Conformal Cu coating on electrospun nanofibers for three-dimensional electro-conductive networks

Fuze Jiang $^{1,2}$, Wenbo Ju $^{2}$, Zhengyuan Pan $^{1,2,3}$, Luchan Lin $^{2}$, Yang Yue$^{1,2}$, Yi-Bo Zhao $^{1,2}$, Congju Li $^{4}$, Frank Clemens $^{2}$, Corsin Battaglia $^{2}$, Jing Wang $^{1,2,*}$

F. Jiang, Z. Pan, Dr. Y. Yue, Y.-B. Zhao, Prof. J. Wang
Institute of Environmental Engineering
ETH Zürich
Stefano-Franscini-Platz 3, 8093 Zürich, Switzerland
E-mail: jing.wang@ifu.baug.ethz.ch

F. Jiang, Dr. W. Ju, Z. Pan, Dr. L. Lin, Dr. Y. Yue, Y.-B. Zhao, Dr. F. Clemens, Dr. C. Battaglia, Prof. J. Wang
Empa, Swiss Federal Laboratories for Materials Science and Technology
Überland Strasse 129, 8600 Dübendorf, Switzerland

Z. Pan
School of Light Industry and Engineering
South China University of Technology
Guangzhou 510640, China

Prof. C. Li
School of Energy and Environmental Engineering
University of Science and Technology Beijing
Beijing 100083, China

Keywords: electroless copper plating, polydopamine, electrospun nanofiber, conformality, three-dimensional electrode

Abstract

Electro-conductive nanofiber networks with high flexibility have potential applications as gas diffusion electrodes (GDEs) in flexible electrochemical devices. Here, we develop flexible GDEs, based on a versatile method of conformally coating a Cu layer on membranes consisting of stacked electrospun nonconductive polymer nanofibers. The Cu coating, comprising of fine-grained Cu crystals, has an average thickness of circa 50 nm and a root-mean-square roughness of circa 5.3 nm, maintaining the topography of polymer nanofibers. For nanofiber membranes with a thickness ranging in a micrometer scale, the conformal Cu layer coats all nanofibers in the outermost layers as well as in the bulk of the membrane. All demonstrated Cu coated nanofiber networks have sheet resistance $< 2.4 \, \Omega\cdot\text{cm}$, and gas permeability in the order of $10^{-13}$ to...
10^{-15} m^2, which are comparable to some commercialized carbon based micro-/nanofiber GDEs. Particularly, these conductive nanofiber networks have excellent bending durability, with negligible conductivity degradation after 10000 bending test cycles. The high conductivity, gas permeability, and flexibility of these three-dimensional nanofiber networks allow for potential applications into various flexible electrochemical devices.

1. Introduction

Electro-conductive micro- / nanofiber networks are capable of conjoining solid, liquid, and gaseous (three-phase) interfaces, and thus have been widely used as gas diffusion electrodes (GDEs) in many applications, such as environmental sensing,[1] wearable and flexible electronics,[2-5] and electrochemical energy conversion.[6-7] Carbon fiber based networks, including non-woven carbon papers and woven carbon cloths, are commonly used as rigid GDEs,[8-9] while carbon nanotube based GDEs have recorded applications in flexible and stretchable electronic devices.[10] In contrast, polymer fiber based conductive networks, which can be made of pure conductive polymers (e.g. polypyrrole),[11] copolymers of conductive / nonconductive compounds,[12] and polymers doped with carbon nanotubes[13-14] or metal nanoparticles and precursors,[15-16] have more favorable mechanical properties for flexible and stretchable devices. An alternative approach is to conformally coat nonconductive polymer fibers by a conductive layer in a nanometer scale to form a conductive network topologically.[2,17-18] Some of the advantages of these conductive networks include mechanical flexibility, tunable porosity and tortuosity, and an unlimited number of compositional and processing possibilities, which allow for adaptations of these electrodes into various flexible devices.[18] This concept of making conductive networks inspires the innovation of three-dimensional GDEs with high flexibility and stretchability, and gas permeable structures possessing functionalized surfaces.
Electrospinning has a proven potential for producing polymer fibers with diameters in the sub-micrometer range.\cite{8} Electrospun nanofiber meshes or mats are used as templates for fabricating metal based conductive networks (see Table 1).\cite{2, 17, 19-24} A metal layer prepared by physical vapor deposition (PVD) is confined to the line of sight of the sputtering target due to the shadowing effect. Thus it forms topologically a metal network on top of polymer nanofibers, which is identified with a two-dimensional conductive network.\cite{2, 19-20}

Conformal metal coating on a three-dimensional structure requires homogeneous growth of a metal layer conforming to the topology of a substrate. Electroless plating, which is based on an autocatalytic process on the surface, is capable of forming metal layers on all surfaces exposed to the plating solution. Several pioneering works demonstrated electroless plating on fibrous materials, including carbon nanofibers,\cite{23} and knitted\cite{22} or nonwoven\cite{17, 24-25} polymer fibers (see Table 1). Lin et al. have successfully deposited a conformal Cu layer on three-dimensional knitted polymer microfibers (circa 20 $\mu$m in diameter).\cite{22} However, for polymer nanofibers, electroless metal plating is limited to the surface of dispersed nanofibers\cite{23}, or the outermost layers of nanofiber mats.\cite{24-25} The conformal metal coating on three-dimensional nanofiber mats is seldom reported. The challenges come from inhomogeneous distribution of noble metal nuclei (e.g. Pd/Sn, Ag/Sn) on the substrate, insufficient mass transport, and different reaction kinetics due to different local environments.\cite{26-28} Moreover, nanofibers have relatively low tolerance to surface roughness. In order to address these challenges, a systematic improvement in surface activation, mass transport, and surface roughness control should be achieved. Lee et al.\cite{29} introduced self-assembled polydopamine (pDA) as a surface activation material for versatile electroless metal plating. The pDA layer coats the substrate conformally, providing uniform active sites for metal ion adsorption and metal nucleation.\cite{30-31} Macroconvection and microstructure design advantage the mass transport in pores among nanofibers.\cite{32} The deposition controlled by its kinetics instead of mass transport can approach identical growth rate.\cite{33}
In this work, we demonstrate a versatile method for producing three-dimensional conductive networks by conformally coating a Cu layer on pDA activated polymer nanofibers. Electrospun polyacrylonitrile (PAN), polycaprolactam (nylon), polyvinylidene fluoride (PVDF), and expanded polytetrafluoroethylene (ePTFE) nanofiber membranes are employed as substrates, in order to investigate the versatility of this coating method on polymers with different hydrophilicity. The electrospun polymer nanofibers, both in the outermost layers and in the bulk of the membrane, are conformally coated by a Cu layer with an average thickness of circa 50 nm. The root-mean-square (RMS) roughness of deposited Cu layers remains lower than circa 5.3 nm. The nanofiber networks with well-balanced combination of electrical conductivity, gas permeability, mechanical flexibility, and electrode active area satisfy the requirements for GDEs possibly used in flexible electrochemical devices.

2. Results and Discussion

2.1. Characterization of Polymer Nanofiber Membranes

A scheme of fabricating Cu coated electrospun nanofiber networks is presented in Figure 1. The detailed description of each step is in the experimental section. PAN, nylon, and PVDF nanofiber membranes are prepared by electrospinning, while ePTFE membranes are fabricated by biaxially stretching a PTFE membrane. The top-view SEM images of the four kinds of nanofiber membranes are shown in Figure 2a1 to 2d1, respectively. The corresponding high-resolution SEM images are shown in Figure 2a2 to 2d2. During hot lamination, fused junctions form in electrospun nanofiber membranes due to pressing of molten polymers (see regions marked by yellow circles in Figure 2a1, 2b1, and 2c1). The fused junctions enhance the mechanical strength of membranes, and improve the connections of nanofibers in different layers. The microstructure of ePTFE membrane is comprised of nodes and radially distributed nanofibers (Figure 2d1), which is different to those of the other three kinds of membranes. The diameters of the four kinds of nanofibers are quantified by analyzing the top-
view SEM images, following Gaussian distributions. The mean values of Gaussian fittings are noted in Figure 2a to 2d. For nylon and ePTFE nanofibers, the mean values of diameters are smaller than 100 nm. In contrast, the diameters of PAN and PVDF nanofibers distribute mainly in the several hundred nanometer range. The water wettability of the four kinds of nanofiber membranes are analyzed by water contact angles shown in Figure S1a to S1d in the Supporting Information (SI). PAN and nylon nanofiber membranes are identified with hydrophilic materials, according to the criterion of contact angles smaller than 90°. In contrast, PVDF and ePTFE nanofiber membranes are hydrophobic. The order of wettability of the four kinds of nanofiber membranes from high to low is shown in Figure S1e in SI.

2.2. Polydopamine Coated Polymer Nanofibers

The surfaces of all the four kinds of polymer nanofibers are activated by grafting a self-assembled pDA layer formed by a dopamine polymerization process. The pDA possesses the ability of binding versatile substrates. The growth of pDA on nanofibers consists of three stages: (1) sub-monolayer growth, (2) formation of a complete and conformal pDA layer, and (3) growth of three-dimensional pDA agglomerates. The growth of pDA to the second stage is optimal for further conformal Cu coating. Both the sub-monolayer pDA coating and the formation of pDA agglomerates can significantly increase the surface roughness of Cu coating via influencing the initial nucleation conditions. However, the precise control of pDA growth to the second stage is challenging in practice, especially for preparing large-scale samples.

Figure 3a1 to 3d1 show the SEM images of pDA coated nanofibers with overgrown pDA agglomerates. The agglomerates, protruding from the surface of nanofibers and growing into the pores, have changed at least the morphology of outermost layers of nanofiber membranes. In the ePTFE membrane, pDA forms thin films among nanofibers in addition to particulate agglomerates (Figure 3d1).
An ultrasonic treatment of the pDA activated nanofibers is applied to selectively remove overgrown pDA agglomerates, remaining the completely and conformally coated pDA layers. Conformal pDA layers have higher structure stability as compared with pDA agglomerates, so that they have higher tolerance to mechanical peeling under ultrasonication.\cite{37,39} Figure 3a\textsubscript{2} to 3d\textsubscript{2} show the pDA activated nanofibers after ultrasonic treatments. Very rare pDA particles can be observed on the surface. For pDA activated ePTFE, some pDA thin films among nanofibers still exist after ultrasonication (Figure 3d\textsubscript{2}), indicating the high mechanical strength of pDA layers and the strong binding of pDA with ePTFE. The reason for higher mechanical strength of pDA layers as compared with that of pDA agglomerates is still unknown. Lee et al.\cite{29} reported that the thickening of pDA thin films had a saturated value of circa 50 nm. The further polymerization of dopamine follows the mechanism of forming random pDA agglomerates instead of pDA layers.\cite{37-38} Thus we consider that the order degree of pDA plays a significant role in mechanical strength. In contrast with less-ordered pDA agglomerates, well-ordered pDA thin films have enhanced mechanical strength. The diameter distributions of pDA activated electrospun nanofibers are shown in Figure S2 in SI. After pDA coating, the mean values of diameters remain similar, or increase slightly, for all the three kinds of electrospun nanofibers, indicating a negligible thickness of the pDA layer.

2.3. Cu Deposition on Polymer Nanofibers

Electroless Cu coating on pDA activated polymer nanofibers is performed in a precursor consisting of 50 mM CuCl\textsubscript{2} and 50 mM ethylenediamine tetraacetic acid (EDTA). The bath additive EDTA sequesters Cu\textsuperscript{2+} ions to form a chelated compound [CuEDTA]\textsuperscript{2-}. The redox pair [CuEDTA]\textsuperscript{2-} / Cu\textsuperscript{0} has a standard electrode potential of -0.216 V vs. standard hydrogen electrode (SHE), which is 0.556 V more negative than that of the redox pair Cu\textsuperscript{2+} / Cu\textsuperscript{0} (+0.340 V vs. SHE).\cite{26} Thus with the same reducing agent the reduction of [CuEDTA]\textsuperscript{2-} to Cu\textsuperscript{0} is kinetically slow. The concentration of free Cu\textsuperscript{2+} ions is estimated to be 22 nM by chemical equilibrium modelling. In the heterogeneous process, Cu\textsuperscript{2+} ions are adsorbed by the active sites
provided by the catecholamine group in pDA layers, then the adsorbed Cu$^{2+}$ ions are chemically reduced to metallic Cu by borane dimethylamine complex (DMAB) in neutral media. The process can be expressed by two half reactions as below:

\[
3\text{Cu}^{2+} + 6e^- \rightarrow 3\text{Cu}
\]

\[
2(\text{CH}_3)_2\text{NH}:\text{BH}_3 + 6\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{BO}_3 + 6\text{H}^+ + 2(\text{CH}_3)_2\text{NH} + 3\text{H}_2 + 6e^-
\]

In the reaction, hydrogen (H$_2$) forms as a byproduct. Cu deposition is characterized by three sequential phases: (1) nucleation, (2) growth of crystallites, and (3) coalescence of crystallites into a continuous layer. The time-dependent morphology of Cu deposits is investigated using PAN nanofibers as substrates. Figure 4 shows the SEM images and the corresponding sketches of Cu coated PAN (Cu-PAN) nanofibers after 1-hour, 2-hour, and 4-hour Cu deposition. After 1-hour deposition (Figure 4a), small isolated grains form on the pDA layer. According to the high contrast between the particulate structure and the uncovered surface of nanofibers in the high-resolution SEM image (inset in Figure 4a), we assign these small grains to Cu, and the uncovered surface to PAN. Here, Cu grains do not coalesce to a complete Cu layer. Due to the substrate effect from the pDA layer, well-ordered nanoscale Cu grains form and grow with an increasing film thickness. The coalescence of those segregated grains leads to form small grains boundaries which locally reduce the resistance across the boundary. Figure 4b shows the SEM images of nanofibers after 2-hour Cu deposition. The Cu-PAN has a fibrous topography with little amount of particulate deposits on top. In the high-resolution SEM image (inset in Figure 4b), there is slightly discernable contrast among different regions on nanofibers, indicating a uniform composition on the surface. In this phase, Cu crystals coalesce to a complete layer, and the Cu layer coats the PAN nanofibers conformally. Similarly, a conformal Cu layer forms on nylon or PVDF nanofibers after 2-hour deposition (Figure S3a and 3b in SI). On PTFE nanofibers, Cu deposits on the pDA thin films among PTFE nanofibers, in addition to the pDA coated PTFE nanofibers (Figure S3c in SI), forming Cu plates in the outermost layers of the nanofiber mat. Further extension of deposition time results in the formation of Cu...
clusters (Figure 4c). The clusters agglomerate on nanofibers and in pores, covering the original fibrous structure. In the high-resolution SEM image (inset in Figure 4c), the Cu clusters are identified with aggregates of Cu nanocrystals, possessing a porous structure. The growth of Cu clusters is influenced by the reaction conditions, the adsorbed H2 bubbles, and the crystal texture underneath.[30, 42, 45] Well-ordered Cu grains on a pDA layer coalesce to a conformal Cu layer. In contrast, the further growth of Cu clusters on the Cu texture is templated by H2 bubbles adsorbed at the solid / liquid interface, leading to porous structures.[46] The Cu clusters can be removed by ultrasonic treatment, while the conformal Cu layer shows high tolerance to ultrasonication. Therefore, the pDA layer is considered to have a substrate effect on the growth of directly bound Cu grains, and the substrate effect vanishes from the secondary contact. The binding strength of the pDA layer to Cu grains seems not to be weakened by the H2 produced in the reaction.

2.4. Characterization of Deposited Cu Layers

For an individual Cu coated nanofiber, a core-shell structure, i.e., a polymer nanofiber core and a Cu/pDA shell, can be deduced from the fabrication process, and is confirmed by the cross-sectional SEM image of Cu coated PVDF (Cu-PVDF) nanofibers (Figure 5a). Based on the assumptions of uniform Cu coating along the radial direction and negligible pDA thickness, the diameter of a Cu coated nanofiber equals the sum of the initial diameter of the polymer nanofiber, and the double thickness of the Cu layer. Figure 5b compares the diameter distributions of PVDF nanofibers before and after Cu coating. The experimental data are fitted with Gaussian functions. The diameters of PVDF nanofibers have a mean value of 272 nm, while the mean value increases to 366 nm after Cu coating, corresponding to a circa 47 nm thick Cu layer. For Cu coated PAN and nylon nanofibers, the mean values of diameters increase from 372 to 478 nm, and from 90 to 174 nm, respectively, corresponding to a 53 nm Cu layer on PAN and a 43 nm Cu layer on nylon (Figure S4a and S4b in SI). Interestingly, the thickness of Cu layers on the three kinds of electrospun nanofibers falls into the range of 42 to 53 nm.
after a 2-hour deposition, and it is not strongly influenced by the original diameters of the polymer nanofibers. The thickness of Cu layers agrees very well with the work of Cu deposition on a pDA activated polymer sheets by Merkel et al.[30] Nakahara and Okinaka [47] proposed that Cu deposits initiated as fine-grained crystals on the catalytically active sites. The fine-grained crystals had sizes in the range of 50 to 200 nm, which agreed with the size of anomalously grown grains.[48] Thus we consider that the conformal Cu layer with a thickness ranging from 42 to 53 nm is comprised of fine-grained crystals which contact directly with the pDA layer.

Figure 5c shows the X-ray diffraction (XRD) patterns of PVDF, pDA activated PVDF (pDA-PVDF), and Cu-PVDF nanofibers. A diffraction peak at 36.5˚ (marked as a triangle in Figure 5c) can be observed in all the three patterns, which is assigned to the crystalline nature of fused junctions in the PVDF membrane. The pattern of Cu-PVDF consists of the main peaks of Cu crystalline phases and a small peak of Cu$_2$O (220), confirming the deposits mainly as metallic Cu. The formation of Cu$_2$O leads to a charging effect and surface potential variations as compared with pure Cu coated nanofiber.[44] Similar XRD patterns are obtained for Cu coated nylon (Cu-nylon) and Cu-PAN nanofibers (Figure S5 in SI).

A Cu-PVDF membrane with a geometric area of 0.79 cm$^2$ is assembled as an electrode for investigating the electrochemical properties of the Cu surface. The cyclic voltammograms (CVs) of the Cu-PVDF electrode are measured in an Ar saturated 0.1 M KHCO$_3$ solution (pH 8.8) (Figure 5d). In the CV for the Cu redox reaction (orange curve in Figure 5d), the oxidation peaks with onsets at 0.07 V and 0.38 V can be observed, corresponding to the adsorption of hydroxide ion on Cu and the formation of Cu$_2$O, respectively.[49] The reduction peak in the potential range from 0.5 to 0.24 V can be assigned to the reduction of Cu$_2$O. In the CV for the H$_2$ evolution reaction (HER) (blue curve in Figure 5d), the Cu surface is active for the HER at potentials < -0.2 V vs. reversible hydrogen electrode (RHE). The double layer capacitance ($C_{dl}$) of the Cu-PVDF electrode is determined by a series of CVs at various scan rates measured in the double layer potential range (Figure S6a in SI). Figure S6b in SI shows the linear fitting of
the double layer currents plotted against the scan rates, deducing a $C_{dl}$ of 983.4 µF. The $C_{dl}$ is divided by a value of 28 µF·cm$^{-2}$\cite{46,50} resulting in the electrochemical surface area of 35.12 cm$^2$. As compared with the geometric area of 0.79 cm$^2$, the porous Cu-PVDF electrode provides a 45 times larger surface active area.

### 2.5. Conformality of Cu Coating on Nanofibers

Nanofibers after conformal Cu coating maintain their initial topography, and their surface has a relatively low roughness. Figure 6a shows a top-view SEM image of Cu-PVDF. The surface of Cu-PVDF nanofibers is continuous and smooth. Figure 6b shows the atomic force microscopy (AFM) topographic image. In the selected region in Figure 6b, a high-resolution AFM image is captured, and shown in Figure 6c. The RMS roughness of this region is circa 5.3 nm, indirectly confirming the formation of small Cu grain boundaries as the grain size ($d$) in the direction of film thickness (Cu-PVDF) reaches to circa 47 nm\cite{43}. Both the top-view SEM and AFM images confirm the conformal Cu coating on PVDF nanofibers in the outermost layer of the membrane.

An 8-µm-thick Cu-PVDF membrane is encapsulated in epoxy resin, then the sample is mechanically polished to expose a cross-section of the membrane for investigating the coating quality on polymer nanofibers in the bulk of the membrane. Figure 7a shows a cross-sectional SEM image of the sample. Nanofibers, both in the outermost layers and in the bulk, show a similar structure of a bright circle surrounding a dark core. The elemental mapping of the cross-section shows that Cu distributes mainly along the bright circles (Figure 7b), while fluorine (F) locates in dark cores (Figure 7c). Since F stems from the PVDF, the F-rich regions are considered to be PVDF nanofibers. The elemental mapping confirms the core-shell structure of each Cu-PVDF nanofiber throughout the bulk of the membrane.

The success of a conformal Cu coating on a three-dimensional fibrous structure is attributed to the use of pDA activator, and the appropriate control of reaction conditions. In addition, high compactness of electrospun nanofiber membranes is required for a high quality of conformal
Cu coating. Two PVDF nanofiber membranes with different levels of compactness are monitored with an inverted microscope during electroless Cu plating. H₂ produced in the heterogeneous reduction coalesce to H₂ bubbles.¹⁵¹ H₂ bubbles trapped in pores among nanofibers force the expansion of the less compact PVDF nanofiber membrane, leading to blisters (Figure 8a, and Movie S1 in SI). The nanofibers surrounding a H₂ bubble lose partial contacts with the solution, resulting in insufficient mass transport. Thus H₂ bubble blockage increases the inhomogeneity of Cu coating. In contrast, for the compact PVDF membrane treated by hot lamination, the formation of big blisters is efficiently suppressed by the constraint of nanofibers (Figure 8b). Movie 2 in SI shows the frequent release of small H₂ bubbles from loose parts of the nanofiber membrane. Strainful nanofibers prevent the growth of H₂ bubbles, and force them to detach from nanofibers at small sizes (Figure 8c). This phenomenon can be identified with structure-enhanced microconvection. Combining a strong macroconvection in the solution, the H₂ bubble detachment and the reactant supply can be significantly improved, facilitating the homogeneous growth of a Cu layer.

2.6. Electrical Conductivity, Bending Durability and Gas Permeability

The sheet resistance (Rs) of Cu coated nanofibers is characterized by a four-point probe setup. The Rs of Cu-PVDF is lower than 2.4 Ω. For Cu-nylon and Cu-PAN, the Rs is lower than 1.9 Ω and 2.2 Ω, respectively, which is similar to or even lower than those of carbon based nanofiber mats (see Table 2).²²,⁵²-⁵³ Conformally Cu coated nanofiber networks are conductive not only in the same plane, but also between the two opposite surfaces. Figure 9a and 9b demonstrates a Cu-PVDF sheet (5 cm × 8 cm) as an electrical conductor in a circuit. The connection of two pins either in the same plane (Figure 9a), or on two opposite surfaces (Figure 9b), is able to close the circuit for lightening of a red light-emitting diode. The Rs of Cu coated nanofibers remains similar after 7-month storage under ambient conditions (see Table S2 in SI). A bending test is performed on a Cu-PVDF electrode. The geometry and testing parameters are illustrated as insets in Figure 9c. The ohmic resistance of the Cu-PVDF electrode is measured
along the longitudinal direction, showing an initial resistance of 3.3 Ω. After repetitive bending for 10000 cycles, the resistance increases slightly to 4.5 Ω. Interestingly, the resistance increases by 0.8 Ω in the first 1000 bending cycles, while from 1000 to 10000 cycles it increases only by 0.4 Ω, indicating an enhanced resistance to fracture of the Cu layer. The Cu coated nanofiber networks are therefore capable of being used as bending-durable electrodes.

Air pressure drop through an 8-µm-thick Cu-PVDF electrode is measured at different air face velocities from 9.96 to 99.60 cm·min⁻¹. Figure 10a shows the pressure drop through the electrode as a function of air face velocity. Here we observe a linear pressure drop response versus the air face velocity. The intrinsic permeability of 1.56 × 10⁻¹⁴ m² for air is extracted applying Darcy's law.[54] The geometric parameters of the Cu-PVDF electrode, including the diameter distribution and the membrane thickness, are acquired by analyzing the top-view and cross-sectional SEM images. Based on the intrinsic permeability and the geometric parameters, a virtual 3D fibrous model for the Cu-PVDF electrode is generated using the PaperGeo module in GeoDict (inset in Figure 10a). The details for modelling and simulations are provided in the SI. The pore size distribution of Cu-PVDF is estimated by fitting spheres into the pore volume among nanofibers based on the virtual fibrous model.[55] Typical pore sizes range from 0.5 to 1 µm (Figure S7a in SI). The porosity of the Cu-PVDF electrode is ~ 77%. The simulated air pressure drop across the Cu-PVDF fibrous model agrees very well with the experimental results (Figure 10a). A 3D air flow field is simulated based on the virtual Cu-PVDF fibrous model at an air face velocity of 44.3 cm·min⁻¹ (see Figure 10b). Big pores provide more effective pathways for air flow. At the face velocity of 44.3 cm·min⁻¹, the simulated pressure drop is 98.6 Pa. The intrinsic permeability of Cu-nylon and that of Cu-PAN is 4.31 × 10⁻¹⁵ m² and 2.41 × 10⁻¹³ m², respectively (Figure S7b in SI). The three kinds of Cu coated electrospun nanofibers have intrinsic permeability in the order of 10⁻¹³ to 10⁻¹⁵ m², which is comparable to that of carbon-based nanofiber mats prepared by pyrolyzing electrospun polymer nanofibers (see Table 2). Despite of similar electrical conductivity and gas permeability, Cu coated nanofibers
allow various modifications of surface composition via Cu alloying, rather than carbon based nanofibers. Thus they are capable of being used as a model substrate for supporting active materials for electrochemical processes under gas diffusion conditions. Five intrinsic properties of four kinds of three-dimensional GDEs are compared in Figure 11. The criteria for rating the scores are listed in Table S3 and S4 in SI. The Cu coated nanofiber networks have predominant advantages in fiber diameter and bending durability. The electrodes based on the conformal coating technique shown in this work have been successfully demonstrated in the application of GDEs with a Sn/Cu surface for electrochemical CO₂ reduction reaction.[56]

3. Summary and Perspective

Three-dimensional conductive networks are successfully produced by pDA assisted electroless Cu coating on polymer nanofiber membranes. The self-assembled pDA activation layer provides uniform active sites to adsorb Cu ions and catalyze Cu deposition. Via substrate effect, this activation layer influences the growth of Cu fine-grained crystals, leading to a smooth, continuous and conformal Cu coating. The Cu layer has an average thickness of circa 50 nm, and a root-mean-square roughness of circa 5.3 nm. For nanofiber membranes with a thickness ranging in a micrometer scale, the conformal Cu layer coats all nanofibers in the outermost layers as well as in the bulk of the membrane. This work demonstrates a successful pathway of conformal Cu coating on stacked nanofibers.

Cu coated nanofiber networks possess low sheet resistance (< 2.4 Ω/□) and high gas permeability (circa 2.41 × 10⁻¹³ m² for air). Their performance in some criteria are comparable to commercialized carbon based micro- / nanofiber GDEs. A conductive Cu layer in a nanometer scale coats a flexible polymer core. This particular core-shell structure maintains the inherent flexibility in polymer and conductivity in metal, enabling the conductive networks to have flexibility. In fact, a Cu-PVDF electrode shows excellent bending durability, with negligible conductivity degradation after 10000 bending test cycles. The conductive nanofiber networks are therefore suitable for potential applications as GDEs in flexible devices.
This versatile method for producing flexible GDEs facilitates the adjustment of electrodes in many parameters, including electrode thickness, fiber diameter, porosity, fiber composition, and coating composition. This concept may trigger the development of flexible electrochemical devices for environmental and healthcare sensing, and harvest, convection, and storage of renewable energy.

4. Experimental Section

The details of chemicals and materials, fabrication of PAN, nylon, and PVDF nanofiber membranes (Table S1 in SI), and electroless Cu plating on polymer nanofibers are provided in the SI.

The PVDF nanofiber membranes with different levels of compactness were used as substrates for investigating the evolution of H\textsubscript{2} bubbles in nanofiber membranes during electroless Cu plating. The evolution of H\textsubscript{2} bubbles was monitored with an inverted microscope (OCM-1, KREN & Sohn GmbH). Photos and videos were recorded by a high-speed video camera at 100x magnification (ODC-832, KREN & Sohn GmbH).

Environmental scanning electron microscopy (ESEM, Quanta 650 ESEM, Thermo Fisher Scientific, Inc.) was employed to visualize the morphology of materials (Everhart-Thornley Detector, ETD), to analyze elements (energy dispersive X-ray spectroscopy detector, EDS), and to image the spatial distribution of elements (EDS elemental mapping). The surface roughness of Cu/pDA PVDF nanofibers was analyzed by AFM (Bruker Dimension Icon3).

XRD patterns were collected on a Bruker D8 diffractometer equipped with a Göebel mirror selecting Cu K\textalpha radiation (\(\lambda = 1.5406 \text{ Å}\)).

The sheet resistance of Cu/pDA polymer nanofiber membranes was analyzed with a four-point probe setup (PRO4, Microworld, Inc.). The distance between two adjacent probes was 0.04 inches. For each sample, 30 positions were randomly selected for measurements. The sheet resistance \(R_s\) was calculated according to Equation (2):
\[ R_s = \frac{\pi}{\ln 2} \frac{V}{I} \]  

where \( V \) and \( I \) are the measured voltage and current, respectively.

The bending-durability tests were performed with a home-built bending test bench. The dimension of a testing sample is 4.5 cm \( \times \) 2.5 cm. During the test, the sample was repetitively bent along the longitudinal direction. In one bending cycle, the distance between the two fixing points was first reduced to 1.0 cm, and then was stretched to 4.5 cm. The ohmic resistance of the sample was measured along the longitudinal direction with a voltammetric meter.

Cyclic voltammetry was performed in a three-electrode cell with electrochemical workstation (VersaSTAT 4, Princeton Applied Research). A Pt wire was used as the counter electrode, and a leakless Ag/AgCl electrode (SI Analytics, 3 M KCl) was employed as the reference. Ar-saturated 0.1 M KHCO\(_3\) solutions were used as electrolyte.

A single-channel test section, which was formed by a gasket sandwiched between two back plates, was used for measuring the pressure drop across the Cu/pDA polymer nanofiber membranes. A mass flow controller (Aalborg TIO totalizer) regulated air flow rates. The pressure drop between the entrance and exit of the test section was measured directly with a pressure transducer (PX409, Omega, Inc.) The commercial GeoDict (Math2Market GmbH) software package was employed for modelling and simulation of Cu/pDA polymer nanofiber membranes and their gas permeability. More details are shown in the SI.

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

**Acknowledgements**
F.J. and W.J. contributed equally to this work. F.J. and Y.Z. acknowledge financial support from Chinese Scholarship Council (CSC). F.J. and W.J. thank Dr. Huan Ma, Dr. Sebastian Tutu and Dr. Xiaoshuang Li for helpful discussions.
References


[41] D. Plana, *Doctor of Philosophy*, The University of Manchester, **2010**.


Table 1. Compared parameters of electrically conductive polymer micro- / nanofibers obtained by different coating methods.

<table>
<thead>
<tr>
<th>Material</th>
<th>Dimension</th>
<th>Template</th>
<th>Coating method</th>
<th>Diameter</th>
<th>Coating thickness</th>
<th>Resistance / Resistivity</th>
<th>Bending durability [cycle]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au nanotrough [19]</td>
<td>One layer (2D)</td>
<td>Electrospun PVA a) / PVP c) NFs</td>
<td>PVD d)</td>
<td>400 [nm]</td>
<td>80 [nm]</td>
<td>2 [Ω□]</td>
<td>&gt; 1000</td>
</tr>
<tr>
<td>Au nanomesh [2]</td>
<td>One layer (2D)</td>
<td>Electrospun PVA NFs</td>
<td>PVD</td>
<td>300 - 500 [nm]</td>
<td>70 - 100 [nm]</td>
<td>5.30 × 10⁻⁷ [Ω m]</td>
<td>&gt; 10000</td>
</tr>
<tr>
<td>Metal (Ni, Cu, Ag, Au) / polymer nanofiber mat [20]</td>
<td>Top layer (2D)</td>
<td>Electrospun PAN NFs</td>
<td>PVD &amp; Electroplating (Pt / Pd seeds)</td>
<td>&lt; 1 [μm]</td>
<td>&lt; 1 [μm]</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>Cu / polymer nanomesh [21]</td>
<td>One layer (2D)</td>
<td>Electrospun PAN NFs</td>
<td>Electroplating (Pt seeds)</td>
<td>1.8 [μm]</td>
<td>&gt; 1 [μm]</td>
<td>0.31 - 0.42 [Ω□]</td>
<td>&gt; 1000</td>
</tr>
<tr>
<td>Metal (Cu, Ag) / polymer nanowire [17]</td>
<td>One layer (2D)</td>
<td>Electrospun PVB e) NFs</td>
<td>Electroless plating (Ag seeds)</td>
<td>200 [nm]</td>
<td>70 [nm]</td>
<td>10 [Ω□]</td>
<td>&gt; 1000</td>
</tr>
<tr>
<td>Cu / knitted fabrics [22]</td>
<td>Multilayer (3D)</td>
<td>Knitted fabrics (PA 1) / PU 3) compounds</td>
<td>Electroless plating (pDA + Pd seeds)</td>
<td>20 [μm]</td>
<td>900 [nm]</td>
<td>0.32 [Ω□]</td>
<td>N.A.</td>
</tr>
<tr>
<td>Cu / polymer nanofibers [24]</td>
<td>Top layer (2D)</td>
<td>Electrospun PA6 f) NFs</td>
<td>Electroless plating (Sn + Ag seeds)</td>
<td>300 - 600 [nm]</td>
<td>200 - 300 [nm]</td>
<td>24.41 [Ω□]</td>
<td>N.A.</td>
</tr>
</tbody>
</table>

Abbreviation: a) two-dimension; b) polyvinyl alcohol; c) polyvinylpyrrolidone; d) nanofibers; e) physical vapor deposition; f) Polyaclonitrile; g) polyvinyl butyral; h) three-dimension; i) polyamide; j) polyurethane; k) one-dimension; l) nylon.

Table 2. Compared parameters of 3D electrically conductive micro- / nanofibers.

<table>
<thead>
<tr>
<th>Material</th>
<th>Dimension</th>
<th>Template</th>
<th>Fabrication method</th>
<th>Diameter</th>
<th>Gas permeability [$×10⁻¹⁴ m²$]</th>
<th>Resistance [Ω□]</th>
<th>Bending durability [cycle]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon fiber [25]</td>
<td>Multilayer (3D)</td>
<td>Papers / Fabrics / Electrospun fibers</td>
<td>Carbonization</td>
<td>7 - 14</td>
<td>800 - 5500</td>
<td>0.24 - 0.29</td>
<td>N.A.</td>
</tr>
<tr>
<td>Carbon nanofiber [53]</td>
<td>Multilayer (3D)</td>
<td>Electrospun PAN NFs</td>
<td>Carbonization</td>
<td>0.5 - 1.88</td>
<td>8 - 20</td>
<td>2.70 - 2.90</td>
<td>N.A.</td>
</tr>
<tr>
<td>Cu / knitted fabrics [22]</td>
<td>Multilayer (3D)</td>
<td>Knitted fabrics (PA + PU compounds)</td>
<td>Electroless plating (pDA + Pd seeds)</td>
<td>20</td>
<td>N.A.</td>
<td>0.30</td>
<td>N.A.</td>
</tr>
<tr>
<td>Cu / polymer nanofiber a)</td>
<td>Multilayer (3D)</td>
<td>Electrospun Nylon / PVDF / PAN NFs</td>
<td>Electroless plating (pDA seeds)</td>
<td>0.17 - 0.48</td>
<td>0.43 - 24.10</td>
<td>1.90 - 2.40</td>
<td>&gt; 10000</td>
</tr>
</tbody>
</table>

a) this work.
Figure 1. Scheme of fabricating Cu coated electrospun nanofiber networks. Step 1: electrospinning of a nanofiber membrane; Step 2: hot lamination of an electrospun nanofiber membrane; Step 3: activation of nanofiber surfaces by self-assembled polydopamine layers; Step 4: electroless plating of a Cu layer on electrospun nanofibers.
Figure 2. SEM images of electrospun (a1) PAN, (b1) nylon, (c1) PVDF nanofibers, and (d1) expanded PTFE nanofibers. The fused junctions are marked by yellow circles. (a2-d2) High-resolution SEM images of nanofibers as described in a1-d1, respectively. (a3-d3) Size distributions and the corresponding Gaussian fittings of nanofibers as described in a1-d1, respectively.

Figure 3. SEM images of pDA coated (a1 and a2) PAN, (b1 and b2) nylon, (c1 and c2) PVDF, and (d1 and d2) ePTFE nanofibers before and after ultrasonication in deionized water.
Figure 4. SEM images and the corresponding sketches of Cu coated PAN nanofibers after (a) 1-hour, (b) 2-hour, and (c) 4-hour Cu deposition.
Figure 5. (a) Cross-sectional SEM image of Cu-PVDF nanofibers. The cross-section was prepared by freeze fracture in liquid nitrogen. (b) Size distributions and their Gaussian fittings of diameters of PVDF nanofibers before (blue hexagons and dashed line) and after Cu coatings (orange diamonds and dashed line). (c) XRD patterns of PVDF, pDA-PVDF and Cu-PVDF nanofibers. (d) CVs of a Cu-PVDF electrode in Ar saturated 0.1 M KHCO₃ at a scan rate of 50 mV·s⁻¹.

Figure 6. (a) Top-view SEM image of Cu-PVDF nanofibers, (b) AFM image of Cu-PVDF nanofibers, and (c) high-resolution AFM image captured from the selected region in (b).
**Figure 7.** (a) Cross-sectional SEM image of a Cu-PVDF electrode encapsulated in epoxy resin, and the elemental mapping for (b) Cu and (c) F.

**Figure 8.** Microscopic images of blisters in the (a) less compact, and (b) highly compact PVDF nanofiber membranes during electroless Cu plating. (c) Scheme of hydrogen bubble formation, coalescence and release in nanofibers with different levels of compactness.
Figure 9. Demonstration of a Cu-PVDF electrode (5 cm × 8 cm) as an electrical conductor in a closed circuit by (a) pinning on the same surface, and (b) pinning on two opposite surfaces. (c) Ohmic resistance of a Cu-PVDF electrode after selected bending cycles in a bending-durability test. The dimension of the Cu-PVDF electrode and the testing parameters are illustrated with insets in (c).

Figure 10. (a) Measured and simulated air pressure drops through a Cu-PVDF membrane at different air face velocities. A virtual three-dimensional fibrous model is generated with GeoDict (inset). (b) Simulated air flow field in the Cu-PVDF membrane at a face velocity of 44.3 cm·min⁻¹.
Figure 11. Comparative analysis of 3D electrically conductive micro-/nanofibers.
A versatile method allows for producing three-dimensional electrode-conductive networks by conformally coating a Cu layer on stacked electrospun polymer nanofibers. The high conductivity, gas permeability, and flexibility of these three-dimensional nanofiber networks allow for potential applications into various flexible electrochemical devices.

F. Jiang, W. Ju, Z. Pan, L. Lin, Y. Yue, Y.-B. Zhao, C. Li, F. Clemens, C. Battaglia, J. Wang

**Conformal Cu coating on electrospun nanofibers for three-dimensional electro-conductive networks**

TOC figure