Conductive Electrospun Nanofiber Mats

Subjects: Nanoscience & Nanotechnology
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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. Here we give an overview of the most recent applications of such conductive electrospun nanofiber mats.

Keywords: electrospinning ; conductive nanofibers ; conductive solution ; conductive polymers ; conductive coating

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]. This results in a strong use of combinations of magnetic loss materials like magnetic metals with dielectric loss materials like carbon in different modifications for the preparation of lightweight EM composite absorbers, as depicted in Figure 1[2][3][4][5]. Nanofiber mats electrospun from other combinations such as ZnO/C are also reported to show good microwave absorption[6].

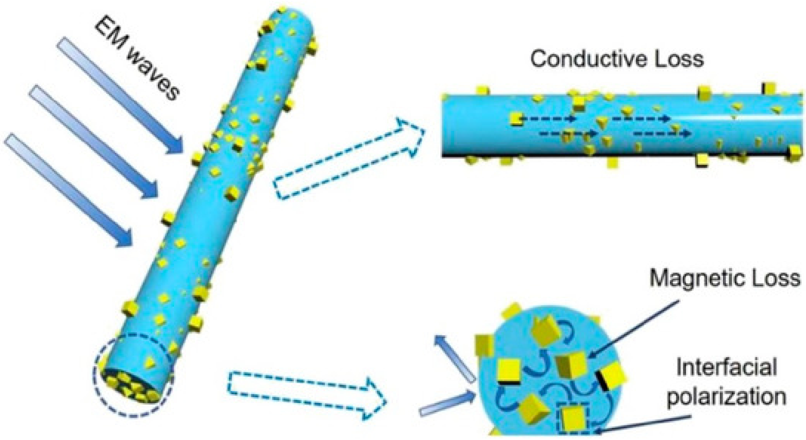

Figure 1. Electromagnetic wave absorption due to magnetic and dielectric losses. Reprinted from , with permission from Elsevier[2].

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[7], carbon nanotubes[8] or graphene aerogel[9][10]. 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[11].

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 (Fig. 2), 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[12].

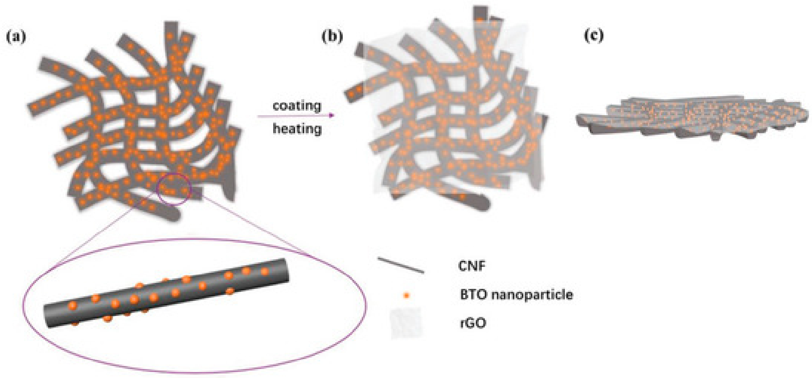

Figure 2. Pure $BaTiO_3$@CNF interlayer and interlayer loaded with rGO. Reprinted from[12] , with permission from WILEY-VCH Verlag GmbH & Co. KGaA. (**a**) $BaTiO_3$@CNF interlayer; (**b**) rGO/$BaTiO_3$@CNF interlayer in top view; (**c**) rGO/$BaTiO_3$@CNF interlayer in side view.

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[13].

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[14]. Döpke et al. suggested producing conductive magnetic nanofiber mats for data storage and transfer[15].

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[16][17]. In general, scaffolds with embedded conductive materials often show advances against non-conductive nanofiber mats, whether prepared with PAni, PPy or CNTs[18][19][20].

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[21]. 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[22]. 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[23]. 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[24]. For the same purpose, Walker et al. suggested using electrospun gelatin methacryloyl with bio-ionic liquid to combine adhesive and conductive properties[25].

Cell proliferation and gene expression could also be optimized by doping PAni scaffolds with graphene oxide and plasma treatment to hydrophilize the fiber surface[26]. Attachment, spreading and proliferation of fibroblasts and endothelial cells was optimized by tailoring the concentration of multilayer graphene flakes in electrospun polyurethane nanofiber mats[27]. Embedding reduced graphene oxide in electrospun poly(ester amide) (PEA) and PEA/chitosan scaffolds increased cardiac differentiation[28]. 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 (Figure 3)[29].

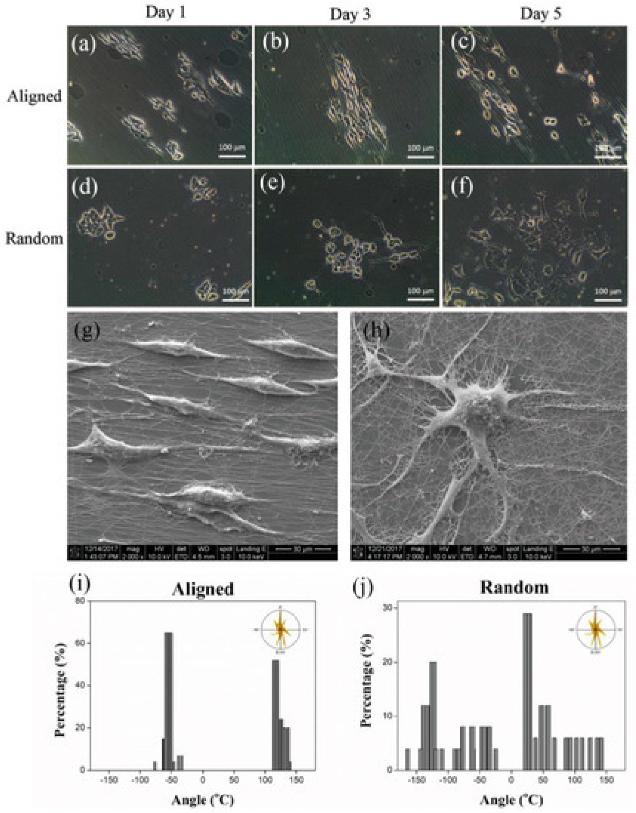

Figure 3. PC12 cells grown on aligned (**a**–**c**,**g**) and random nanofibers (**d**–**f**,**h**), resulting in oriented or random neurites (**i**,**j**). Reprinted from[29] , with permission from WILEY-VCH Verlag GmbH & Co. KGaA.

Osteoblast cells were found to grow and proliferate well on electrospun poly(L-lactic acid)/PAni/p-toluene sulfonic acid nanofiber mats[30]. Keratinocytes were shown to grow on electrospun PAN/PPy and PAN/PPy/CNT nanofiber mats[31]. 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[32].

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 (Fig. 4)[33]. The optimum number of layers resulted in a sheet resistance around 150 Ω, reduced from approximately 550 Ω for a single coating layer[33][34]. 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[35].

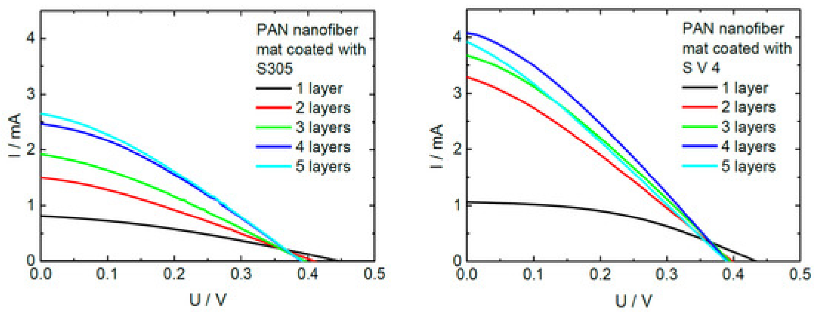

Figure 4. Current-voltage curves of DSSCs, prepared with different PEDOT:PSS counter electrodes. Reprinted from[33], originally published under a CC BY license.

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[36]. 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[37].

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[38]. 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[39]. 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[40]. 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[41]. 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 (Figure 5)[42].

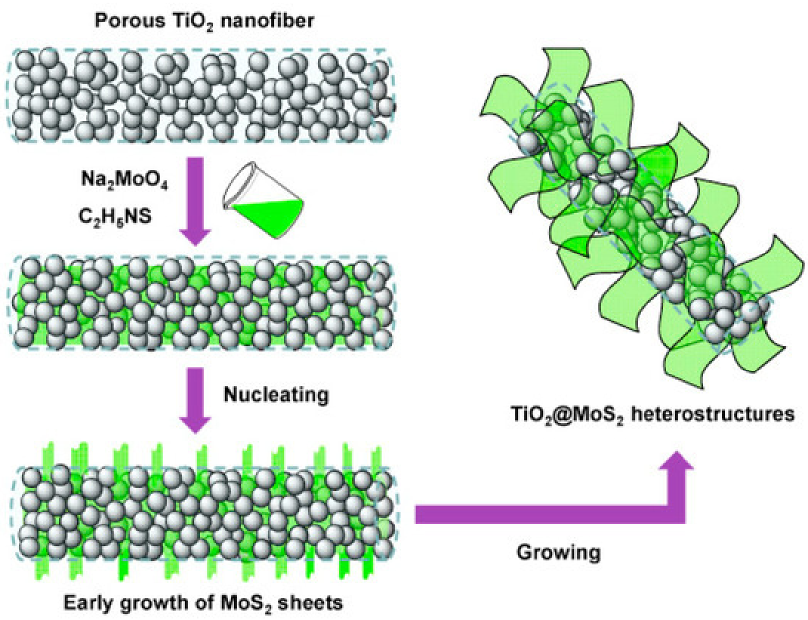

Figure 5. Nucleation and growth of MoS_2 nanosheets on porous TiO_2 nanofibers. Reprinted from[42] , with permission from Elsevier.

7. Sensors

Lee et al. used electrospun WO_3 nanofibers coated with RuO_2 nanorods as a sensor for H_2O_2 and L-ascorbic acid. They could show that by the addition of the RuO_2 nanorods, the electrocatalytic activity was increased, and the sensing abilities were significantly improved in comparison with pure WO_3 nanofibers, as shown in Figure 6[43].

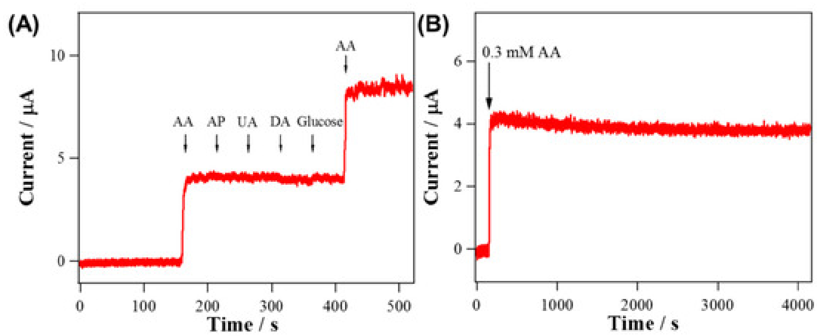

Figure 6. The amperometric response of the WO_3 nanofiber with RuO_2 nanorods, showing the stability for detection of L-ascorbic acid (AA) against additions of diverse chemicals (**A**) and against time (**B**). Reprinted from[43], originally published under a CC BY license.

To sense dopamine, Ozoemena et al. used electrospun PAN/onion-like carbon nanofibers and found a high conductivity and sensitivity of the resulting nanofibers[44]. 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[45].

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[46]. Yang et al. coated highly conductive MXene sheets on electrospun PU nanofibers mats to produce highly sensitive strain sensors[47]. Flexible strain sensors with up to 1000% elongation were prepared from conductively coated electrospun styrenebutadiene-styrene copolymer[48]. 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[49]. 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[50].

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[51]. 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.

Table 1. Examples of electrical conductivities of nanofiber mats mentioned in this paper, sorted by conductivity.

Nanofiber Materials	**Conductivity/(S/cm)**	**Ref.**
PVA/polyaniline	$0.35 \cdot \times 10^{-9}$	[52]
Multi-wall CNTs in polystyrene	10^{-8}	[53]
Polypyrrole/poly(butyl acrylate-co-methyl methacrylate)	$0.5 \cdot \times 10^{-6}$	[54]
Polyethylene terephthalate/graphene oxide	$1 \cdot \times 10^{-6}$	[24]
Glucose-gelatin coated with polypyrrole	$3 \cdot \times 10^{-6}$	[32]
Multi-wall CNTs in a polyurethane/silk	$60 \cdot \times 10^{-6}$	[55]
PCL/PAni	$80 \cdot \times 10^{-6}$	[23]
Camphoric acid doped PAni/poly(ethylene oxide)	10^{-6}–10^{-4}	[56]
PAN coated with multi-wall CNTs	$3 \cdot \times 10^{-3}$	[57]
Multi-wall CNTs/polyurethane	10^{-5}–10^{-2}	[58]
Poly(caprolactone)/PAni	10^{-4}–10^{-1}	[23]
Poly(L-lactide acid) coated with chitosan/ polypyrrole	0.01	[59]
Fe_3O_4/polylactic acid-glycolic acid coated with pyrrole	0.58	[59]
Graphite in polystyrene	1	[60]
Polyamide-6 nanofiber mats coated with PAni	1	[14]
Trimethylethoxysilane/graphene	20	[61]
PEDOT	60	[62]

PU coated with p-toluenesulfonate doped PPy	276	[63]
Silver nanowires in polyvinyl alcohol	650	[64]
Poly(vinylidene fluoride-co-trifluoro ethylene) coated with multi-wall CNTs and reduced graphene oxide	4000	[65]

Generally, possible applications of electrospun nanofibers vary from biomedicine to sensors to batteries to hydrogen evolution. Similarly, the range of conductivities achievable with different methods is wide. This entry gives an overview of some recent applications.

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