Mussel-Inspired Flexible, Durable, and Conductive Fibers Manufacturing for Finger-Monitoring Sensors

Chuang Zhu, Xinyi Guan, Xi Wang, Yi Li, Evelyn Chalmers and Xuqing Liu*

School of Materials, University of Manchester, Oxford Road, Manchester M13 9PL, UK
E-mail: xuqing.liu@manchester.ac.uk

Keywords: polydopamine, conductive fibers, electroless deposition, surface catalysis, finger-monitoring sensors

Here we report a bio-inspired facile and versatile method for fabricating highly durable, washable and electrically conductive fibers and yarns. Self-polymerized dopamine plays as adherent layers for substrates and then captures Pd$^{2+}$ catalyst for subsequent metal deposition on substrates. The Pd$^{2+}$ ions are chelated and partially reduced to nanoparticles by polydopamine (PDA)-modified substrates and the catalytic performance is investigated in surface electroless deposition. Importantly, this is the first report about PDA as both ligand and enhancement in Pd catalyst system, and the mechanism of their excellent catalytic performance is studied by XPS. This approach can be extended as a general method for fabricating conductors from all kinds of substrates, and precursory research about PDA/Pd catalyst application in surface catalysis.

1. Introduction

In recent years, fiber-based wearable electronics such as fiber-shaped energy harvesting and storage devices, wearable displays, deformable antenna and fiber computers/processors have attracted a great deal of attention.\textsuperscript{[1-6]} For realizing these devices, one critical step is the fabrication of conductive components such as interconnects on flexible and stretchable fibers/fiber assemblies.\textsuperscript{[7]} Although several novel materials, including conductive polymers, carbon nanotubes (CNTs) and graphene were developed in recent decades, metal is still considered as the best coating material in terms of conductivity, stability, compatibility and
Compared with other substrate materials such as plastics and elastomers, fibers and paper have the unique porous structures. Thus, the desired coating materials should penetrate into the fibrous structures. Several attempts have been made to metalize fibers such as thermal evaporation, atomic layer deposition, magnetron sputtering and galvanic deposition. But the fabrication via above-listed methods does not have chemical bonds or other tethering force between the metallic layers and the surface of fibers. The inherently poor adhesion between metal nanoparticles and flexible substrates limits the widespread application of conductive fibers. Additionally, for flexible substrates with the particular 3D structure, such as sponges, the electro-conductivity is poorly containable because the 3D structure, as a spatial mask, decreases the uniformity and continuity of the deposited metal films initiated by gravity. Recently, Liu et al. reported the polymer-assisted metal deposition by surface-initiated atomic transfer radical polymerization (SI-ATRP). The designed polymer interface introduces covalent bonds between the surface of fibers and grafted polymer brushes and viscoelastic and high-swelling intrinsic properties of polymers provide the nanometer-scale mechanical interlocking of deposited nanoparticles within brushes. Although the resultant conductive yarns are highly durable and washable, the polymerization requires an inert N₂ protection and complex steps. Moreover, the target substrates have to contain abundant hydroxyl groups. On the other hand, with the booming development of novel materials, which can be employed in wearable electronics as their variety of performances, how to develop a new surface modification method which can be used in virtually any substrate and create conductive composites is important.

According to Lee’s report, dopamine which mimics the adhesive chemistry of mussel plaque detachment allows the spontaneous deposition of nanoscale-thin, surface-adherent films of poly(dopamine) (PDA) on virtually all material surfaces such as polymers, ceramics, semiconductors and novel metals by simple dip-coating in an alkaline solution. More importantly, Secondary reactions can be used to produce a variety of ad-layers on the top of
PDA, including metal films by electroless metallization.[21] In some reports, silver (Ag) was coated on different fibers, such as polyester (PET), meta-aramid, glass, cotton and polyurethane, via PDA-assisted electroless deposition (ELD).[22-26] However, in accordance with Zheng’s review work,[27] silver, as a conductive coating material, is much more expensive than copper and nickel. More importantly, according to the European Commission and its non-food Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR), there are still some arguments related to the toxicity of silver nanoparticles and additional adverse effects caused by the use of silver nanoparticles should be further evaluated. To address the challenges, we report here a simple, versatile and scalable approach for preparing highly durable, washable and electrically conductive fibers and yarns by electroless nickel (Ni) plating on fiber surfaces modified with PDA as adhesive layers. Copper (Cu) can be an alternative coating choice due to the high conductivity and low price. However, the oxidation of the Cu layer can cause the slow decrease in conductivity when the sample is placed in air. Thus, nickel, as an air-stable conductive metal, is mainly discussed in this report. In detail, PDA that tethers one end on the surface via covalent and noncovalent bonds is firstly grown from fibers by dip-doping in tris buffer. Subsequently the grafted PDA interface anchors the catalyst in an aqueous solution. The captured catalyst final activates electroless plating metallization. The as-made conductive yarns can be demonstrated as interconnects to power light-emitting diodes (LEDs) and also can be used to track finger motions. In principle, this effective approach can be extended as a general method for producing conductors from all kinds of substrates.

2. Results and Discussion

2.1 The Graft of PDA onto Substrates and Catalyst Immobilization
As proof-of-concept, we synthesized PDA by pH-induced polymerization, which strongly adheres to the surface of various substrates and provides a platform for secondary reactions. The PDA modification can control the coating thickness by varying deposition time and is recognized as an environmentally-friendly chemical approach. The procedure is illustrated in Scheme 1. In a typical experiment, we first immobilized the PDA interface on fiber surfaces by dip-doping in tris buffer for 24 h at room temperature. Then, the samples were washed with DI water several times and dried with a N₂ gas stream.

Scheme 1. Scheme illustration of processes for preparing conductive fibers by dopamine functionalization and electroless deposition.

Fourier transform infrared spectroscopy (FTIR) was applied in this work to confirm the successful PDA-coating process. From Figure 1a, cotton as a natural cellulose, without any treatment and modified by PDA were compared. The new peak at 1612 cm⁻¹ is attributed to
the N-H bending vibration in primary amine groups of PDA. From Figure 1b, PET as one of the most widely used synthetic fibers, without any surface modification and modified by PDA were analyzed and attributed. The new peak at 1232 cm$^{-1}$ is attributed to the C-O stretching vibration in catechol groups of PDA. The peaks at 1635 cm$^{-1}$ and 3284 cm$^{-1}$ are attributed to N-H bending state and N-H stretching state in primary amine groups of PDA, respectively. The successful wrapping of PDA on wool surface is also detected by FTIR (see Figure S1, Supporting Information).

After PDA modification, the PDA-coated samples were immersed into a 5 mM (NH$_4$)$_2$PdCl$_4$ aqueous solution for 2 h, where Pd$^{2+}$ moieties were anchored within the PDA interface. The captured palladium moieties/particles provide effective catalytic sides for subsequent ELD. The proposed mechanism of dopamine polymerization has been known but when adding Pd (II) to PDA-modified substrates, the binding mechanism between PDA and Pd (II) should be explained. Thus, X-ray Photoelectron Spectroscopy (XPS) was applied to investigate the surface composition of the Pd/PDA-PET composite. The XPS survey spectrum reveals region

Figure 1. Transmittance FTIR spectrum of a) cotton substrates and b) PET samples, modified by PDA (red) and under control (black).
The C 1s spectrum in Figure 2a shows three peaks assigned to C-C (284.8 eV), C-O/C-N (286.4 eV) and C=O (288.9 eV) species originating from the PDA layer. From the N 1s spectrum (Figure 2b), the peak at 402.0 eV was assigned to the component of primary amine (R-NH$_2$), which is associated with dopamine. The peak at 399.7 eV was attributed to the secondary amine component (-R-NH-R), which is associated with both PDA and accepted intermediates. The peak at 398.6 eV was assigned to the tertiary/aromatic amine functionality, which was associated with 5,6-dihydroxylindole (DHI) and 5,6-indole-quinone. Additionally, the O 1s region in Figure 2c is fit with two oxygen signals assigned to C=O (531.9 eV) and C-O (533.2 eV) species, which were from the PDA layer. In Pd 3d region (Figure 2d), two spin-orbital doublets (Pd 3d$_{5/2}$ and Pd 3d$_{3/2}$ peaks) are shown, indicating there are two electronic states of palladium, i.e. Pd (0) (binding energy 333.9 and 343.3 eV) and Pd (II) (binding energy 339.1 and 346.4 eV). This confirms that Pd$^{2+}$ ions were chelated by the primary amine groups of PDA and the catechol groups of PDA reduced some Pd$^{2+}$ ions into Pd nanoparticles, which were encapsulated within PDA layers.

It is interesting to note that in comparison with previous reports, there is an increase of the binding energy of palladium in our report. The first reason for the increase in binding energy is due to the electronic environment around Pd catalysts. PDA, due to the characteristics of its π bond, causes the outer electrons of the palladium ions to participate in the π-metal stacking, resulting in an increase in binding energy. On the other hand, it is important that the palladium nanoparticles we reported were reduced by PDA, not further reduced by other reducing agents such as sodium borohydride. Therefore, the reduced palladium nanoparticles were nearly not agglomerated, resulting in the larger binding energy. The smaller catalytic nanoparticles also contribute to the larger specific surface area of catalytic region, leading to the increased performance of the catalyst in the followed ELD. To prove that, extra NaBH$_4$ was added in the catalyst solution to further reduce...
palladium ions into palladium particles on the surface of PDA-PET and when this sample was immersed in the ELD bath, only a few weak bubbles were formed, suggesting a very low reaction rate. Therefore, on the surface of a substrate, PDA plays a role of reducing and stabilizing palladium ions with an adhesive force. Importantly, the stabilized Pd$^{2+}$ can enhance the catalytic action in ELD, causing the good performance of metal coating.

Figure 2. X-ray photoelectron spectroscopic (XPS) spectrum of a) C 1s, b) N 1s, c) O 1s and d) Pd 3d for the Pd/PDA-PET sample.

2.2 Surface Characterization

Since the surface morphology of the obtained copper or nickel coatings may affect the electrical, mechanical and optical properties of the conductive fibers that are produced, scanning electron microscopy (SEM) was employed to characterize the morphology of thin
copper or nickel films in detail. The SEM photographs of the nickel coating on cotton (c, e) and PET (d, f) fibers and pure cotton (a) and PET (b) fibers are shown in Figure 3. Compared with Figure 3c, e, d, f, a significant change on the surface of raw materials (Figure 3a, b) can be observed after nickel electroless plating. And it can be clearly seen that uniform and continuous nickel nanoparticles were compactly dispersed on the surface of PET and cotton fibers. The homogeneous distribution of Ni nanoparticles on the fiber surface would enhance the electrical performance of as-made conductive fibers. Additionally, the longer ELD time caused the bigger size of nickel nanoparticles. The detailed change of the size of nickel nanoparticles on cotton fibers with the increased ELD time is also analyzed by SEM (see Figure S3, Supporting Information).

Particularly, for cotton fibers which have the natural hollow structure, conventional methods initiated by gravity such as physical vapor deposition and chemical vapor deposition can only coat metal nanoparticles on the outer layer of cotton fibers because of the directional limitation. This causes that the coating layer is not continuous and fully covered on multidirectional surfaces. However, in this report, cotton fibers are immersed into aqueous solutions throughout, which ensures the inner layer can be modified by PDA and coated with nickel nanoparticles in ELD. Figure 4 shows that the nickel particles deposited not only on the upper surface of the fibers, but also on the surface of inner fibers. And electrical properties of the prepared metallic cotton yarns and fabrics would be enhanced by this integral and continuous coating.
Figure 3. SEM photographs of cotton and PET fibers a,b) without any treatment and c,d,e,f) with the nickel coating (electroless plating time for cotton and PET is 10 min).

Figure 4. SEM photographs of nickel-coated cotton fibers with the unique hollow structure (electroless plating time is 10 min).
X-ray diffraction (XRD) is a conventional and simple technique to reveal the size and the shape of the unit cell for any crystalline compound. In previous reports,\(^{[19, 33]}\) no discussions were related to the size and the shape of deposited nickel nanoparticles on the surface of fibers. Accordingly, this report reveals the XRD patterns of nickel particles on the cotton surface at different ELD time. From Figure 5a, the main peak at 2\(\theta\) value of 44.48 degrees was observed from these two patterns. According to the standard powder diffraction card of Joint Committee on Powder Diffraction Standards (JCPDS), the value corresponds to the (111) crystal plane of Ni. Based on the PDF card of the JADE-SCAN software, the characteristic face-centered cubic crystalline structure of deposited nickel particles was also identified, implying the excellent conductivity of as-made nickel-deposited fibers. According to the Scherrer equation, the average size of nickel nanoparticles when the ELD time is 30 min and 60 min is 16.6 nm in both cases. However, the size of nickel nanoparticles is clearly bigger when the ELD time is longer based on the SEM photographs as shown in the supporting information. To further investigate this, low-voltage scanning electron microscopy (LVSEM), as an intuitive measurement, was used to determine the size of nickel nanoparticles when ELD is 60 min. The low-voltage mode ensures more detailed information of the surface morphology but images are less three dimensional. From Figure 5b,c, it can be clearly observed that the grown big spheres are comprised of small nanoparticles, which are estimated to be 16-17 nm, which is coincident with XRD results. This means that nickel nanoparticles are deposited on fibers with the same size along the ELD, resulting in the uniform coating. Importantly, these granular nanoparticles are homogeneously and continuously arranged on the fiber surface with a compact distribution, leading to the perfect conductive property of nickel-plated composites.
Figure 5. a) The XRD spectrum of the Nickel/PET composite. The SEM photographs of nickel-coated PET fibers at the low-voltage mode: b) electroless plating time is 30 min and c) 60 min.

2.3 Electrical Conductivity and Mechanical Durability

Compared with bare textile fibers which are well-known to be insulated, the as-made Ni-coated fibers are electrically conductive. In this report, four types of conductive yarns are produced, including wool, cotton, nylon and PET and the digital images of yarns are recorded (see Figure S4, Supporting Information). From Figure 6a, the electrical surface resistance of the cotton yarn decreases with increasing plating time, reaching as low as 0.05 Ω/cm at 60 min ELD. And longer plating leads to heavier samples due to the increasing amount of plated metallic nanoparticles (see Figure S5, Supporting information). However, a saturation plateau occurs at ~60 min. This can be attributed to catalyst poisoning. Clearly, extending the depositing time resulted in a conspicuous decrease in resistance, but a more brittle and stiff
film with increased thickness. This can be explained by the decreased contact resistance between plated nanoparticles when they are more tightly packed with longer depositing time. However, no evidence is shown to prove this hypothesis.\textsuperscript{[34]} Luckily, we found three different types of distributions of nickel nanoparticles on a single fiber using field emission gun scanning electron microscopy (FEG-SEM). The surface morphology of Ni nanoparticles on the cotton fiber when the ELD time is 15 min is shown in \textbf{Figure 6b} and it perfectly confirms the assumption. From the yellow area of the image, nickel nanoparticles were dispersed at a low rate of compact distribution, which can be defined as the first layer of nickel coating. Based on the blue area of the photograph, the plated nickel particles were more continuous on the surface of the cotton fiber, leading to the decreased resistance. This can be defined as the second layer. When depositing time increased further, nickel nanoparticles were more densely aggregated on the second layer, leading to the further decrease in resistance and the formation of subsequent layers such as the cyan area of the FEG-SEM image. With increased ELD time, the coated nickel film on fibers was thicker and more compact, creating higher conductivity at the expense of flexibility.
Figure 6. a) The conductivity test of the prepared conductive cotton yarns at different plating time. b) The FEG-SEM photograph of Ni nanoparticles on cotton fibers (Electroless plating time is 15 min).

The electrical stability under multiple cycles of bending and washing is one of the most critical challenges of conductive yarns and fabrics. To investigate this, washing cycles using simple hand washing and squeeze-drying and mechanical bending cycles using simple hand bending with a radius of 15 mm were employed to test the rubbing and bending robustness, respectively. No obvious increase of surface resistivity on the Ni/cotton conductive yarn was observed after five washing and drying cycles or two thousand simple mechanical bending cycles (see Figure S6, Supporting Information). This was due to the chemical bonds between the surface of fibers and the coated PDA layers.

2.4 Demonstrations of Ni conductive yarns

One of the most important applications for the as-prepared conductive yarns is used as conductive wires in electronic circuits because of their high conductivity and robustness. As a demonstration, a simple circuit was built by bridging a 9 V battery and one electrical contact of a blue light emitting diode (LED) with prepared conductive yarns. When the blue LED
contacted the alkaline battery, the LED turned on immediately and illuminated for more than 20 min until the contact was disconnected (see Figure S7, Supporting information). On the other hand, because of the high sensitivity to strain, these conductive yarns can be used as a strain sensor to monitor tiny motions of the finger. As a proof-of-concept, we sewed nickel-coated cotton yarns into four finger parts of a commercial glove, as shown in Figure 7a. When the finger bent/unbent at different gestures, the conductive yarns sewn into glove were stretched/released, causing the increased/decreased contact area between conductive fibers (see Figure S8, Supporting information). This gave corresponding resistance signal (obviously the larger/smaller area of contact between conductive cotton fibers would lead to the decrease/increase in resistance), detected by Keithley 2400 Source Meter. Three different hand gestures, including releasing, grasping and holding, are tested in this experiment, as illustrated in Figure 7b. From Figure 7c, the resistance showed a quick decrease during bending fingers and the resistance recovered to its original value during unbending fingers. We could successfully monitor the motions of the finger through recording the resistance signal changes versus hand gestures. More importantly, these conductive yarns also can be attached to the finger parts of the robotic hand to track the robotic finger movements, as shown in Figure 7d,e. From Figure 7f, when the gesture of robotic hand changed from releasing to grasping, the resistance of attached conductive yarns reduced correspondingly because the stretching caused more internal connections between conductive staple fibers. And when the gesture of robotic hand changed from grasping to releasing, the resistance of attached conductive yarns increased since releasing reestablished the conductive network in the nickel layer.
Figure 7. a) Digital photographs of conductive yarns sewn into the four finger parts of a glove. b) Digital photographs of three typical finger movements, including releasing, grasping and holding. c) The resistance changes vs hand gestures when fingers move. d) Digital photographs of conductive yarns attached to the four finger parts of a robotic hand. e) Digital photographs of two typical finger movements, including releasing and grasping. f) The resistance changes vs hand gestures when the robotic hand moves.
3. Conclusion

In conclusion, this study demonstrates a novel, facile and versatile approach for preparing durable, flexible and electrically conductive yarns. PDA nano-films are first coated on fiber surfaces by immersing them into an alkaline aqueous solution. PDA-modified fibers then anchor the catalyst via ion chelation and finally metal nanoparticles are deposited onto the catalytic area, resulting in the formation of polymer-bridged conductive composites. This in-situ plating method ensures that metallic nanoparticles are distributed on the surface of fibers continuously and uniformly. In addition, as the PDA coating serves as an adhesive layer, this leads to the superior electrical stability of as-made conductive yarns under repeated bending and washing cycles. Such manufactured conductive yarns can be used as the flexible electrical conductor in electrical circuits to power a LED and also a strain-stress sensor to monitor finger movements. The bioinspired polymerization of dopamine can be used for multifunctional coatings. Thus, PDA-assisted ELD can be a universal method for coating nickel or copper nanoparticles on virtually all material surfaces. PDA-assisted ELD is also a low-energy and green method throughout and the low price of nickel and copper makes them perfect coating materials for producing conductive yarns on a large scale. Such conductive yarns should develop a wide variety of applications in fiber-based wearable electronics, radiation and electromagnetic protection, energy, architecture and biomedical industries. Moreover, PDA/Pd catalyst was firstly employed in surface-catalyzed reactions and show better performance than isolated Pd catalyst, and PDA as both adhesion and enhancement will show broadened application in other surface catalytic reaction.

4. Experimental Section

*Materials:* Dopamine hydrochloride, Ammonium tetrachloropalladate(II) [(NH₄)₂PdCl₄] and all other chemicals were purchased from Sigma-Aldrich. All textile substrates were obtained from the Dye House at the University of Manchester. Each fiber substrate was ultrasonically
cleaned in acetone and distilled (DI) water for 30 min, respectively, then dried with a N\textsubscript{2} gas stream.

Dopamine Spontaneous Polymerization on the surface of fibers: Dopamine was dissolved in 0.01 mol/L tris (hydroxymethyl) aminomethane (pH 8.5) buffer to prepare a dopamine solution (2 g/L). Cleaned substrates were dipped into the solution and the non-specific micro-particle deposition on surfaces was prevented by stirring and/or vertical sample orientation. The pH-induced oxidation of dopamine changed the color of the solution to dark brown. After a predetermined reaction time of 24 h, the adherent PDA film coated surfaces were filtered and rinsed thoroughly with ultrapure water and dried with a N\textsubscript{2} gas stream.

Metallization by ELD: The modified samples were immersed into a 5mM (NH\textsubscript{4})\textsubscript{2}PdCl\textsubscript{4} aqueous solution and placed in a dark environment for 15 min to load catalysts by chelation and reduction, followed by thorough rinsing with DI water to remove the physical absorption of catalyst inks. The Ni electroless plating was performed in an ELD bath containing 4:1 volumetric proportion of nickel-to-reductant stocks at room temperature. A nickel stock solution consisting of 10 g/L lactic acid, 20 g/L sodium citrate and 40 g/L nickel sulfate hexahydrate was prepared in advance. A fresh reductant solution containing 1 g/L dimethylamine borane (DMAB) in DI water was prepared separately. After mixing, the solution was adjusted with ammonia to pH \textasciitilde8. After ELD, all samples were washed several times and dried with compressed air.

Characterization: The surface morphology of the samples was characterized by scanning electron microscopy (ZEISS Ultra-55 and TESCAN Mira3). The surface resistance was measured by a 2-point probe method with a Keithley 2400 Source Meter. The self-polymerization of dopamine in solution was investigated by UV-visible spectroscopy (M550 Double Beam Scanning UV/Visible Spectrophotometer). The coating of PDA on fibers was tested by Fourier transform infrared spectroscopy (NICOLET 5700 FTIR). The size and the
shape of the unit cell for metallic particles on the fiber surface were determined by X-ray
diffraction (PANalytical X'Pert Pro X'Celerator diffractometer).

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

Acknowledgements
We would like to thank the support of the EU Horizon 2020 and University of Manchester
through projects with project codes 644268-ETEXWELD-H2020-MSCA-RISE-2014,
AA14512 (UMRI project “Graphene-Smart Textiles E-Healthcare Network”) and the British
Cotton Growing Association Work People’s Collection Fund for funding the project
“Protective Efficiency of Respiratory Protective Equipment (RPE) against Byssinosis for
Cotton Workers”.

Received: ((will be filled in by the editorial staff))
Revised: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

References
[1] Z. Yang, J. Deng, X. Sun, H. Li, H. Peng, Adv. Mater. 2014, 26, 2643.
[2] J. Ren, Y. Zhang, W. Bai, X. Chen, Z. Zhang, X. Fang, W. Weng, Y. Wang, H. Peng,
Angew. Chem. 2014, 126, 7998.
[3] Z. Zhang, X. Chen, P. Chen, G. Guan, L. Qiu, H. Lin, Z. Yang, W. Bai, Y. Luo, H.
Peng, Adv. Mater. 2014, 26, 466.
[4] Z. T. Li, Z. L. Wang, Adv. Mater. 2011, 23, 84.
[5] F. Clemens, M. Wegmann, T. Graule, A. Mathewson, T. Healy, J. Donnelly, A.
Ullsperger, W. Hartmann, C. Papadas, Adv. Eng. Mater. 2003, 5, 682.
[6] Z. Wei, S. Lin, L. Qiao, C. Song, W. Fei, T. Xiao-Ming, Adv. Mater. 2014, 26, 5310.
[7] C. Zhu, Y. Li, X. Liu, Polymers 2018, 10, 573.
[8] X. Liu, X. Zhou, Y. Li, Z. Zheng, Chem. - Asian J. 2012, 7, 862.
[9] Y. Zhang, T. Mao, H. Wu, L. Cheng, L. Zheng, Adv. Mater. Interfaces 2017, 4,
1601123.
[10] H. M. Lee, J. Y. Seo, A. Jung, S.-Y. Choi, S. H. Ko, J. Jo, S. B. Park, D. Park, ACS
Appl. Mater. Interfaces 2014, 6, 15480.
[11] H. M. Lee, H. B. Lee, D. S. Jung, J.-Y. Yun, S. H. Ko, S. B. Park, Langmuir 2012, 28,
13127.
[12] H. M. Lee, S. Y. Choi, A. Jung, S. H. Ko, Angew. Chem. 2013, 125, 7872.
[13] N. L. Silva, L. Gonçalves, H. Carvalho, J. Mater. Sci.: Mater. Electron. 2013, 24, 635.
[14] J. S. Jur, W. J. Sweet, C. J. Oldham, G. N. Parsons, Adv. Funct. Mater. 2011, 21, 1993.
[15] D. K. Diop, L. Simonot, N. Destouches, G. Abadias, F. Pailloux, P. Guérin, D. Babonneau, *Adv. Mater. Interfaces* **2015**, 2, 1500134.

[16] B. K. Little, Y. Li, V. Cammarata, R. Broughton, G. Mills, *ACS Appl. Mater. Interfaces* **2011**, 3, 1965.

[17] S. Gimpel, U. Mohring, H. Muller, A. Neudeck, W. Scheibner, *J. Ind. Text.* **2004**, 33, 179.

[18] Y. Yu, J. Zeng, C. Chen, Z. Xie, R. Guo, Z. Liu, X. Zhou, Y. Yang, Z. Zheng, *Adv. Mater.* **2014**, 26, 810.

[19] X. Liu, H. Chang, Y. Li, W. T. Huck, Z. Zheng, *ACS Appl. Mater. Interfaces* **2010**, 2, 529.

[20] H. Lee, S. M. Dellatore, W. M. Miller, P. B. Messersmith, *science* **2007**, 318, 426.

[21] J. H. Ryu, P. B. Messersmith, H. Lee, *ACS Appl. Mater. Interfaces* **2018**, 10, 7523.

[22] C. Xu, M. Tian, L. Liu, H. Zou, L. Zhang, W. Wang, *J. Electrochem. Soc.* **2012**, 159, D217.

[23] W. Wang, R. Li, M. Tian, L. Liu, H. Zou, X. Zhao, L. Zhang, *ACS Appl. Mater. Interfaces* **2013**, 5, 2062.

[24] H. Liu, L.-I. Zhu, Y. He, B.-w. Cheng, *Mater. Des.* **2017**, 113, 254.

[25] H. Liu, L. Zhu, J. Xue, L. Hao, J. Li, Y. He, B. Cheng, *J. Nanomater.* **2016**, 2016.

[26] W. Wang, W. Cheng, M. Tian, H. Zou, L. Li, L. Zhang, *Electrochim. Acta* **2012**, 79, 37.

[27] D. Wang, Y. Zhang, X. Lu, Z. Ma, C. Xie, Z. Zheng, *Chem. Soc. Rev.* **2018**.

[28] J. Xi, J. Xiao, F. Xiao, Y. Jin, Y. Dong, F. Jing, S. Wang, *Sci. Rep.* **2016**, 6, 21904.

[29] R. A. Zangmeister, T. A. Morris, M. J. Tarlov, *Langmuir* **2013**, 29, 8619.

[30] S. Hong, Y. S. Na, S. Choi, I. T. Song, W. Y. Kim, H. Lee, *Adv. Funct. Mater.* **2012**, 22, 4711.

[31] H. Yang, S. Kang, H. Zou, J. Jin, J. Ma, S. Li, *RSC Adv.* **2016**, 6, 90462.

[32] I. Aruna, B. Mehta, L. Malhotra, S. Shivaprasad, *J. Appl. Phys.* **2008**, 104, 064308.

[33] X. Wang, C. Yan, H. Hu, X. Zhou, R. Guo, X. Liu, Z. Xie, Z. Huang, Z. Zheng, *Chem. - Asian J.* **2014**, 9, 2170.

[34] X. Wang, H. Hu, Y. Shen, X. Zhou, Z. Zheng, *Adv. Mater.* **2011**, 23, 3090.