Strain-Invariant, Highly Water Stable All-Organic Soft Conductors Based on Ultralight Multi-Layered Foam-Like Framework Structures

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Soft and flexible conductors are essential for the development of soft robots, wearable electronics, electronic tissue, and implants. However, conventional soft conductors are inherently characterized by a large change in conductance upon mechanical deformation or under alternating environmental conditions, e.g., humidity, drastically limiting their application potential. This work demonstrates a novel concept for the development of strain-invariant, highly elastic and highly water stable all-organic soft conductors, overcoming the limitations of previous strain-invariant soft conductors. For the first time, thin film deposition technologies are combined in a three-dimensional fashion, resulting in micro- and nano-engineered, multi-layered (<50 nm), ultra-lightweight (<15 mg cm\(^{-3}\)) foam-like framework structures based on Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) and Polytetrafluoroethylene (PTFE), characterized by a highly strain-invariant conductivity (≈184 S/m) between 80% compressive and 25% tensile strain. Both the initial electrical and mechanical properties are retained during long-term cycling, even after 2000 cycles at 50% compression. Furthermore, the PTFE thin film renders the framework structure highly hydrophobic, resulting in stable electrical properties, even when immersed in water for a month. Such innovative multi-scaled and multi-layered functional materials are of interest for a broad range of applications in soft electronics, energy storage and conversion, sensing, water and air purification, as well as biomedicine.

1. Introduction

Today’s electronics, such as smart phones or laptops, are typically based on semiconducting and metallic conductors. However, due to their rigid nature, the application of these conventional electronic components in fields of wearable electronics, soft robotics, as well as electronic implants is limited. In order to develop innovative functional electronic devices, that can naturally interact with soft living matter or improve human-machine interaction, new soft (bio-)electronic materials and components such as actuators, sensors, as well as soft and flexible conductors have to be designed.\[1–4\] Conventional approaches for the fabrication of soft and flexible conductors include geometric engineering of non-stretchable conductors into stretchable patterns,\[5,6\] incorporation of conductive fillers, such as carbon nanomaterials, into an elastomeric matrix\[7\] or the plastination of conductive polymer (CP) thin films through additives.\[8\] Advanced fabrication methods include the use of aerogels and multi-scaled framework structures based on conductive nanomaterials, e.g. Graphene or Carbon Nanotubes,\[9–11\] as well as conductive polymers (CPs).\[12–14\] Especially, the latter provides a) the intrinsic capacity for both compressive and tensile strains without failure, b) high conductivities at ultra-light weight, and c) adjustable mechanical compliance. Further benefits are breathability, high specific surface area, improved mass and charge transport and higher availability of active sites.\[12\] While

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in combination these properties make three-dimensional (3D) aerogels, foams and framework structures promising candidates for the development of high-performance soft conductors, their electrical properties are extremely susceptible to mechanical deformation or changes in environmental conditions, e.g. humidity. For example, 3D CP foams, framework structures and aerogels are typically characterized by a piezo-resistive effect, i.e., a change in resistance upon mechanical deformation. This effect is often utilized to create strain and force sensors based on CPs.[15–18] Furthermore, 3D porous framework structures are prone to changes in their mechanical response, which for example manifests as cyclic softening, i.e., the decrease in stress at a given strain upon repeated deformation.[13,19,20] And finally, the conductivity of CP foam-like structures and their composites are prone to water absorption, which can be utilized for sensing applications,[21–23] but makes its electrical properties dependent on ambient humidity.

However, for applications in the fields of soft robotics, wearable electronics and electronic tissue technologies constant electrical and mechanical characteristics of conductors, irrespective of deformation state or environmental conditions, e.g. humidity, are of uttermost importance. For example, a reliable electrical readout, and control of electronic components, such as sensors and actuators, connected or integrated into a single soft matrix, can only be achieved by a strain-invariant response of the conductor, i.e., a constant resistance upon deformation. Furthermore, if the soft conductor is a load-bearing component or is used to drive an actuator in soft robotics, a response with constant mechanical properties is required.

In this work we present a novel approach, in which we combine wet-chemical and dry-chemical thin film technologies in a 3D fashion to develop innovative multi-scaled and dual-layered foam-like composite framework structures. We show, that the as prepared composites are characterized by a set of properties that surpass that of the individual materials, enabling completely new functionalities and thus application scenarios. As a first demonstration of this concept, in this work we focus on the development of multi-scaled framework structures based on Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and Polytetrafluoroethylene (PTFE). Utilizing a ceramic template, highly porous (porosity up to 99.6%) and highly conductive (≈184 S m⁻¹) PEDOT:PSS framework structures are fabricated by a wet chemical approach, consisting of thin films (<50 nm) in the form of a network of interconnected hollow microtubes. The approach is based on the synthesis of multi-scaled framework structures of PEDOT:PSS, which forms a network of interconnected hollow microtubes. This 3D macroscopic thin film structure is further functionalized with an insulating PTFE thin film coating of on average ≈23 ± 10 nm via initiated chemical vapor deposition (iCVD), a vapor based free-radical polymerization technique, that has emerged as a highly efficient method for conformal polymer coatings down to nanoscale thicknesses even in complex 3D geometries.[24–27] Similar to conventional wire insulation, the applied PTFE thin film coating acts as an insulting layer between the PEDOT:PSS microtubes. Thereby, the previously piezo-resistive PEDOT:PSS framework structure is converted into a strain-invariant soft conductor with constant conductivity between 80% compressive and 25% tensile strain, without changing the overall morphology of the framework structure. Both, the initial electrical and mechanical properties are retained during long-term cycling at 50% compression. Furthermore, the PTFE thin film coating results in an enhancement of the mechanical flexibility and stability of the PEDOT:PSS framework structure. Lastly, the PTFE functionalization greatly reduces water absorption, which enables constant electrical properties even after 30 days immersed in water. Whereas other state-of-the-art strain-invariant conductors may feature one of the previously mentioned characteristics, the here presented approach excels in all of them (see Tables S1 to S3, Supporting Information), thereby overcoming the aforementioned limitations of aerogels and foam-like framework structures for soft electronics.

2. Results

2.1. Synthesis

The schematic synthesis route for the PEDOT:PSS framework structure (Aero-PEDOT:PSS) and its subsequent functionalization via iCVD is shown in Figure 1A. The synthesis uses highly porous (>94%) sacrificial templates of interconnected zinc oxide (ZnO) microrods, which have proven to be a suitable pathway for the dry-chemical and wet-chemical assembly of nanomaterials into macroscopic and lightweight 3D networks.[9,10,28] The ZnO templates are prepared by a molding process (Figure 1A, Step 1), in which the geometry as well as density of the final template can be controlled. Infiltration of an aqueous PEDOT:PSS solution by dripping leads to a homogenous distribution throughout the porous network (Figure 1B and Video S1, Supporting Information; for further details see Methods). Divinyl sulfone (DVS) is used as low temperature cross-linking reagent, as it allows evaporation of the solvent without strong capillary forces damaging the framework structure.[29,30] After evaporation of the solvent a thin film of PEDOT:PSS remains on the ZnO microrods (Figure 1A, Step 2). The homogeneity of the thin film deposition without any filtration effect was confirmed through detailed scanning electron microscopy (SEM) studies (Figure S1, Supporting Information). The film thickness and therefore total density of the resulting material can be controlled by either adjusting the concentration of PEDOT:PSS in the solutions or the amount of infiltrations. Freestanding Aero-PEDOT:PSS frameworks are then obtained by wet-chemical etch-removal of the sacrificial ZnO and critical point drying (Figure 1A, Step 3). With densities between 3.8 and 15.0 mg cm⁻³ the obtained framework structures are highly porous (>99.8%) and ultra-lightweight, i.e., readily attach to nearby objects such as tissue paper (Figure 1C). Furthermore, the template-based approach can be utilized to fabricate framework structures that can be specifically controlled in their macroscopic size and geometry (Figure 1D).

By controlling the amount of infiltrated PEDOT:PSS during synthesis the density (3.8–15.0 mg cm⁻³) and the corresponding conductivity (22.9–174.8 S m⁻¹) of Aero-PEDOT:PSS can be adjusted (Figure 1E; measurement setup see Figure S2, Supporting Information). While the conductivity could also be controlled by changing the density of the initial ZnO network, since the addition of ZnO microrods equals more electrical
pathways, this parameter was kept constant in this work. As highlighted by the conductivity of PEDOT:PSS-ZnO prior to etching (Figure 1E), the etching is bifunctional, since it not only removes the sacrificial ZnO template, but also increases the conductivity by 59% on average. X-ray photoelectron spectroscopy (XPS) analysis of the ratios between the Sulfur 2p peaks of PEDOT and PSS confirms, that the mechanism is the removal of non-conductive PSS through etching, which reduces the ratio between PSS and PEDOT by ~5.56% (Inset Figure 1E; detailed deconvolution given in Figure S3, Supporting Information). Finally, the as-prepared Aero-PEDOT:PSS framework structures are functionalized with a thin layer of PTFE via iCVD (Figure 1A, Step 4, and Figure 1F). Here, the monomer gas hexafluoropropylene oxide (HPFO) (orange) is thermally...
decomposed at a hot filament into a trifluoroacetyl fluoride byproduct (white) and difluorocarbene (red). The PTFE thin film is then formed by adsorption and chain-growth of the difluorocarbene on the previously synthesized Aero-PEDOT:PSS (blue). The film growth is furthermore accelerated through addition of the thermally activated initiator perfluorobutane-sulfonylfluoride (PFBSF) (not shown). The resulting film thickness can be controlled via process parameters such as deposition rate or deposition time of the process. Besides a detailed experimental description of the iCVD process in the Methods, an in-depth description of the process and its governing parameters is given elsewhere.[24,34]

2.2. Morphology and Chemical Characterization

For all subsequent investigations of the properties of the here demonstrated porous conductors, Aero-PEDOT:PSS with a density of ≈25 g cm⁻³ has been used and the deposition parameters for the iCVD functionalization were kept constant. Scanning electron microscopy (SEM) was used to investigate the resulting microstructure of Aero-PEDOT:PSS and Aero-PTFE-PEDOT:PSS. The non-functionalized Aero-PEDOT:PSS (Figure 2A) consists of a network of interconnected hollow microtubes resembling the tetrapodal ZnO structure of the template with partial sail-like formation in between the microtubes (detailed image overview see Figure S4, Supporting Information). The iCVD PTFE deposition does not change the overall morphology of the network (Figure 2B). The comparison of individual Aero-PEDOT:PSS arms before and after PTFE coating shows no distinct differences in SEM and indicate a thin and conformal coating (Figure S5, Supporting Information).

A more detailed investigation of the nanostructure of the PEDOT:PSS films with and without iCVD deposition of PTFE was carried out using transmission electron microscopy (TEM). Due to the highly flexible nature of Aero-PEDOT:PSS and Aero-PTFE-PEDOT:PSS extraction of single microrods suitable for TEM analysis is not feasible. Instead, structures with intact ZnO cores yet identical coatings of PEDOT:PSS and subsequent iCVD PTFE deposition were investigated. The amorphous polymer shell can readily be distinguished from the crystalline ZnO core by mass-thickness as well as diffraction contrast (Figure 2C,D) in bright field (BF) TEM. Thus, the thickness of the PEDOT:PSS and PTFE-PEDOT:PSS thin films can be determined from the change in gray values within the TEM micrograph. Investigation of numerous microrods yields ≈16 ± 3 nm thickness for the PEDOT:PSS layer. As stated previously, a small amount of PSS is assumed to be removed in the process of ZnO etching. Thus, the thickness in Aero-PEDOT:PSS is assumed to be slightly less than the value determined here. After iCVD coating a clear increase in average polymer shell thickness of ≈23 ± 10 nm is determined, giving an average of ≈39 ± 10 nm for the PTFEPEDOT:PSSZnO system.

Both polymers possess a unique element, i.e., sulfur (S) for PEDOT:PSS and fluorine (F) for PTFE. Therefore, the presence of the polymers can be inferred from the presence of S and F in the shell respectively. Spatially resolved energy dispersive X-ray spectroscopy (EDX) via scanning TEM (STEM) EDX mapping of a microrod coated with both PEDOT:PSS and PTFE (Inset Figure 2D) clearly shows a shell containing both S and F around the ZnO core with an outer layer containing no S. Accordingly, the successful iCVD deposition of PTFE on PEDOT:PSS is strongly supported. However, the difference in average shell thickness before and after iCVD coating with PTFE (≈23 ± 10 nm) is much larger than this apparent PTFE layer thickness of ≈3 nm. It can thus be concluded that at least partial intermixing of the polymers takes place. In order to unambiguously verify PTFE deposition additional investigation via complementary methods was performed.

To investigate the chemical structure of PEDOT:PSS before and after PTFE functionalization Fourier transformation infrared spectroscopy (FTIR) was used. Figure 2E shows the FTIR spectra of PEDOT:PSS (blue) and PTFE-PEDOT:PSS (red) between 2000 and 500 cm⁻¹ (wide spectra see Figure S6, Supporting Information). In both cases characteristic absorption peaks of PEDOT:PSS are present. The peaks at 1583 and 1537 cm⁻¹ are related to the C≡C stretch in PSS and PEDOT respectively. At 1307 cm⁻¹ the C≡C stretch and at 1137 cm⁻¹ the C=O−C stretch of PEDOT can be seen (all peaks given in Table S4, Supporting Information).[33,35] A successful cross-linking reaction between DVS and PSS to form vinyl sulfone ethyl sulfate is confirmed by the signature peak at 1270 cm⁻¹ (not indicated).[29,30] The highlighted area shows the differences introduced by the PTFE deposition. While the peak ≈1220 cm⁻¹ corresponds to asymmetrical C-F2 stretching, its overlap with the C-O-C absorption band of PEDOT at 1207 cm⁻¹ allows no clear identification without deconvolution. However, the unique peak at 1163 cm⁻¹ is attributed to symmetrical C-F2 stretching of PTFE, thus indicating a successful deposition of PTFE.[36,37] This is additionally confirmed by XPS, since for Aero-PTFE-PEDOT:PSS typical Fluorine peaks with F KLL at 833.5 and 859.5 eV (Figure S7, Supporting Information) and F 1s at 688.9 eV (Figure S8, Supporting Information) appear. Furthermore, the carbon C 1s spectrum shows the presence of a C-F2 peak at 292.0 eV attributed to PTFE (Figure 2F), which is not present in unfunctionalized Aero-PEDOT:PSS (Figure S9, Supporting Information).[24,36] Noticeably, for a PTFE film thickness exceeding the signal depth in XPS (<10 nm) the C 1s spectrum is expected to be dominated by the C-F2 contribution, which is not the case here. A possible explanation is that the porosity created by the etch-removal of PSS allows for local intermixing of PTFE and PEDOT:PSS, thus reducing the overall film thickness in Aero-PTFE-PEDOT:PSS. While the exact nanostructure in Aero-PTFE-PEDOT:PSS is yet to be determined, the functionalization nevertheless leads to drastic changes in its physical properties compared to its unfunctionalized counterpart, as will be demonstrated in the following paragraphs.

2.3. Strain-Invariant Conductance and Elasticity

The electrical and mechanical properties of samples with an initial density of ≈7.5 mg cm⁻³ and a corresponding conductivity of 377 ± 70 S m⁻¹ were tested before and after PTFE deposition using a custom made setup (Figure S9, Supporting Information). The stress–strain curves for different compression cycles (40–80%) for Aero-PEDOT:PSS (Figure 3A) and
Aero-PTFE-PEDOT:PSS (Figure 3B) both show the typical response of porous 3D framework structures. A minor linear regime (I) is followed by a plateau region (II) and finally a strong non-linear behavior in the densification region (III). Compared to Aero-PEDOT:PSS the maximum stress at 80% compression increases for Aero-PTFE-PEDOT:PSS from 22.7 kPa to 24.1 kPa, while the Young’s modulus increases from 0.92 kPa to 7.92 kPa. Because of the high porosity these values are considerably lower than for bulk PEDOT:PSS (765 MPa) or bulk PTFE (2.3 GPa), making them suitable for tissue compliant electronics. Overall, the PTFE coating gives rise to reversible compression up to 80% with a low residual strain of 2% compared to 60% for Aero-PEDOT:PSS (Figure 3C and Video S2, Supporting Information). The explanation for this is based on the densification and formation of new interconnections between structural elements of...
Figure 3. A) Compressive stress–strain curve between 40% and 80% compression for Aero-PEDOT:PSS. B) Compressive stress–strain curve between 40% and 80% compression for Aero-PTFE-PEDOT:PSS. C) Photographic series highlighting the response to 80% compression for Aero-PTFE-PEDOT:PSS (left) and Aero-PEDOT:PSS (right). Scale bar (red) is 6 mm. D) Schematic depiction of compression process and the formation of new interconnections (white circles) upon densification of the network elements. E) Normalized resistance $R/R_0$ versus subsequent compression cycles (40%–80%) for Aero-PEDOT:PSS. F) Normalized resistance $R/R_0$ versus subsequent compression cycles (40%–80%) for Aero-PTFE-PEDOT:PSS. G) Tensile stress–strain curve until material failure for Aero-PEDOT:PSS and Aero-PTFE-PEDOT:PSS. H) Normalized resistance $R/R_0$ versus tensile strain for Aero-PEDOT:PSS and Aero-PTFE-PEDOT:PSS.
the network upon compression (Figure 3D). In the absence of a PTFE barrier layer, as is the case for Aero–PEDOT:PSS, adhesive forces between the new connections reduce the elastic restoring force and lead to plastic deformation and/or rupture upon unloading. The PTFE encapsulation of the PEDOT:PSS network partially negates this effect due to the extremely low surface energy of PTFE.\(^{[40]}\) Additionally, PTFE acts as insulating layer due its low dielectric constant,\(^{[24,40]}\) which can be seen in the distinct differences in the normalized electrical resistance \(R/R_0\) for consecutive compression cycles (40%-80%) for Aero–PEDOT:PSS (Figure 3E) and Aero–PTFE–PEDOT:PSS (Figure 3F). The non-linear piezoresistive response of Aero–PEDOT:PSS with \(R/R_0 = 0.30\) at 80% compression is caused by the formation of new conductive pathways during compression. A net increase in resistance upon uploading is associated with the reduction of conductive pathways due to residual strain or material failure. Aero–PTFE–PEDOT:PSS on the other hand is highly strain-invariant over a wide range with \(R/R_0 = 0.95\) at 80% compression. The stark contrast in behavior is indirect proof for the completeness of PTFE coverage throughout the PEDOT:PSS framework structure. Since a soft conductor component ideally should be able to withstand both compressive and tensile load, maximum tensile strain tests were performed (Figure 3G). For Aero–PEDOT:PSS an ultimate tensile strength of 0.62 kPa and strain at fracture of 16.1% can be seen. The stretchability for Aero–PTFE–PEDOT:PSS is improved to a tensile strength of 2.16 kPa and fracture at 47.9% strain. Almost no change in the elastic modulus between Aero–PTFE–PEDOT:PSS and Aero–PEDOT:PSS can be observed, which is in agreement with previous investigations on the mechanical properties of framework structures based on hollow microtubes,\(^{[41]}\) where it was shown that for low strains the elasticity of the framework structures is determined by its microstructure. Aero–PEDOT:PSS is clearly piezoresistive at any given tensile strain, while Aero–PTFE–PEDOT:PSS remains strain-invariant up until 25% strain with \(R/R_0 = 1.04\) (Figure 3H). In comparison to PEDOT:PSS thin films the 3D porous structure therefore features two advantages: First, it improves the stretchability with an elongation at break of up to \(\approx 16\)% and \(\approx 48\)% respectively compared to a commonly reported \(\approx 5\)% for PEDOT:PSS thin films.\(^{[19]}\) And second, by taking the compression into account Aero–PTFE–PEDOT:PSS shows stable electrical properties over a wide range of deformation of up 105%. The combination of both large scale deformation and strain-invariant conduction could not have been obtained through conventionally used PEDOT:PSS thin films or their composites.

The long-term stability of the materials was tested for 2000 cycles at 50% compression. The stress–strain curves for the first and last cycle show less residual strain for Aero–PTFE–PEDOT:PSS (4.5%) compared to Aero–PEDOT:PSS (35.1%) (Figure 4A). Aero–PTFE–PEDOT:PSS is prone to changes in its mechanical properties (Figure 4B), indicated by a decrease in stress at maximum compression (\(\sigma = 3.2\) kPa, \(\sigma/\sigma_0 = 0.84\)) and a decrease in the energy loss coefficient \(Q_c\), i.e., the area ratio between loading and unloading curve with respect to the loading curve, from 0.63 to 0.30 (calculation see Supporting Section 8). Aero–PTFE–PEDOT:PSS shows a constant maximum stress (\(\sigma_0 = 5.06\) kPa, \(\sigma_{\text{rel}} / \sigma_0 = 0.98\)) and a constant loss coefficient (\(Q_0 = 0.28\), \(Q_{\text{rel}}/Q_0 = 0.96\)). Compared to the literature, Aero–PTFE–PEDOT:PSS shows remarkably stable mechanical properties without any cyclic softening, outperforming any other porous or aeromaterial so far reported (see Table S1, Supporting Information). The normalized resistance \(R/R_0\) versus compression for the 1st and 2000th cycle for both materials is given in Figure 4C (exemplary raw data given in Figure S10, Supporting Information). The piezoresistive Aero–PTFE–PEDOT:PSS suffers from a continuous increase in resistance at all compression ranges due to ongoing plastic deformation. On the other hand, Aero–PTFE–PEDOT:PSS is highly stable with only minor deviations at maximum compression. While \(R/R_0\) at zero compression shows no change, the resistance at 50% compression changes from 0.98 on the first to 0.95 on the last cycle (Figure 4D). Compared to the literature, the cyclic stability in its electrical response of Aero–PTFE–PEDOT:PSS matches that of the most stable strain-invariant conductors reported so far (Table S2, Supporting Information). While Chen et al. reported a strain-invariant PEDOT:PSS-BIBSAT foam with similar performance and structure, this approach however suffers from a 4-fold increase in resistance even after 20 min in water.\(^{[13]}\)

### 2.4. Water Stability

Contact angle measurements were performed to determine the wetting characteristics before and after PTFE functionalization. In case of Aero–PEDOT:PSS no contact angle can be measured, since the water droplet is immediately absorbed upon contact (Figure 5A and Video S3, Supporting Information). On the other hand, Aero–PTFE–PEDOT:PSS is strongly hydrophobic with an average contact angle of \(\approx 139 \pm 4\)°, which remains stable over a duration of 10 min and longer. To test the effect of the functionalization on the swelling behavior, the swelling ratio \(m/m_0\) was measured for different samples for up to 30 days in water (Figure 5B). As Aero–PTFE–PEDOT:PSS is too hydrophobic to be submerged in water without force (Videos S4 and S5, Supporting Information), the samples were held under water using a porous sieve. Aero–PEDOT:PSS with a final swelling ratio of 12.94 is prone to quick swelling, which leads to visible bulging of the samples (Figure 5B, left photograph). On the other hand the strong hydrophobicity of Aero–PTFE–PEDOT:PSS is highlighted by the formation of a distinct air layer underwater (Figure 5B, right photograph), and a drastic reduction in water uptake with \(m/m_0 = 1.21\) after 30 days. Finally, the electrical characteristics for Aero–PEDOT:PSS and Aero–PTFE–PEDOT:PSS were measured for samples immersed in water for 30 days using a custom made setup (Figure 5C). After 30 days, the final normalized resistance \(R/R_0\) for Aero–PEDOT:PSS is at 2.30 due to water absorption, whereas it is only 1.24 for Aero–PTFE–PEDOT:PSS (Figure 5D), highlighting the good protective properties against swelling. Our approach matches the water stability of the best performing other approaches (see Table S3, Supporting Information), which however either sacrifice the benefits of a 3D porous network by using an elastomeric filler\(^{[42]}\) or maintain the porosity, but show strain-variant conductance.\(^{[43]}\)
3. Conclusion

In summary, we demonstrate a new concept for the development of an ultralight, strain-invariant and highly water stable soft conductor. The concept is based on the coating of piezoresistive microtubular framework structures by a nanoscopic insulating polymer layer, by which the macroscopic properties of the framework structure, such as mechanical, electrical, as well as wetting characteristics, can be tailored in a controlled manner. We specifically demonstrate, that ultra-light weight (< 15 mg cm⁻³), piezo-resistive PEDOT:PSS framework structures with a conductivity of up to 184 S m⁻¹, can be converted into strain-invariant soft conductors with constant conductivity between 80% compressive and 25% tensile strain by coating them with a nanoscopic insulating thin film (~23 nm) of PTFE. While the coating results only in a negligible weight increase, it enhances the mechanical flexibility and stability of the PEDOT:PSS framework structure, additionally providing highly hydrophobic properties. In combination, these properties overcome previous limitations of strain-invariant soft conductors with stable electrical properties, resulting in an attractive functional material system for application in the fields of soft robotics, wearable electronics, as well as electronic tissue and implants. Especially for the field of electronic tissue and implants the here demonstrated conductor can act as a soft, flexible and biologically inert wire to connect different electronic devices, such as actuators (e.g., artificial muscles) and sensors. Here, both the constant electrical as well as mechanical response are of utmost importance for reliable performance. Second, as mechanically compliant 3D porous networks have a high potential to form intimate surfaces with organic tissue and host cells, adjustments to the wettability of the functionalized...
surfaces of the conductor can enable the fabrication of interpenetrating composite materials and biohybrid electronic devices. One approach to control the wettability is readily available in iCVD, since it allows one-step depositions of nanoscale gradient copolymer thin films, that change from one polymer to another within the same film.[27] For example, even the transition from a hydrophobic insulator into a hydrophilic hydrogel is possible. Alternatively, simple and effective protocols for the hydrophilization of hydrophobic surfaces like PTFE via Polydopamine functionalization have been reported.[44] While in this study, we focus on strain-invariant all organic soft conductors based on PEDOT:PSS and PTFE, this concept can be further transferred to tailor the properties of other ultra-lightweight framework materials and open porous aerogels, e.g. based on carbon or related nanomaterials, which have already demonstrated huge potential in a wide variety of applications, such as energy conversion, energy storage, thermal management, sensing, catalysis, water and air purification, as well as biomedicine. In summary, the here demonstrated concept represents a versatile approach to develop innovative functional soft materials and composites, by altering the macroscopic and microscopic properties of porous materials by a nanoscopic thin film coating process in 3D.

4. Experimental Section

Preparation of ZnO Networks: ZnO tetrapods were prepared by flame transport synthesis, which has been described in great detail elsewhere.[43,44] In short, sacrificial 3D networks of ZnO were prepared by mold forming ZnO tetrapods powder into the desired geometry. After subsequent sintering for 5 h at 1150 °C in ambient conditions mechanically stable, interconnected ZnO networks were obtained.

Preparation of PEDOT:PSS Solutions: Prior to usage PEDOT:PSS solution (Heraeus Clevios PH1000) was tip sonicated and filtered with a PES syringe filter (0.45 µm pore size). Aqueous solutions between 0.1 to 0.6 wt% PEDOT:PSS were made by mixing a given volume of the pristine solution with deionized water and 5% v/v ethylene glycol, 3% v/v EtOH and 5% v/v divinyl sulfone (DVS) as cross-linking reagent. After heavy stirring for 3 min the solutions were immediately used. The

Figure 5. A) Water contact angle measurement for Aero-PEDOT:PSS (top) and Aero-PTFE-PEDOT:PSS (bottom). Aero-PEDOT:PSS absorbs the droplet immediately, whereas the functionalized material shows a stable contact angle of ≈138°. B) Swelling ratios of Aero-PEDOT:PSS and Aero-PTFE-PEDOT:PSS after immersion in water for up to 30 days. The photographs indicate the swelling behavior. While bulging due to swelling is observed for Aero-PEDOT:PSS (white arrows), for Aero-PTFE-PEDOT:PSS a distinctive layer of air forms under water (red arrows), which highlights the strong hydrophobicity obtained through the PTFE coating. C) Experimental setup for IV-measurement immersed in water (bottom) and photograph of the setup (top). The porous samples are immersed in deionized water after being contacted with two metal electrodes. D) Normalized resistance \( R/R_0 \) for Aero-PEDOT:PSS and Aero-PTFE-PEDOT:PSS after 30 days in water demonstrating the improved water stability of Aero-PTFE-PEDOT:PSS.
solutions were kept at a fridge in between infiltration cycles. For each new sample series fresh solution was prepared.

**Synthesis of Free-Standing 3D PEDOT:PSS Networks:** The deposition of PEDOT:PSS onto the ZnO arms was carried out by dripping the freshly prepared PEDOT:PSS solution onto the template until the respective free volume was filled. After evaporation of the solvent and initiation of the cross-linking reaction on a hot-plate (4 h, 55 °C, air) the infiltration process was repeated multiple times. After completion of all infiltration and drying cycles, the networks were completely immersed in aqueous acid solution of 10 m HCl for 24 h. After repeated rinsing with deionized H2O and pure EtOH, the samples were dried by critical point drying (EMS 3000).

**CVD Coating of Aero-PEDOT:PSS:** The fabricated Aero-PEDOT:PSS samples were coated with a PTFE thin film via initiated chemical vapor deposition (iCVD). The monomer HFPO was combined with the initiator PFBSF for this purpose. Details on the iCVD reactor used can be found in the literature.[25] The samples were coated in a continuous flow process. The substrate temperature of 20 °C was maintained by a thermostat (CC-K8, Huber) and a power of 72 Watt was applied to the NiCr filament (Goodfellow) array during the deposition by a power supply (Polars 65-10, Knurr-Heinzinger). The process pressure of 50 Pa in the reactor was maintained by a butterfly valve (VAT, 615, instruments) attached to the reactor. The vacuum was generated by a rotary van pump (Duol 10, Pfeiffer Vacuum). The Monomer HFPO (0.5 sccm) was supplied to the reactor via a mass flow controller (MC, Alicat scientific) and the initiator PFBSF (0.1 sccm) was delivered to the reactor via needle valve (Varian).

**Conductivity Measurements:** Cylindrical samples (height 6 mm, diameter 6 mm) were attached to a custom made electrode holder (see Figure S1, Supporting Information) via silver conductive paste. Afterward, linear voltage sweeps using a Keithley 2401 in 4 wire sense mode were performed. The conductivity for each sample was calculated from averaging the slope from 10 sweeps and 3 different samples.

**Electromechanical Characterization:** Cylindrical samples (6 mm height, 6 mm diameter) were used for all electromechanical characterization tests. By using silver adhesive paste, Aero-PTFE-PEDOT:PSS samples were contacted to a thin strip of copper foil featuring a one-sided removable protective layer prior to functionalization. Afterward, removal of the protective layer allows for electrical contact post functionalization. All samples were contacted to a custom made electromechanical characterization setup (Märzhäuser Wetzlar HS 6.3 micromanipulator, burster 9235/36 force sensor) via silver conductive paste (see Figure S9, Supporting Information). All measurements were performed at a voltage of 0.5 V.

**Fourier Transform Infrared Spectroscopy (FTIR):** A solution with 0.25 wt.% PEDOT:PSS was used to deposit thin films via spin-coating (Laurell WS-650-23B) on 20×20 mm Silicon substrates. Prior to deposition the Si substrates were immersed in Piranha solution to increase hydrophilicity. After spin-coating at 400 rpm for 1 min, the samples were dried at 65 °C on a hot plate for 6 h. The resulting film thickness of ~400 nm was measured by profilometry (Bruker DektakXT). PTFE functionalization was performed via iCVD by depositing for 30 min at 72 W with flows for PFBSF of 0.1 sccm and HFPO of 0.5 sccm. FT-IR spectra of functionalized and non-functionalized samples were obtained in a range from 4000 to 500 cm⁻¹ in air (Bruker INVENIO). Background correction and peak analysis was performed using Origin 2022 software.

**X-Ray Photoelectron Spectroscopy (XPS):** For XPS analysis (Omicron Nanotechnology GmbH, Al Kα X-ray anode, 240 W power) aero-samples with a geometry of 10 × 10 × 2 mm samples were prepared. Prior to analysis a thin strip of 100 nm gold was sputter-deposited on the edge of the samples for binding energy reference. For binding energy calibration the Au 4f⁷/₂ peak (84.00 eV) was used as reference value. Peak analysis was performed using the CasaXPS software.

**Electrical Characterization Underwater:** Cylindrical samples (6 mm height, 6 mm diameter) were contacted to a custom made electromechanical characterization setup (Figure 5C). At first the UI-curves were measured using a constant voltage of 0.5 V for 1000 min. Afterward, the conductivity and resistance values per day were calculated by taking the average from 10 linear voltage sweeps from ~0.5 to +0.5 V.

**Contact Angle Measurement:** For contact angle measurements samples with a geometry of 30×10×2 mm were fabricated. Static contact angle measurements (OCA 30, Dataphysics) were performed by depositing 10 µL droplets of deionized water onto the surface.

**Swelling Behavior:** For the estimation of water uptake cylindrical samples (6 mm height, 6 mm diameter) were immersed in deionized water. Aero-PTFE-PEDOT:PSS were held under water by a porous sieve. After the respective amount of days, samples were removed from the water, put on tissue to remove excess water for a fixed amount of time (1 min) and their weight was measured using a microscale (Sartorius Micro MCi). Swelling ratios were calculated by comparison to the initial weight in dry state.

**Microstructure:** An SEM Ultra 55 (Zeiss) had been used to perform scanning electron microscopy at a scanning distance of 3 mm and acceleration voltage of 3 kV. Samples were glued to custom made holders prior to measurements.

**Transmission Electron Microscopy (TEM):** TEM analysis had been performed with a FEI Tecnai F30 S Twin operated at 300 kV. Samples were prepared for TEM analysis by gentle grinding a small portion of a template submerged in n-Butanol in a mortar. The resulting suspension was drop coated onto lacey carbon coated copper TEM grids. After drying in air single microrods were readily available for analysis. By simultaneously utilizing material of all areas from a cross sectional template a random selection of microrods was achieved. Film thicknesses had been estimated by taking 4–7 measurement points at 12 separate locations for each sample. To enhance image contrast, an objective aperture was placed around the primary beam reflection for true bright field TEM imaging.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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