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Multifunctional Composite Nanofibers

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Abstract

Multi-functional fibrous materials are a new family of fiber materials whose physical and chemical properties are sensitive to the change in the environment such as temperature, pressure, electric field, magnetic field, optical wavelength, adsorbed gas molecules and the pH value. This paper introduces a new approach to translate functions from nanoparticles to advanced fibrous structures by co-electrospinning of composite nanofibers. To illustrate this composite nanofiber concept an example of nanofibers that have tailorable, electrical and magnetic functions is shown.

Keywords: Functional Materials; Nanofibers; Co-electrospinning; Nanocomposite; Lignin Nanofiber

1 Introduction

Multi-functional materials are a new family of materials whose physical and chemical properties are sensitive to the change in the environment such as temperature, pressure, electric field, magnetic field, optical wavelength, adsorbed gas molecules and the pH value. The functional materials utilize the native properties and functions of their own to achieve an intelligent action [1]. Multi-functional materials in the form of fibers bring additional attribute as a carrier of the functions to higher order structures ranging from medical devices to clean water filters, to electrodes for rechargeable batteries and solar cells [2].

In the search for multi-functional material concepts one can find abundant of clues in nature. In fact multifunctionality is a norm rather than exception in living systems. Fibrous materials in nanometer scale are the fundamental building blocks of living systems. From the 1.5 nm double helix strand of DNA molecules, including cytoskeleton filaments with diameters around 30 nm, to sensory cells such as hair cells and rod cells of the eyes, nanoscale fibers form the Extra-cellular Matrices (ECM) or the multifunctional structural backbone for tissues and organs [2]. Specific junctions between these cells conduct electrical and chemical signals that result from various kinds of stimulation. The signals direct normal functions of the cells such as energy storage, information storage and retrieval, tissue regeneration, and sensing. Analogous to nature's design, nanofibers and their composites can provide fundamental building blocks for the construction of

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devices and structures that perform unique new functions. The areas expected to be impacted by the nanofiber based technology include drug delivery systems and scaffolds for tissue engineering, wires, super capacitors, transistors and diodes for information technology, systems for energy transport, conversion and storage, as well as smart structural composites for medical devices [2-3].

Some research studies have been done on multi-functional electrospun composite nanofiber fabrication and applied in different fields. In structural composite areas, for example, Carbon Nanotubes (CNT) reinforced Polyacrylonitrile (PAN) nanocomposite fiber has been fabricated by Ko *et al.* previously. It has been shown that co-electrospinning provides an excellent means for the translation of the mechanical properties of CNT to polymer fibril matrix by the inclusion of a small amount of CNT [4]. Multifunctional composite nanofibers can also be used in electrical and electronic application area. Lithium ion battery anode has been prepared by electrospinning of Poly(acrylonitrile-co-acrylamide) (PANAM) and silicon nanoparticles [5]. Using the process of electrospinning, nanofiber materials as a transparent conductor have been developed and their performance for applications in solar cell applications has been explored [5]. Electospun fiber could make soft magnetic materials with high saturation magnetization and high permeability for Electromagnetic Interference (EMI) shielding applications [6-8]. Bayat *et al.* developed electromagnetic nanofibers through incorporation of magnetic nanoparticles (Fe_3O_4) to PAN by electrospinning [6]. The electrical conductivity increased with the increase of carbonization temperature and Fe_3O_4 nanoparticles content in the carbon matrix. Chen *et al.* [7] fabricated cobalt ferrite ($CoFe_2O_4$)-embedded Polyacrylonitrile (PAN) carbon nanofibers. The saturation magnetization of this carbon fiber was 45 emu/g and it also demonstrated superparmagnetic behavior. Castillo *et al.* [8] designed a multifunctional core-shell fiber mat by co-electrospinning process. They used a fluorescent pH-sensitive copolymer (NP1(X)) as the outer fluid. Two different suspension, one is a polymethyl methacrylate (PMMA) melt magnetic nanoparticles (EDMA/MMA/-Fe_3O_4-OA-NP), and another is O_2 indicator (PtOEP) suspension, as the inner fluid. Thus, the core is magnetic and optically sensitive to O_2 and the shell is sensitive to pH. In biomedical area, multifunctional composite nanofibers have been tested out. An example of antibacterial fibers with silver nanoparticles has been studied [9]. It has been found that the Ag/PLLA fibrous membranes showed strong antibacterial properties. Thus, Ag/PLLA fibrous membrane can be used as an antibacterial scaffold for tissue engineering. Li *et al.* [10] developed a poly (L-lactic acid) (PLLA)/keratin composite nonwoven fibrous membrane as ECM for bone tissue engineering. Their testing results showed that the cell had higher viability and differentiation on PLLA/keratin membranes than on pure PLLA membranes. Li *et al.* further developed a keratin/hydroxyapatite (HA) nanocomposite then put it into electrospun PLLA fiberous membrane to mimic the natural mineralized nanofibrial counterparts. The result indicated that the keratin-HA could enhance the human osteoblast cell adhesion and formation on the PLLA-keratin-HA membranes [11-12]. Electrospun nanofibers are also an ideally scaffold for forming a hierarchically organized multifunctional components [13]. Bai *et al.* [14] assembled a TiO_2/PVP electrospun nanofiber/ZnO nanorod hierarchically multifunctional membrane for water filtration. It had several advantages such as high permeate flux and high antibacterial capacity. Lim *et al.* [15] combined sol-gel process and electrospinning technique to make Methyltriethoxysilane (MTES) organic-inorganic hybrid fabrics with thermally stable superhydrophobicity. The electrospun MTES fiber exhibited large water contact angle on surface and still maintained superhydrophobicity after heat treatment at high temperature. Summarily, multifunctional composite nanofibers preparation becomes very promising general method to transfer functions from nanoparticles to polymer and

hence to enhance materials overall performance value.

In this paper we illustrate a new approach to translate functions from nanoparticles to advanced fibrous structures by the co-electrospinning process. The paper concludes with examples of the development of electromagnetic nanofiber.

2 Materials and Methods

2.1 The Electrospinning Process

Although the effect of fiber diameter on the performance and processibility of fibrous structures have long been recognized the practical generation of fibers down to the nanometer scale was not realized until the rediscovery and popularization of the electrospinning technology by Professor Darrell Reneker almost a decade ago [16]. The ability to create nanoscale fibers from a broad range of polymeric materials in a relatively simple manner using the electrospinning process coupled with the rapid growth of nanotechnology in the recent years have greatly accelerated the growth of nanofiber technology. Although there are several alternate methods for generating fibers in a nanometer scale, none matches the popularity of the electrospinning technology due largely to the great simplicity of the electrospinning process. In this paper we will focus on the electrospinning technology.

Techniques for electrostatic generation of ultra-fine fibers ("electrospinning") has been known since the 1930's [17]. In this non-mechanical, electrostatic technique a high electric field is generated in a polymer solution contained in a glass syringe with a capillary tip and a metallic collection screen. When the voltage reaches a critical value, the charge overcomes the surface tension of the deformed drop of the suspended polymer solution formed on the tip of the syringe and a jet of ultra fine fibers is produced. The electrically charged jet undergoes a series of electrically induced bending instabilities during its passage to the collection screen that results in the hyper-stretching of the jet. This stretching process is accompanied by the rapid evaporation of the solvent molecules that reduces the diameter of the jet in a cone shape radius. The dry fibers are accumulated on the surface of the collection screen resulting in a non-woven mesh of nano to micron diameter fibers. A schematic drawing of the electrospinning process is shown in Fig. 1. The process can be adjusted to control the fiber diameter by varying the electric field strength and polymer solution concentration, while the duration of electrospinning controls the thickness of fiber deposition. According to Rutledge *et al.* [21], the diameter of electrospun fibers is governed by the following equation:

$$d = \left[\gamma\varepsilon\frac{Q^2}{I^2}\frac{2}{\pi(2\ln\chi - 3)}\right]^{1/3} \tag{1}$$

where d = fiber diameter; γ = surface tension; ε = dielectric constant; Q = flow rate; I = current carried by the fiber; and χ = ratio of the initial jet length to the nozzle diameter.

The fiber diameter can be controlled by adjusting the flow rate, the conductivity of the spinning line, and the spinneret diameter. Fiber diameter can be minimized by increasing the current carrying capability of the fiber through introduction of a conductive filler such as carbon black, carbon nanotube, metallic atoms or mixing with an intrinsically conductive polymer. An increase of current carrying capability of the fiber (I) by 32 times will bring about ten-fold decrease in

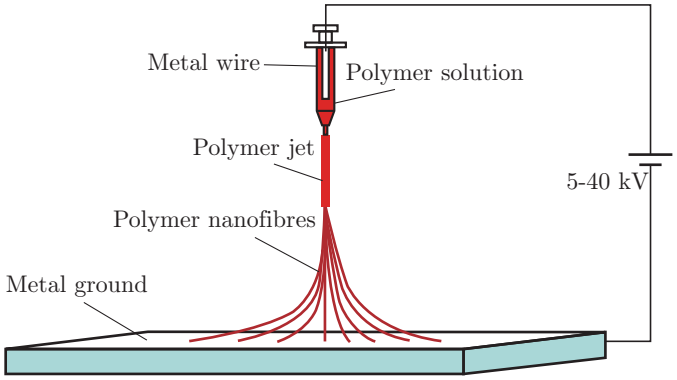


Fig. 1: The electrospinning process

fiber diameter. Alternatively, if the current, I, is kept constant, one can bring about a ten-fold decrease in fiber diameter by reducing the flow rate by 32 times. Reducing the spinneret nozzle diameter can also bring about a reduction in fiber diameter. When the χ value increases from 10 to 1000, the diameter of the fiber will decrease by approximately 2 times.

While the Rutledge equation provides a reasonable link between fiber diameter and process control parameters, it ignores the intrinsic properties of the spinning dope such as molecular conformation, which relates to the polymer concentration and molecular weight. To address this issue we introduce a dimensionless parameter, the Berry number (Be) [22] expressed in terms of the product of intrinsic viscosity, $[\eta]$, and the concentration K of the polymer spinning dope.

$$Be = [\eta] \times K \tag{2}$$

Buildig on the concept of the Berry number Ko and Yamashita found a simple law governing the formation of nanofibers from various polymers by relating fiber diameter to the Berry number as expressed by the following equation [23]:

$$D = A(Be)^C \tag{3}$$

where A and C are constants. That is to say, the diameter D of the nanofiber is shown to have a power law relationship to the Berry number.

2.2 The Concept of Composite Nanofibers

Nanoparticles of various geometries and shapes can be combined with a suitable polymer matrix to form composite nanofibers. Among various available nanomaterials in 0-D, 1-D, and 2-D geometry as illustrated in Fig. 2 and summarized in Table 1, magnetic nanoparticles, quantum dots, photocatalytic nanoparticles and carbon nanotubes are excellent examples of nanoparticles that can be incorporated into electrospinning process to fabricate composites fibers with interesting functions. We demonstrated that the nanocomposites fibers produced by co-electrospinning can mechanically stabilize particles and capable of transforming into complicated structures while maintaining the nanoparticles properties. The nanoparticle embedded nanocomposite fibers not only improve mechanical properties but also introduce new functions in the form of fibers. Iron oxide nanoparticles can be used for biomedical applications, electromagnetic interference shielding, catalyst and sensors [24]. Quantum dots such as CdS, CdSe and ZnS can be used in semiconductive devices, biological labeling and optical switches [25, 26]. TiO_2 particle has been known

for its strong photocatalytic properties for filtration and antibacterial applications [27]. Carbon nanotubes has brought a great attention for its superb mechanical and electrical properties [28]. Creating nanocomposite fibers through the electrospinning process using nanosize particles has been previously explored and successfully demonstrated as shown in the following examples. Previous work of Carbon Nanotubes (CNT) nanocomposite fabrication by Ko *et al.* showed that co-electrospinning provides an excellent means for the translation of the mechanical properties of CNT to polymer fibril matrix by the inclusion of a small amount of CNT. For example, a 4 to 5 fold increase of mechanical properties was found with the introduction of less than 1.5% by weight of CNT to the PAN matrix nanocomposite fibers [4]. In order to explore the feasibility of using nanocomposites as interior materials for buildings and houses, such as shoji paper, wallpaper, and fusuma paper, the thermal insulation properties of nanocomposites consisting of Cloisite 15A-nanoclay reinforced PVDF in film and fibrous forms, were evaluated. A 10X higher thermal insulation values was observed for the nanoclay filler nanofibrous structures [28]. Goto *et al.* demonstrated that the incorporation of silica particles into PA66 nanofibers led to significant improvement of the tensile properties. They also found that PAN/silica composite nanofibers synthesized by blending PAN and APES showed good adsorption property with hydrophilic molecules of BTB, i.e. PAN/APES composite nanofibers efficiently captured the hydrophobic molecules [29]. Carbon free selective permeable membranes were developed by Ko *et al.* using TiO_2 filled polyurathane nanofibers. These composite fiber membranes were demonstrated to be capable of repelling Chem/Bio agents while allowing the body moisture vapor to escape [30]. Yang and Ko developed antimicrobial fibrous scaffolds using photocatalytic composite nanofibers by coelectrospinning of 60 nm TiO_2 nanoparticles with PVDF. The photocatalytic effect was confirmed using methylene blue dye bleaching caused by TiO_2. A 3wt% of TiO_2 content in the fiber was found to be effective in the antiviral activity in the E. Coli culture. It was also found from bovine osteoblast culture that higher amount of TiO_2 particles facilitate higher cell attachment and proliferation [31]. By introducing a small amount of carbon nanotube into PEDT, an intrinsically conducive polymer, a ten-fold increase in electrical conductivity was demonstrated by Ko *et al.* for the co-electrospun nanofiber mats [32].

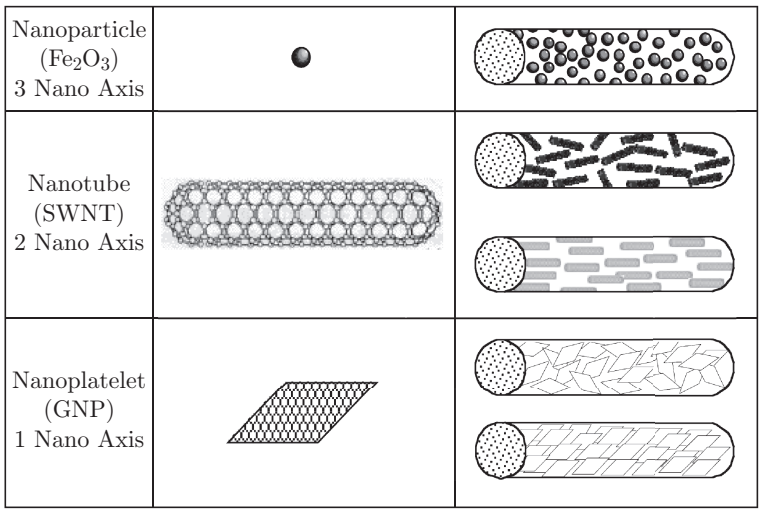


Fig. 2: Geometry of nanoparticles for co-electrospinning

Table 1: Functions of composite nanofibers

Function	Nanoparticles	Polymer
Mechanical	CNT, GNP	PAN, PVDF, Cellulose
Thermal	clay	PAN
Electrical	CNT	PEDT, SBS
Magnetic	Fe_3O_4	PVDF, PCL, PAN, PEO
Optical	CdS (quantum dot)	PEO
Biological antimicrobial	Ag, TiO_2	PCL, PLGA
Physical hydrophillicity	SiO_2	PAN, PA66
Photocatalytic	TiO_2	PU

3 Results

It should be noted that multifunctional composite nanofibers preparation becomes very promising general method to transfer functions from nanoparticles to polymer and hence to enhance materials overall performance/price value. To illustrate this composite nanofiber concept, an example of multifunctional composite nanofibers from lignin that have tailorable, electrical and magnetic functions is shown below.

Electromagnetic nanofibers from lignin were successfully prepared and characterized. Specifically, Softwood Kraft Lignin (SKL) based carbon nanofibres with electromagnetic properties were successfully prepared by electrospinning and by subsequent carbonization. The magnetic properties were incorporated to lignin composite nanofiber by embedding magnetic nanoparticles through the direct dispersion method and by in situ synthesis method.

In the direct dispersion method, iron oxide nanoparticles was suspended in DMF and then 35 w.t.% SKL lignin/PEO (lignin: PEO = 99:1 by weight) was added to the iron oxide-DMF ssuspension system. The iron oxide nanoparticles-DMF-lignin-PEO was sonicated for another 2 hours and then cooled to room temperature before subsequent electrospinning them into nanofiber mats. Stabilization of the as-spun fibers was performed by heating the fibers to 250 °C in air at a heating rate of 1 °C/min and held for 1 hour. Carbonization and the growth of magnetic iron oxide nanoparticles were achieved by treating the thermalstabilized fibers at 10 °C/min to 900 °C under Nitrogen and held for 1 hour.

Fe_3O_4 nanoparticles were directly dispersed to the lignin based carbon nanofiber matrix. The morphologies of the lignin based carbon nanofibre and the distribution of the directly dispersed Fe_3O_4 nanoparticles within the composite nanofiber were studied using SEM and TEM, as shown in Fig. 3. Fiber average diameters are 440 ± 90 nm. It can be seen that iron oxide nanoparticles agglomeration occurred.

The conductivity of the 5% Fe_3O_4 lignin based composite carbon nanofibres (carbonized at 900 °C) were 4∼6 S/cm, which is comparable to that of PAN based composite carbon nanofibres at 6∼8 S/cm with 5% Fe_3O_4 carbonized at 900 °C [6]. The magnetic properties of composite nanofibres were characterized using Superconducting Quantum Interference Device (SQUID) at 300K. Fig. 3 also shows the plot of magnetization (M) versus magnetic field (H) (M-H curve), where ferromagnetic hysteresis was observed for the lignin based composite carbon nanofibres. Lignin based composite nanofibres have saturation magnetization Ms = 8.59 emu/g, remanent

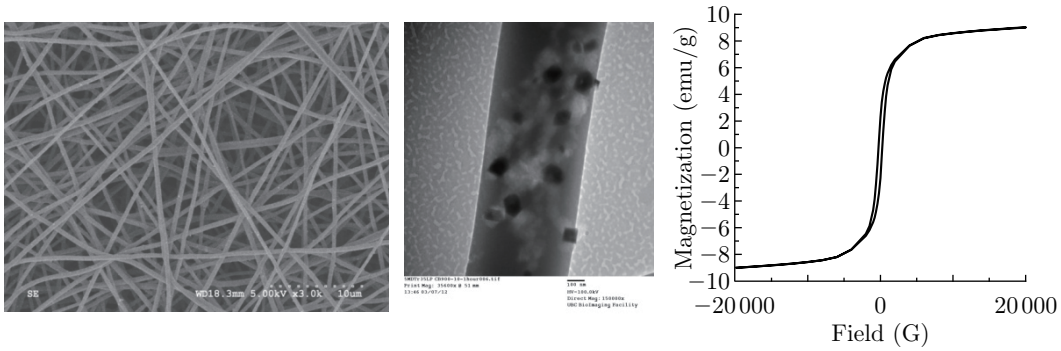


Fig. 3: SEM and TEM images of 5% Fe_3O_4 lignin based composite nanofibre carbonized at 900 °C and its magnetic hysteresis loop M-H curve

magnetization Mr = 2.24 emu/g and coercivity Hc = 250 Oe, which are similar to that of PAN based composite nanofibres, Ms = 7.5 emu/g, Mr = 2.62 emu/g and Hc =240 Oe [6].

For the in-situ synthesized magnetic carbon nanofiber from lignin, iron oxide nanoparticles precursor, Iron (III) acetylacetonate, (AAI) was dissolved in DMF and then 35 w.t.% SKL lignin/PEO (lignin:PEO = 99:1 by weight) was added to the AAI-DMF solution. The AAI-DMF-lignin-PEO solution was heated to 80 °C for 2 hours. The solutions were cooled to room temperature and electrospun into nanofiber mats. Stabilization of the as-spun fibers was performed by heating the fibers to 250 °C in air at a heating rate of 1 °C/min and held for 1 hour. Carbonization and the growth of magnetic iron oxide nanoparticles were achieved by treating the thermalstabilized fibers at 10 °C/min to 700 °C and 900 °C under Nitrogen and held for 1 hour.

For the in-situ synthesized magnetic carbon nanofiber from lignin, the morphologies of carbon nanofibres were studied using SEM (Fig. 4), and the presence and distribution of in-situ synthesized magnetic nanoparticles were verified through TEM (Fig. 4). Two examples are discussed below. One is nanofibers with 3% AAI carbonized at 700 °C (3A700). Fiber average diameters are 560 ± 88 nm. It can be seen that iron oxide nanoparticles (sizes about a few nanometers) were uniformly dispersed within the fiber matrix. Second example is nanofibers with 10% AAI carbonized at 900 °C (10A900). Fibers are 814 ± 122 nm in diameter. Iron oxide nanoparticles, about 50 nm, were still uniformly dispersed within the fiber matrix. The advantage of in-situ synthesis method is to permit the uniform dispersion of the nanoparticles within the ultrafine electrospun fibers.

The conductivity of the in-situ synthesized magnetic lignin based carbon nanofibre (0.21∼5.01 S/cm) were found to be at the same level as the in-situ synthesized magnetic PAN based carbon

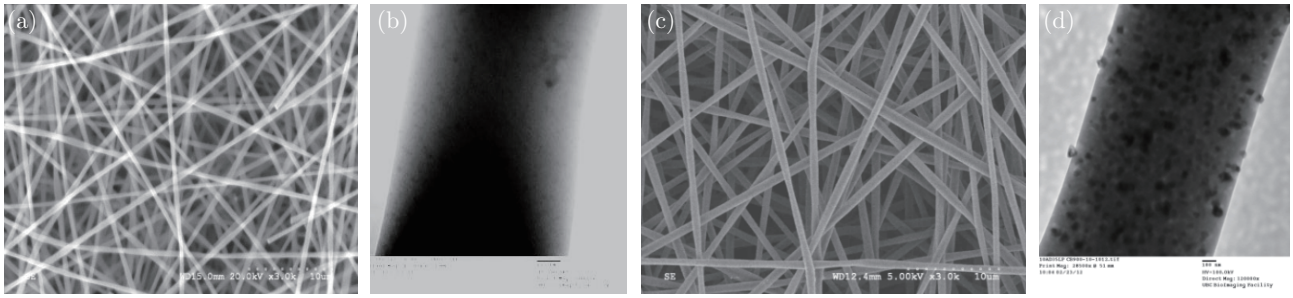


Fig. 4: SEM (a, c) and TEM (b, d) images of 3A700 (a, b) and 10A900 (c, d)

nanofibre (0.38 S/cm) [33]. The magnetic properties of in-situ synthesized lignin based magnetic carbon nanofibre are illustrated in Fig. 5. For 3A700, Ms = 1.26 emu/g, Mr = 0.007 emu/g and Hc = 18 Oe, which corresponds to the iron oxide superparamagnetic properties.10A 900 has Ms = 6.73 emu/g, Mr = 1.77 emu/g and Hc = 108 Oe, which relates to the ferromagnetic properties of iron oxide. It is believed that through the precise control of the processing conditions, both superparamagnetic properties and ferromagnetic properties can be transferred to lignin-based nanofibers.

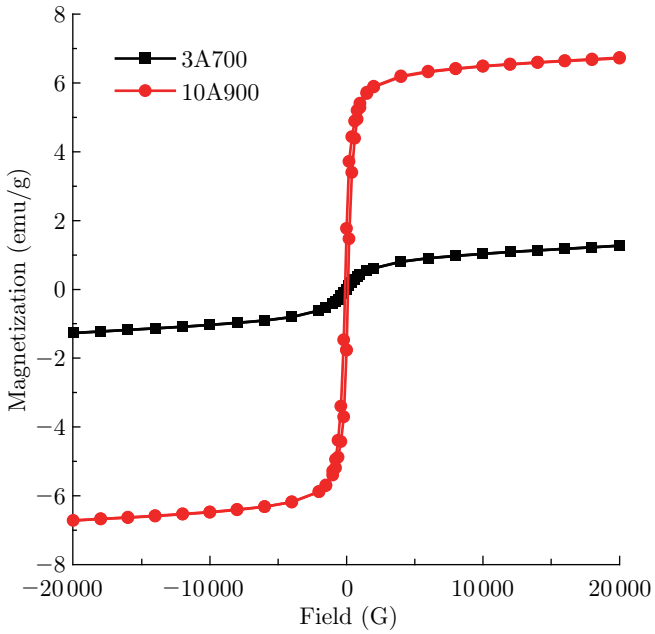


Fig. 5: Magnetic hysteresis loop of 3A700 and 10A900

In summary, through the multifunctional composite nanofibers preparation, functions have been incorporated into lignin. In the papermaking process, lignin is a major by-product, which is removed from wood through the pulping process. Only a small amount is currently used for commercial products, and 98% of lignin is being burnt as fuel. Therefore, multifunctional composite nanofibers from lignin would become new series of value-added lignin-derived products, which would enable low cost lignin entering into the high value advanced application area and would confer great benefits to the forest products industry.

4 Conclusions

In the evolution of fibrous material development we have reached the era of multifunctional nanofibers. Nanoparticular materials in various geometries and shapes possess outstanding functions unavailable in bulk materials. By combining the functional nanoparticles with a polymer matrix and forming composite nanofibers using the co-electrospinning process a processing pathway is now available, enabling the connection of the functional nanoparticle to higher order structures such as yarn, fabric, composites and products.

Experimental evidence shows that the nanoeffects of the nanoparticles can be transferred to fibrous assemblies thus opening up exciting design options for the next generation of high performance sportswear and advanced medical devices

The exciting new opportunities with the enabling nanofibrous materials also will bring about new challenges in quality control and scaleability of process. There is a need for standardization of characterization method for these new materials and new performance properties.

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References

[1] Wang ZL. Functional and smart materials: structural evolution and structure analysis, Plenum Pub Corp, 0306456516, 1998.

[2] Ko FK, Yang H. Functional nanofibre: enabling material for the next generations smart textiles. Journal of Fiber Bioengineering and Informatics 2008; 2(1): 81-92.

[3] Leung V. Biomedical applications of nanofibers. Polymers for Advanced Technologies 2011; 22(3): 350-365.

[4] Ko FK. Electrospinning of continuous carbon nanotube-filled nanofiber yarns. Advanced Materials 2003; 15(14): 1161-1165.

[5] Ritchie J. Electrospun composite nanofiber transparent conductor layer for solar cells. MRS Proceedings 2011; 1323.

[6] Bayat M, Yang H, Ko FK. Electromagnetic properties of electrospun Fe_3O_4/carbon composite nanofibers. Polymer 2011; 52(7): 1645-1653.

[7] Chen IH, Wang CC, Chen CY. Fabrication and characterization of magnetic cobalt ferrite/ polyacrylonitrile and cobalt ferrite/carbon nanofibers by electrospinning. Carbon 2010; 48(3): 604-611.

[8] Castillo M, Antonio L, Sánchez JFF, Gutiérrez. AF. One-step fabrication of multifunctional core-shell fibres by co-electrospinning. Advanced Functional Materials 2011; 21(18): 3488-3495.

[9] Li L. Antibacterial properties of nanosilver PLLA fibrous membranes. J. Nanomaterials 2009; Special edition: 1-5.

[10] Li JS, Li Y, Li L, Mak AFT, Ko FK, Qin L. Preparation and biodegradation of electrospun PLLA/keratin nonwoven fibrous membrane. Polymer Degradation and Stability 2009; 94: 1800-1807.

[11] Li JS, Li Y, Liu X, Zhang J, Zhang Y. Strategy to introduce an hydroxyapatite–keratin nanocomposite into a fibrous membrane for bone tissue engineering. Journal of Materials Chemistry B 2013; 1: 432-437.

[12] Li JS, Liu X, Zhang J, Zhang Y, Han Y, Hu J, Li, Y. Synthesis and characterization of wool keratin/hydroxyapatite nanocomposite. Journal of Biomedical Materials Research Part B-Applied Biomaterials 2012; 100B (4): 896-902.

[13] Teo WE, Ramakrishna S. Electrospun nanofibers as a platform for multifunctional, hierarchically organized nanocomposite. Composites Science and Technology 2009; 69(11): 1804-1817.

[14] Bai H, Liu Z, Sun DD. A hierarchically structured and multifunctional membrane for water treatment. Applied Catalysis B: Environmental 2011; 111: 571-577.

[15] Lim HS, Baek JH, Park K, Shin HS, Kim J, Cho JH. Multifunctional hybrid fabrics with thermally stable superhydrophobicity. Advanced Materials 2010; 22(19): 2138-2141.

[16] Reneker DH. Nanometre diameter fibres of polymer, produced by electrospinning. Nanotechnology 1996; 7: 216-223.

[17] Formhals, Anton *et al.* Process and apparatus for preparing artificial threads U.S. Patent 1,975,504 Issue date: October 2, 1934

[18] Doshi J. Electrospinning process and applications of Electrospun fibers. Journal of electrostatics 1995; 35(2-3): 151-160.

[19] Gibson P. Electrospun fiber mats: transport properties. AIChE journal 1999; 45(1): 190-195.

[20] Ko FK. Laurencin CT, Borden MD, Reneker DH. of Proceedings, Annual Meeting, Biomaterials Research Society, San Diego, 1998 Apr.

[21] Rutledge G. Fridrikh S. Proceedings of Texcomp 6, Philadelphia, PA, 2002 Sep.

[22] Dresselhaus S. Carbon Nanotubes: Synthesis, Structure, Properties, and Applications, 2001 Springer.

[23] Yamashita Y, 山下義肝. Electrospinning "エレクトロスピニング最前線-ナノファイバー創製への挑戦, 繊維社, 2007. ISBN 978-4-9902580-1-6.

[24] Jiwon L. Preparation of ultrafine Fe_3O_4 particles by precipitation in the presence of PVA at high pl-I [J], Journal of Colloid and Interface Science 1996; 177(2): 490-494.

[25] Qi L. Synthesis and characterization of CdS nanoparticles stabilized by double-hydrophilic block copolymers. Nano Letters 2001; 1(2): 61-65.

[26] Murray C. Synthesis and characterization of monodisperse nanocrystals and close-packed nanocrystal assemblies. Annual Review of Materials Science 2000; 30(1): 545-610.

[27] Trapalis C. TiO_2Fe^{3+} nanostructured thin films with antibacterial properties. Thin Solid Films 2003; 433(1): 186-190.

[28] Inoue T, Dillon D, Li CY, Ko FK. Nanoclay reinforced PVDF nanocomposites. Proceddings of Proc. of the 33rd Textile Research Symposium (Ed.) 2004; 15-19.

[29] Goto T, Ono Y, Kotaki M, Ko FK. Morphology and properties of silica-based composite nanofibers. Proceddings of Proceedings of the Seventh Joint Canada-Japan Workshop on Composites 2008.

[30] Ko FK, Argawall RYH, Katz H. Electrospinning of improved CB protective fibrous materials, Proceddings of Proceedings, Texhtextil Atlanta 2004.

[31] Yang HJ, Ko FK. Multifunctional composite nanofibers. Proceddings of Seventh Joint Canada-Japan Workshop on Composites, Poon C. e. a. 2008.

[32] Ko FK. Wearable electronics and photonics, chap. Electrostatically Generated Nanofibres for Wearable Electronics, 2005 Woodhead Publishing Ltd., Cambridge, UK.

[33] Panels JE. Synthesis and characterization of magnetically active carbon nanofiber/iron oxide composites with hierarchical pore structures. Nanotechnology 2008; 19(45): 1-7.