shows AFM zoom images as acquired from a solvent casted sample of the conductive PANI-PEG-PVDF blend. A subgranular structure can be identified at smaller scale (Fig. 3c,d). The needle network structure (bright zones) as well as the dark zones show similar granularity in phase contrast images (Fig. 3d).

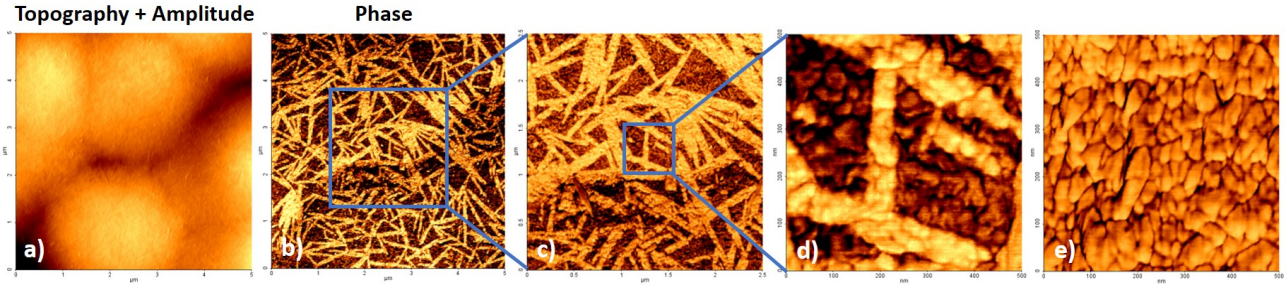

Fig. 3. AFM images PANI-PEG-PVDF. a) topography with amplitude signal (5 µm x µm), b)-d) phase contrast images: b) phase contrast of a), c) zoom 2.5 µm x 2.5 µm, d) zoom 500 nm x 500 nm, e) PANI-PVDF (without PEG and without heating) 500 nm x 500 nm (phase contrast).

Comparison with the PANI-PVDF blend (Fig. 3e) shows a similar granular structure, without needle like structures. We attribute the bright needle structures to conducting zones of PANI-PEG-PVDF blends at the surface and between grains. The formation of the needle like network is favoured by PEG, and by heating of the substrate during deposition and drying. The difference in phase contrast indicates a difference in the stiffness at the surface in these zones, which could be explained by possible incorporation of PEG in the needle area, as well as by a change in the crystallinity which may be at the origin of the conductivity of the PANI-PEG-PVDF blend.

In comparison, we found that PANI-PVDF films without PEG, when prepared by solvent casting on heated glass substrates, led a to less homogeneous distribution of PANI. The granular structure observed for PANI-PVDF films is also in optical microscopy very similar to the one of PANI-PEG-PVDF films. However, large crystalline PANI particles (sizes between 10 µm and 20 µm), partially embedded in PVDF are found on the PANI-PVDF samples (not shown here), contrary to the PANI-PEG-PVDF samples where PANI is homogeneously distributed. Complementary investigations are needed to fully understand the local chemical composition and crystallinity of the needle structure.

PANI coated electrospun PVDF membranes. Fig. 4 shows examples of PANI-PVDF nanofiber membranes and representative microscopy images of their surface for coatings performed in acid PANI-ES and PANI-EB solutions. While we observe in case of PANI-ES, the formation of detaching powder agglomerates at the surface of the PVDF membranes upon immersion (Fig. 4a), the use of the acid PANI-EB DMAc solution (prepared as described in the experimental section), leads to a rather homogeneous distribution of PANI on the membrane surface as can be appreciated by the greenish colour of the nanofiber membrane (Fig. 4b). Some zones appear dark green; some zones are light greenish. Furthermore, the PANI stays attached to the membrane also when scratching or weeping over the membrane surface.

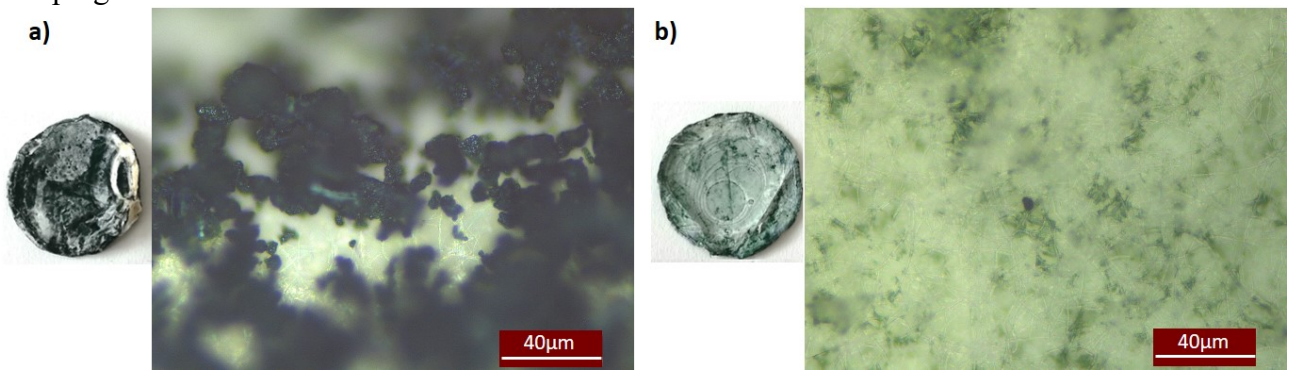

Fig. 4. Electrospun PVDF membranes (diameter 25 mm) upon immersion in acid PANI solutions prepared from a) PANI-ES, b) PANI-EB.

Electrical four-point measurements on PANI-PVDF membranes produced from the PANI-EB acid solution show an average sheet resistance of $3.3 \cdot 10^6$ Ω/sq, (values range from 1.2 $\cdot 10^6$ Ω/sq to $6.6 \cdot 10^6$ Ω/sq depending on probing positions). To the contrary, PANI-PVDF membranes produced from the PANI-ES solution do not show any sufficient conductivity for measurements by four-point probing, indeed, two-point probing with a multimeter shows infinite resistance.

As PANI stays mechanically attached to PVDF (Fig. 4b) for electrode fabrication from the acid PANI-EB solution, we further investigate the PANI incorporation at the membrane surface by analysing the phase contrast images acquired by AFM. Figure 5 shows AFM data of a PANI-PVDF membrane as produced by immersion in the acid PANI-EB solution. The nanofiber network at the membrane surface is clearly observed at a scan size 30 µm x 30 µm (Fig. 5a). The phase contrast images show material incorporation in the membrane. At smaller scan size ((Fig. 5b), 2.5 µm x 2.5 µm) merged submicrometric grains are observed.

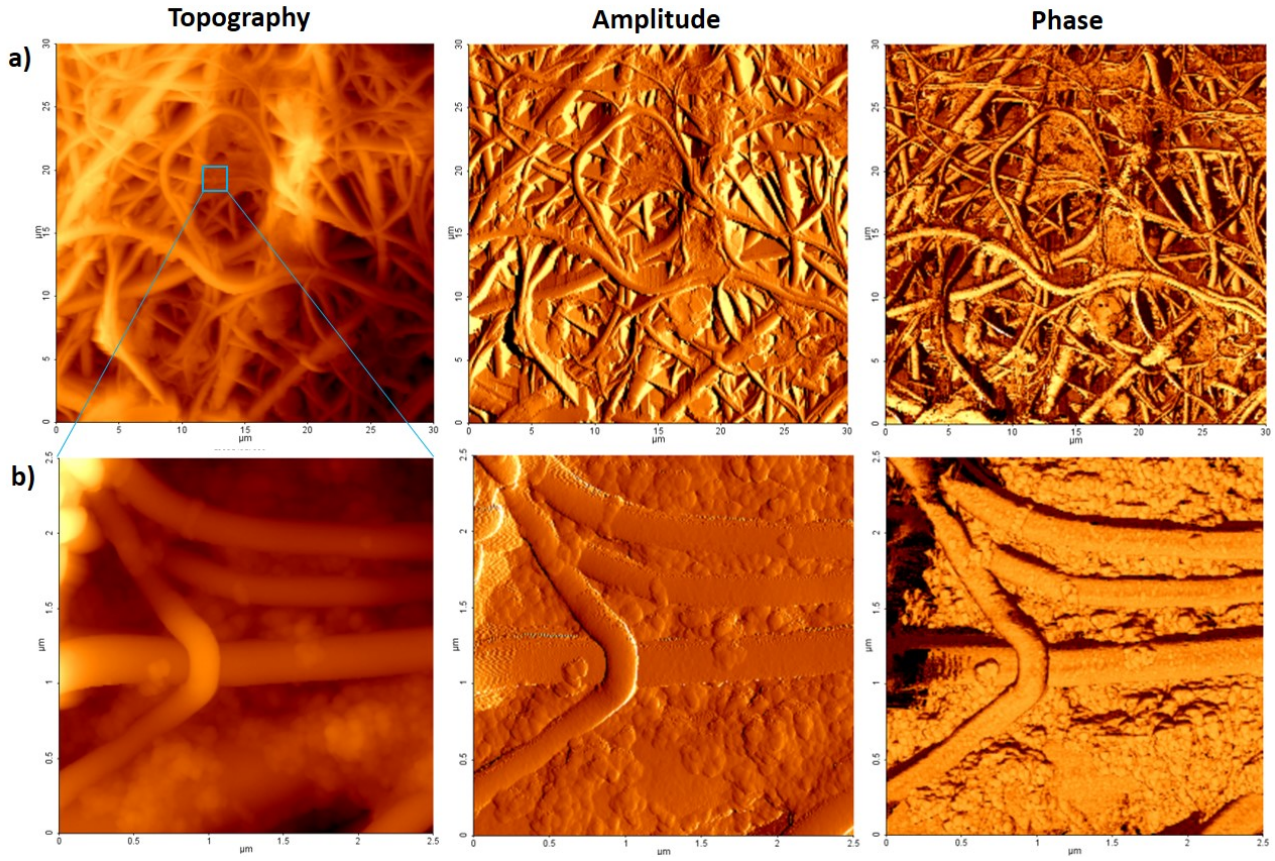

Fig. 5. AFM data (topography, amplitude and phase signals) of a PANI-PVDF membrane as produced from immersion of an electrospun PVDF membrane into the acid PANI-EB solution. The nanofiber network at the membrane surface is clearly observed at a scan size 30 µm x 30 µm (a). The phase contrast image shows material incorporation in the membrane. At smaller scan size ((b), 2.5 µm x 2.5 µm) merged submicrometric grains are observed, which can be attributed to PANI incorporated into the membrane at the surface of the fibers.

We attributed the observed merged granular structure to PANI. The grains are found dense and partially merged forming connected area between the fibres of the network (Fig. 4a). Although DMAc is also a solvent for PVDF, the PVDF nanofibers with smooth surface are still clearly recognized in the AFM data (Fig. 5), thus the PVDF nanofiber surface is not dissolved or attacked during immersion in the acid PANI-EB solution at ambient temperature. PANI-PVDF blending, if any, takes thus place only at the surface of the nanofibers were PANI attaches.

Most PANI grain structures are found merged, forming dense zones that are trapped in between the PVDF nanofiber network at the surface of the PVDF membrane. The appearance of the granular structure is consistent with the one of synthesised PANI nanoparticles observed in scanning electron microscopy [20] and also compares with observations of PVDF nanofiber coating by *in situ* oxidative polymerization reactions of aniline [14] Therefore, we conclude that the observed granular structure in between the nanofiber network (Fig. 5), provides the pathways for electrical conductivity. The obtained PANI-PVDF membranes are flexible and foldable.

For individual PANI grains attached to the polymer nanofiber surface, as observed in Fig. 5b, the appearance in AFM phase contrast compares well to SEM observation of Khalifa et al. [19] who have studied electrospun blend composites based on PANI and halloysite nanotubes in a PVDF matrix.

The results show that our direct coating of PVDF nanofiber membranes with PANI using PANI-EB in acid solution provides a highly promising route for the manufacturing of flexible conductive electrodes. Further studies using higher PANI concentration and optimising temperature, as well as possible sonication during immersion are expected to further decrease the sheet resistance of the electrodes and to allow for reduced immersion duration.

Summary

In summary, we have successfully developed two material formulation and fabrication routes for metal-free and carbon-free flexible electrodes based on PANI-PVDF blends.

First, our developed blend formulation based on PANI-ES and PEG as additives in PVDF for solvent casting on a heated glass substrate, allows for the production of conducting free-standing flexible thin films. Without any mechanical pressing, our films exhibit electrical conductivities that compare well with values reported for pressed PANI-PVDF wafers of similar PANI load. A percolation network structure, attributed to PANI is revealed in atomic force microscopy phase contrast images. Further investigation is needed, to elucidate how PEG and the heating process lead to the observed conductivity enhancement.

Second, we developed a processing protocol for successful coating of PVDF nanofiber membranes using an acid PANI-EB solution.

Our novel metal-free and carbon-free flexible electrode materials are highly promising for further optimization of the PANI load and processing parameters in view of upscaling and tailored manufacturing for applications as flexible electrodes in biomedicine, sports, flexible robotics, and bio-signal monitoring.

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