Applications of Conductive Electrospun Nanofiber Mats

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Conductive nanofiber mats can be used in a broad variety of applications, such as electromagnetic shielding, sensors, multifunctional textile surfaces, organic photovoltaics, or biomedicine. While nanofibers or nanofiber from pure or blended polymers can in many cases unambiguously be prepared by electrospinning, creating conductive nanofibers is often more challenging.

Keywords: electrospinning ; conductive nanofibers

1. Electromagnetic Shielding

One of the large areas in which electrospun nanofiber mats are used is electromagnetic shielding. Typically, lightweight electromagnetic (EM) wave absorbers are prepared as heterogeneous structures from magnetic and dielectric loss materials, with the heterogeneous structure supporting the interaction between an electromagnetic wave and absorber [1].

2. Energy Storage

Another application of conductive nanofiber mats are electrodes of lithium-ion batteries. Here again, metallic and carbon-based materials are often combined to gain a sufficient conductivity. Typically, the anode is prepared from $MgFe_2O_4$ in combination with graphene [2], carbon nanotubes [3] or graphene aerogel [4][5]. MoS_2/carbon nanofiber membranes were prepared by needle-based electrospinning and carbonization of the PAN-based precursor and used as binder-free anodes for sodium-ion batteries [6].

Interlayers for Li-S batteries were prepared by Zhang et al., combining a reduced graphene oxide layer with $BaTiO_3$ decorated carbon nanofibers prepared by electrospinning and subsequent calcination, resulting in low resistances around 30 Ω in the fresh state and around 6 Ω after cycling, resulting in a high rate performance and cycling performance [7].

Supercapacitors, on the other hand, can be created by firstly electrospinning TiO_2 nanofibers from a solution of $Ti(OC_4O_9)_4$ and poly(vinyl pyrrolidone) (PVP), followed by calcination to remove the polymer and retain the pure semiconductive nanofibers. Next, nitridization via ammonia annealing resulted in highly conductive TiN nanofibers. These nanofibers were afterward coated with MnO_2 nanosheets, resulting in increased specific capacitance and cycle stability [8].

3. Electronic Components

Even memristors were produced by conductive nanofiber mats. Lapkin et al. used electrospinning to produce polyamide-6 nanofiber mats on which PAni was polymerized, resulting in a conductivity around 1 S/cm. Combined with a solid polymer electrolyte and a silver counter electrode, a memristor could be realized which showed resistive switching due to a voltage-controlled change in the PAni redox state [9]. Döpke et al. suggested producing conductive magnetic nanofiber mats for data storage and transfer [10].

4. Tissue Engineering and Cell Growth

Tissue engineering generally is often based on electrospun nanofiber mats. In order to engineer cardiac tissue, it is not only necessary to create porous nanofiber scaffolds, but these scaffolds should also mimic the extra-cellular matrix of the target tissue, i.e., should be conductive in case of growing cardiac muscle tissue on them with undisturbed intracellular signaling [11][12]. In general, scaffolds with embedded conductive materials often show advances against non-conductive nanofiber mats, whether prepared with PAni, PPy or CNTs [13][14][15].

Nekouian et al. report on conductive electrospun nanofiber mats, prepared from PCL/PPy/multi-wall CNTs which were used to examine the influence of electrical stimulation on the photoreceptor differentiation of mesenchymal stem cells,

showing that rhodopsin and peripherin gene expressions could significantly be increased by the electrical stimulation [16]. Rahmani et al. used silk fibroin nanofibers filled with conductive reduced graphene oxide, resulting in electrochemical series resistances around 20–30 Ω, to grow conjunctiva mesenchymal stem cells under electrical stimulation and found formation of neuron-like cell morphology and alignment along the electrical field [17]. PCL/PAni scaffolds with conductivities up to approximately 80 µS/cm were used by Garrudo et al. for the cultivation of neural stem cells, showing that the typical cell morphology was retained, and the nanofiber mats were biocompatible [18]. Even lower values of approximately 1 µS/cm were reported by Ghasemi et al. who doped electrospun polyethylene terephthalate (PET) nanofibers with graphene oxide to prepare cardiac patches for cardiac regeneration after myocardial infarcts [19]. For the same purpose, Walker et al. suggested using electrospun gelatin methacryloyl with bio-ionic liquid to combine adhesive and conductive properties [20].

Cell proliferation and gene expression could also be optimized by doping PAni scaffolds with graphene oxide and plasma treatment to hydrophilize the fiber surface [21]. Attachment, spreading and proliferation of fibroblasts and endothelial cells was optimized by tailoring the concentration of multilayer graphene flakes in electrospun polyurethane nanofiber mats [22]. Embedding reduced graphene oxide in electrospun poly(ester amide) (PEA) and PEA/chitosan scaffolds increased cardiac differentiation [23]. Similarly, electrospinning PEO/PEDOT:PSS nanofibers showed a positive effect on neurite outgrowth, i.e., neural differentiation of neuron-like model cells, which is especially interesting since a spin-coated PEO/PEDOT:PSS film showed contact repulsion limiting cell attachment and proliferation.

Osteoblast cells were found to grow and proliferate well on electrospun poly(l-lactic acid)/PAni/p-toluene sulfonic acid nanofiber mats [24]. Keratinocytes were shown to grow on electrospun PAN/PPy and PAN/PPy/CNT nanofiber mats [25]. Coating electrospun polyurethane nanofibers with PAni reduced the water contact angle significantly, resulted in a certain anticoagulant effect and was found supportive for cell adhesion, proliferation, and extension [26].

5. Dye-Sensitized Solar Cells

Counter electrodes of dye-sensitized solar cells (DSSCs) were prepared by coating an electrospun nanofiber mat with PEDOT:PSS. Juhász Junger et al. used several dip-coating steps to optimize the electrode conductivity while partly retaining the nanostructured surface and thus the large contact area with the neighboring layers [27]. The optimum number of layers resulted in a sheet resistance around 150 Ω, reduced from approximately 550 Ω for a single coating layer [27][28]. A similar approach was recently suggested by Kohn et al. who prepared fully electrospun DSSCs with both electrodes prepared by separately dip-coating them in PEDOT:PSS [29].

Eslah and Nouri, on the other hand, used spin-coating of WO_3 nanoparticles on electrospun PAN/PAni nanofibers to prepare counter electrodes of DSSCs [30]. For the possible use in LEDs and solar cells, Jiang et al. developed transparent conductive electrodes by electrospinning copper nanofibers and immersing them in silver ink as a protective layer, resulting in sheet resistances below 10 Ω [31].

6. Hydrogen Evolution

Another interesting application is hydrogen evolution. Sun et al. most recently prepared electrospun carbon/Ni/Mo_2C nanofibers which were used as electrocatalysts in hydrogen evolution reaction in an alkaline electrolyte [32]. Li et al. used nitrogen-doped carbon/Ni nanofibers decorated with Pt for hydrogen evolution, resulting in a high electrochemical activity combined with reduced usage of Pt [33]. Zhang et al. prepared binder-free MoS_2/carbon nanofiber electrodes by electrospinning and carbonization of the resulting nanofibers, allowing them to tailor the porosity chemically, which could be used for electrocatalytic hydrogen production [34]. Rheem et al. used a hierarchical structure of MoS_2 nanosheets on conductive MoO_2 nanofibers, gained by electrospinning, calcination, and sulfurization, to increase the hydrogen evolution reaction [35]. A similar hierarchical structure was prepared earlier by Liu et al. who used porous electrospun TiO_2 nanofibers as a substrate for growing MoS_2 nanosheets perpendicular to the nanofiber surfaces, resulting in high photocatalytic hydrogen production [36].

7. Sensors

To sense dopamine, Ozoemena et al. used electrospun PAN/onion-like carbon nanofibers and found a high conductivity and sensitivity of the resulting nanofibers [37]. By electrospinning polystyrene/polyhydroxibutyrate filled with graphitized carbon and partly doped with porphyrin on an interdigitated electrode, Avossa et al. prepared gas sensors for volatile organic compounds [38].

Shaker et al. developed a polyurethane/PEDOT:PSS electrospun nanofiber mat which exhibited a resistance of approximately 3 kΩ and could be used as a reliable strain gauge sensor [39]. Yang et al. coated highly conductive MXene sheets on electrospun PU nanofibers mats to produce highly sensitive strain sensors [40]. Flexible strain sensors with up to 1000% elongation were prepared from conductively coated electrospun styrenebutadiene-styrene copolymer [41]. A similar stretchability was reached by Ren et al., electrospinning a thermoplastic polyurethane nanofiber mat with a wavelike structure, followed by wrapping CNTs around the nanofibers [42]. Wrapping conductive nanofiber yarn produced from graphene oxide-doped PAN nanofibers with in-situ polymerized PPy around elastic yarns results in high sensitivity and repeatability, in this way enabling detection or breathing or human motion [43].

Harjo et al. developed conductive fiber scaffolds by coating electrospun glucose-gelatin nanofiber mats with polypyrrole and investigated their electro-chemo-mechanical response, showing stable actuation for more than 100 cycles as well as reasonable sensor properties [44]. They found conductivities of approximately 3 µS/cm in the unstretched state and approximately half this value when stretched in aqueous or organic electrolyte solutions.

References

1. Liu, X.F.; Hao, C.C.; Jiang, H.; Zeng, M.; Yu, R.H. Hierarchical NiCo2O4/Co3O4/NiO porous composite: A lightweight el ectromagnetic wave absorber with tunable absorbing performance. J. Mater. Chem. C. 2017, 5, 3770–3778.
2. Yin, Y.H.; Liu, W.F.; Huo, N.N.; Yang, S.T. Synthesis of vesicle-like MgFe2O4/graphene 3D network anode materials wit h enhanced lithium storage performance. ACS Sustain. Chem. Eng. 2017, 5, 563–570.
3. Pereira, C.; Costa, R.S.; Lopes, L.; Bachiller-Baeza, B.; Rodriguez-Ramos, I.; Guerrero-Ruiz, A.; Tavares, P.B.; Freire, C.; Pereira, A.M. Multifunctional mixed valence N-doped 2O4 hybrid nanomaterials: From engineered one-pot coprecipi tation to application in energy storage paper supercapacitors. Nanoscale 2018, 10, 12820–12840.
4. Luo, L.; Chen, Z.; Ke, H.Z.; Sha, S.; Cai, G.M.; Li, D.W.; Yang, H.J.; Yang, X.W.; Zhang, R.Q.; Li, J.Q.; et al. Facile synt hesis of three-dimensional MgFe2O4/graphene aerogel composites for high lithium storage performance and its applic ation in full cell. Mater. Des. 2019, 182, 108043.
5. Brown, E.; Yan, P.L.; Tekik, H.; Elangovan, A.; Wang, J.; Lin, D.; Li, J. 3D printing of hybrid MoS2-graphene aerogels as highly porous electrode materials for sodium ion battery anodes. Mater. Des. 2019, 170, 107689.
6. Xiong, X.Q.; Luo, W.; Hu, X.L.; Chen, C.J.; Qie, L.; Hou, D.F.; Huang, Y.H. Flexible Membranes of MoS2/C Nanofibers by Electrospinning as Binder-Free Anodes for High-Performance Sodium-Ion Batteries. Sci. Rep. 2015, 5, 9254.
7. Zhang, S.Q.; Qin, X.Y.; Liu, Y.M.; Zhang, L.H.; Liu, D.Q.; Xia, Y.; Zhu, H.; Li, B.H.; Kang, F.Y. A Conductive/Ferroelectric Hybrid Interlayer for Highly Improved Trapping of Polysulfides in Lithium-Sulfur Batteries. Adv. Mater. Interfaces 2019, 6, 1900984.
8. Xu, K.B.; Shen, Y.N.; Zhang, K.; Yang, F.; Li, S.J.; Hu, J.Q. Hierarchical assembly of manganese dioxide nanosheets on one-dimensional titanium nitride nanofibers for high-performance supercapacitors. J. Colloid Interface Sci. 2019, 552, 7 12–718.
9. Lapkin, D.A.; Malakhov, S.N.; Demin, V.A.; Chvalun, S.N.; Feigin, L.A. Hybrid polyaniline/polyamide-6 fibers and nonwo ven materials for assembling organic memristive elements. Synth. Met. 2019, 254, 63–67.
10. Döpke, C.; Grothe, T.; Steblinski, P.; Klöcker, M.; Sabantina, L.; Kosmalska, D.; Blachowicz, T.; Ehrmann, A. Magnetic Nanofiber Mats for Data Storage and Transfer. Nanomaterials 2019, 9, 92.
11. Qazi, T.H.; Rai, R.; Dippold, D.; Roether, J.E.; Schubert, D.W.; Rosellini, E.; Barbani, N.; Baccaccini, A.R. Development and characterization of novel electrically conductive PANI–PGS composites for cardiac tissue engineering applications. Acta Biomater. 2014, 10, 2434–2445.
12. Martins, A.M.; Eng, G.; Caridade, G.; Mano, F.; Reis, R.L. Electrically conductive chitosan/carbon scaffolds for cardiac ti ssue engineering. Biomacromolecules 2014, 15, 635–643.
13. Guo, B.; Ma, P.X. Conducting polymers for tissue engineering. Biomacromolecules 2018, 19, 1764–1782.
14. Prabhakaran, M.P.; Ghasemi-Mobarakeh, L.; Jin, G.; Ramakrishna, S. Electrospun conducting polymer nanofibers and electrical stimulation of nerve stem cells. J. Biosci. Bioeng. 2011, 112, 501–507.
15. Wu, Y.; Wang, L.; Guo, B.; Ma, P.X. Interwoven aligned conductive nanofiber yarn/hydrogel composite scaffolds for engi neered 3D cardiac anisotropy. ACS Nano 2017, 11, 5646–5659.
16. Nekouian, S.; Sojoodi, M.; Nadri, S. Fabrication of conductive fibrous scaffold for photoreceptor differentiation of mesen chymal stem cell. J. Cell. Physiol. 2019, 234, 15800–15808.

17. Rahmani, A.; Nadri, S.; Kazemi, H.S.; Mortazavi, Y.; Sojoodi, M. Conductive electrospun scaffolds with electrical stimula tion for neural differentiation of conjunctiva mesenchymal stem cells. Artif. Organs 2019, 43, 780–790.

18. Garrudo, F.F.F.; Chapman, C.A.; Hoffman, P.R.; Udangawa, R.W.; Silva, J.C.; Mikael, P.E.; Rodrigues, C.A.V.; Cabral, J.M.S.; Morgado, J.M.F.; Ferreira, F.C.; et al. Polyaniline-polycaprolactone blended nanofibers for neural cell culture. E ur. Polym. J. 2019, 117, 28–37.

19. Ghasemi, A.; Imani, R.; Yousefzadeh, M.; Bonakdar, S.; Solouk, A.; Fakhrzadeh, H. Studying the Potential Application o f Electrospun Polyethylene Terephthalate/Graphene Oxide Nanofibers as Electroconductive Cardiac Patch. Macromol. Mater. Eng. 2019, 304, 1900187.

20. Walker, B.W.; Lara, R.P.; Yu, C.H.; Sani, E.S.; Kimball, W.; Joyce, S.; Annabi, N. Engineering a naturally-derived adhesi ve and conductive cardiopatch. Biomaterials 2019, 207, 89–101.

21. Almasi, N.; Hosseinzadeh, S.; Hatamie, S.; Sangsari, G.T. Stable conductive and biocompatible scaffold development u sing graphene oxide (GO) doped polyaniline (PANi). Int. J. Polym. Mater. Polym. Biomater. 2019.

22. Bahrami, S.; Solouk, A.; Mirzadeh, H.; Seifalian, A.M. Electroconductive polyurethane/graphene nanocomposite for bio medical applications. Compos. Part B Eng. 2019, 168, 421–431.

23. Stone, H.; Lin, S.G.; Mequanint, K. Preparation and characterization of electrospun rGO-poly(ester amide) conductive s caffolds. Mater. Sci. Eng. C Mater. Biol. Appl. 2019, 98, 324–332.

24. Yao, J.Y.; Chen, Y.F.; Li, W.D.; Chen, X.; Fan, X.D. Fabrication and characterization of electrospun PLLA/PANI/TSA fibe rs. RSC Adv. 2019, 9, 5610–5619.

25. Yardimci, A.I.; Aypek, H.; Ozturk, O.; Yilmaz, S.; Ozcivici, E.; Mese, G.; Selamet, Y. CNT Incorporated Polyacrilonitrile/P olypyrrole Nanofibers as Keratinocytes Scaffold. J. Biomim. Biomater. Biomed. Eng. 2019, 41, 69–81.

26. Li, Y.M.; Zhao, R.; Li, X.; Wang, C.Y.; Bao, H.W.; Wang, S.D.; Fang, J.; Huang, J.Q.; Wang, C. Blood-compatible Polyan iline Coated Electrospun Polyurethane Fiber Scaffolds for Enhanced Adhesion and Proliferation of Human Umbilical Vei n Endothelial Cells. Fibers Polym. 2019, 20, 250–260.

27. Juhász Junger, I.; Wehlage, D.; Böttjer, R.; Grothe, T.; Juhász, L.; Grassmann, C.; Blachowicz, T.; Ehrmann, A. Dye-se nsitized solar cells with electrospun-nanofiber mat based counter electrodes. Materials 2018, 11, 1604.

28. Juhász, L.; Juhász Junger, I. Spectral analysis and parameter identification of textile-based dye-sensitized solar cells. Materials 2018, 11, 1623.

29. Kohn, S.; Wehlage, D.; Juhász Junger, I.; Ehrmann, A. Electrospinning a dye-sensitized solar cell. Catalysts 2019, 9, 9 75.

30. Eslah, S.; Nouri, M. Synthesis and characterization of tungsten trioxide/polyaniline/polyacrylonitrile composite nanofiber s for application as a counter electrode of DSSCs. Russ. J. Electrochem. 2019, 55, 291–304.

31. Jiang, D.H.; Tsai, P.C.; Kuo, C.C.; Jhuang, F.C.; Guo, H.C.; Chen, S.P.; Liao, Y.C.; Satoh, T.; Tung, S.H. Facile Preparat ion of Cu/Ag Core/Shell Electrospun Nanofibers as Highly Stable and Flexible Transparent Conductive Electrodes for O ptoelectronic Devices. ACS Appl. Mater. Interfaces 2019, 11, 10118–10127.

32. Sun, J.H.; Liu, J.N.; Chen, H.; Han, X.; Wu, Y.; He, J.; Han, C.; Yang, G.C.; Shan, Y.P. Strongly coupled Mo2C and Ni n anoparticles with in-situ formed interfaces encapsulated by porous carbon nanofibers for efficient hydrogen evolution re action under alkaline conditions. J. Colloid Interface Sci. 2020, 558, 100–105.

33. Li, M.X.; Zhu, Y.; Song, N.; Wang, C.; Lu, X.F. Fabrication of Pt nanoparticles on nitrogen-doped carbon/Ni nanofibers f or improved hydrogen evolution activity. J. Colloids Interface Sci. 2018, 514, 199–207.

34. Zhang, Z.X.; Wang, Y.X.; Leng, X.X.; Crespi, V.H.; Kang, F.Y.; Lv, R.T. Controllable edge exposure of MoS2 for efficient hydrogen evolution with high current density. ACS Appl. Energy Mater. 2018, 1, 1268–1275.

35. Rheem, Y.; Han, Y.; Lee, K.H.; Choi, S.M.; Myung, N.V. Synthesis of hierarchical MoO2MoS2 nanofibers for electrocatal ytic hydrogen evolution. Nanotechnology 2017, 28, 105605.

36. Liu, C.B.; Wang, L.L.; Tang, Y.H.; Luo, S.L.; Liu, Y.T.; Zhang, S.Q.; Zeng, Y.X.; Xu, Y.Z. Vertical single or few-layer MoS 2 nanosheets rooting into TiO2 nanofibers for highly efficient photocatalytic hydrogen evolution. Appl. Catal. B Environ. 2015, 164, 1–9.

37. Ozoemena, O.C.; Shai, L.J.; Maphumulo, T.; Ozoemena, K.I. Electrochemical Sensing of Dopamine Using Onion-like C arbons and Their Carbon Nanofiber Composites. Electrocatalysts 2019, 10, 381–391.

38. Avossa, J.; Paolesse, R.; Di Natale, C.; Zampetti, E.; Bertoni, G.; De Cesare, F.; Scarascia-Mugnozza, G.; Macagnano, A. Electrospinning of Polystyrene/Polyhydroxybutyrate Nanofibers Doped with Porphyrin and Graphene for Chemiresist or Gas Sensors. Nanomaterials 2019, 9, 280.

39. Shaker, A.; Hassanin, A.H.; Shaalan, N.M.; Hassan, M.A.; Abd El-Moneim, A. Micropatterned flexible strain gauge sensor based on wet electrospun polyurethane/PEDOT: PSS nanofibers. Smart Mater. Struct. 2019, 28, 075029.
40. Yang, K.; Yin, F.X.; Xia, D.; Peng, H.F.; Yang, J.Z.; Yuan, W.J. A highly flexible and multifunctional strain sensor based on a network-structured MXene/polyurethane mat with ultra-high sensitivity and a broad sensing range. Nanoscale 2019, 11, 9949–9957.
41. Khalili, N.; Chu, M.; Naguib, H.E. Solvent-assisted electrospun fibers with ultrahigh stretchability and strain sensing capabilities. Smart Mater. Struct. 2019, 28, 055018.
42. Ren, M.N.; Zhou, Y.J.; Wang, Y.; Zheng, G.Q.; Dai, K.; Liu, C.T.; Shen, C.Y. Highly stretchable and durable strain sensor based on carbon nanotubes decorated thermoplastic polyurethane fibrous network with aligned wavelike structure. Chem. Eng. J. 2019, 360, 762–777.
43. Nan, N.; He, J.X.; You, X.L.; Sun, X.Q.; Zhou, Y.M.; Qi, K.; Shao, W.L.; Liu, F.; Chu, Y.Y.; Ding, B. A Stretchable, Highly Sensitive, and Multimodal Mechanical Fabric Sensor Based on Electrospun Conductive Nanofiber Yarn for Wearable Electronics. Adv. Mater. Technol. 2019, 4, 1088338.
44. Harjo, M.; Zondaka, Z.; Leemets, K.; Järvekülg, M.; Tamm, T.; Kiefer, R. Polypyrrole-coated fiber-scaffolds: Concurrent linear actuation and sensing. J. Appl. Polym. Sci. 2019.
