Magnetic Materials by Concurrent Electrospraying and Electrospinning[1]

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***Abstract*— Both electrospraying and electrospinning use intense electric field for the generation of droplets and fibers respectively. Each of the two techniques has a large number of applications. We aimed at simultaneously or sequentially overlapping the two procedures for the generation of new nanomaterials with magnetic properties. Accordingly, we focused on the concurrent electrospinning of polyvinyl alcohol (PVA) fibers and electrospraying of ferrofluid (ferric oxide nanoparticles in a paraffinic hydrocarbon carrier liquid). A needle-plate configuration was used for the synthesis of new materials by concurrent spraying (negative polarity) and electrospinning (positive polarity). An in-flight self-assembly of the negatively charged ferrofluid droplets and positively charged PVA nanofibers generated a magnetically sensitive nanomaterial structure. The SEM imaging shows the ferric oxide microparticles attached to the scaffold-like structure of nanofibers. In a different procedure, the spraying and electrospinning processes are sequentially applied to a linearly oscillating rectangular collector. The material obtained has PVA fibers embedded in a thin film of ferric oxide produced by electrospraying. This method has the ability to produce thin films with engineered properties.**

I. Introduction

Magnetic materials have a wide variety of applications and diverse methods have been developed for their synthesis [1]. In the present work we simultaneously use electrospraying of ferrofluids and electrospinning of polymers to create new materials with magnetic properties. Ferrofluids [2-4] contain a liquid carrier along with nanoscale ferromagnetic particles (often iron oxides); nano-particles are coated with a thin layer of surfactant so that magnetic particles do not stick together in the liquid carrier. Electrospraying is a method of liquid atomization using an intense electrical field. As the liquid is extracted by electrical forces and also due to the evaporation process, it eventually disperses it into fine droplets. Electrospraying is a significant method for obtaining micro and nano particulates [5]. Although the electrosprays of ferrofluids were occasionally used in conjunction with mass spectrometers, there is scarce information about studying the electrospray of such colloids [6]. Much like electrospraying, electrospinning [7-10] is based on the electric field forces applied to charged liquids. However, due to higher viscosity of the liquid, long chain molecules (polymers), and evaporation, the end result is very different: the fluid is viscous and solidifies in contact with air, creating fibers out of the electrically charged jet of polymer solution. The jet is generated by applying a high voltage across electrodes. The electric forces overcome the viscosity and surface tension of the polymer solution to form a Taylor cone from which fibers are produced. There are important nanofiber applications such as electrical conductors for ultra-small devices, air filtration, textiles, nanofibrous scaffolds (ideal for three-dimensional cell culture and tissue engineering applications [11, 12]. Lately, combining electrospraying and electrospinning has led to new ways of engineering nanomaterials [13, 14]. Concurrent electrospraying and electrospinning have been employed by us in two experimental configurations with the goal of synthesizing new magnetic materials with specific characteristics.

II. EXPERIMENTAL

In order to synthesize magnetic materials, ferrofluid was used for electrospraying or electrospinning in mixtures with PVA. The EFH1 ferrofluid was acquired from Ferrotec Inc. It contains ferric oxide nanoparticles mixtures of magnetite (Fe_3O_4 about 80%) and maghemite (Fe_2O_3 about 20%) with a nominal size of 10 nm and a paraffinic hydrocarbon (petroleum distillate, NOS, clear, combustible liquid, UN 1268, III) used as carrier liquid.
Negative or positive high voltage used for electrospraying and/or electrospinning was generated with a Spellman HVPS, RHR40PN60 (positive 0-40 kV 1.5 mA) and Glassman HVPS, PS/ER10R30-DM22 (negative 0-10 kV 30mA). Harvard Apparatus syringe pumps (single syringe Model 44 or double syringe Model 22) were used to control the flow rate in electrospinning and electrospraying processes.
Two types of experimental setups were employed: A – a static framework where all electrodes are at rest; B – a dynamic framework in which the grounded collector has a linearly oscillatory motion.

A. Concurrent electrospraying and electrospinning in a static framework

Polyvinyl alcohol (PVA) water solutions were prepared for electrospinning and EFH1 ferrofluid was loaded for electrospraying. Concurrent electrospraying of ferrofluid and electrospinning was used with a fixed grounded collector electrode. The schematic of the experimental setup is shown in Fig. 1a. The PVA electrospinning and ferofluid electrospraying nozzles were set perpendicular to each other and 5 cm away from the midpoint of the circular grounded collector plate. The positive high voltage (+20kV) was connected to the electrospinning nozzle - a 16 G blunt needle attached to a 10 mL Kendall Monoject oral syringe. The negative high voltage (-6 kV) was applied to the 25 G electrospraying (blunt) needle. A 0.05ml/min flow rate was insured by the syringe pumps on both electrospraying and electrospinning processes for 5 minutes. An in-flight self-assembled layer of nanofibers and magnetic particles was generated around the collector. SEM imaging of the structure (Fig. 2) reveals micrometer size ferric oxide particles attached to the texture of the PVA nanofiber network. Such structure can be very sensitive to external variations of the magnetic field and may have sensor type applications.

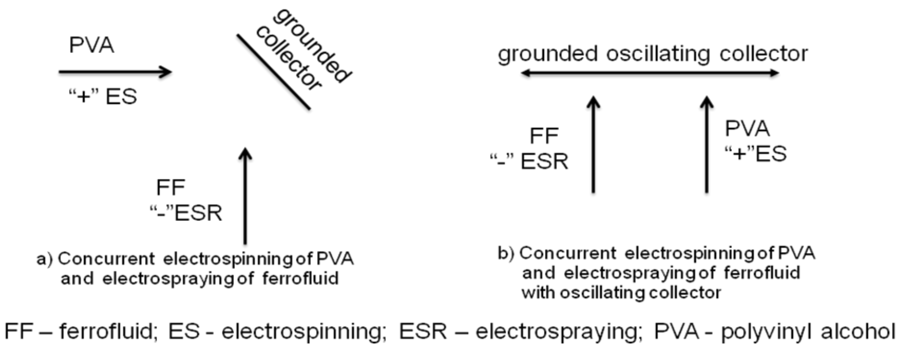


Fig.1 Schematics of the experimental setup.

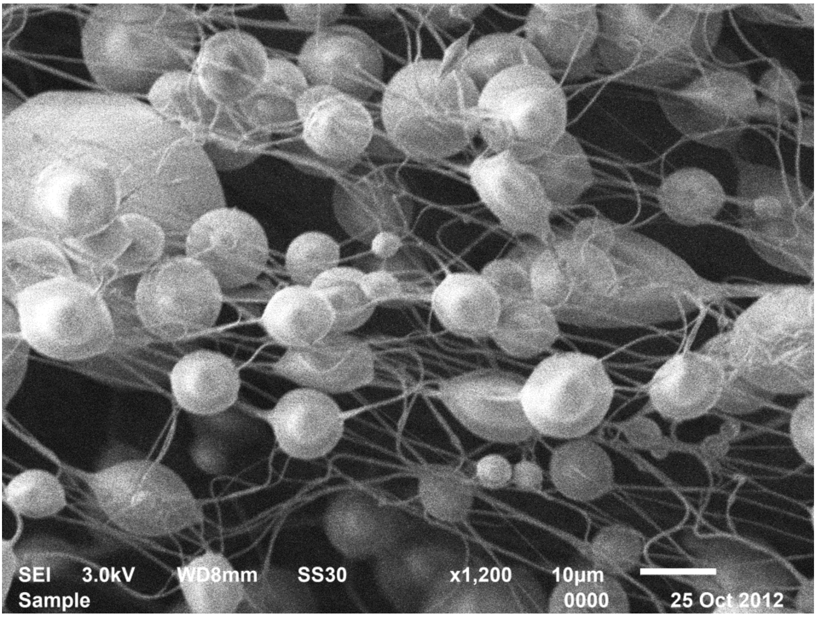


Fig. 2 SEM image of concurrent electrospraying (EFH1 ferrofluid) and PVA electrospinning (8% PVA water solution): +20kV PVA electrospinning, -6 kV ferrofluid electrospray, gap distance 5cm.

B. Concurrent electrospraying and electrospinning in a dynamic framework (linearly oscillating collector)

The ferrofluid syringe and the PVA syringes were set parallel, and horizontally driven by the Harvard Apparatus double syringe pump Model 22 (Fig. 1b). The aligned nozzles (16 G blunt needle for PVA electrospinning and 25 G for electrospray of ferrofluid) were 5 cm from each other and perpendicular to the linearly oscillating grounded collector (4 cm wide collector, oscillatory motion frequency 2 Hz, amplitude 6.4 cm). Tin foil was attached on the collector in order to facilitate the examination of the synthesized material. The positive high voltage (+20kV) was attached to the electrospinning needle. The negative high voltage (-6 kV) was applied to the 25 G electrospraying (blunt) needle.

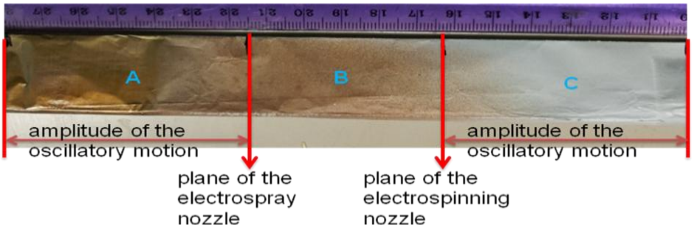
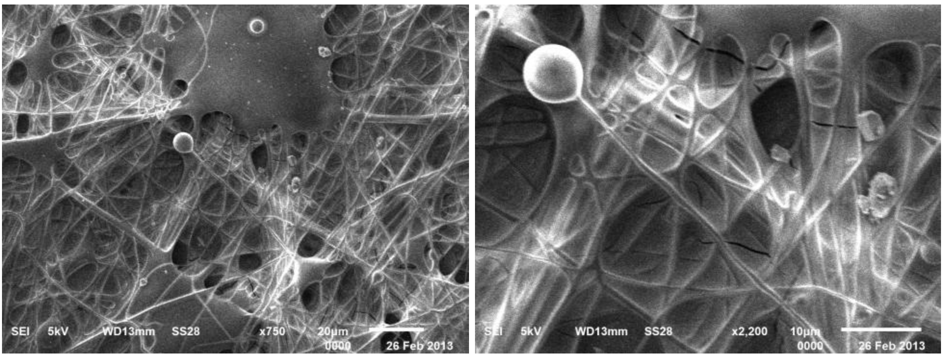


Fig.3 Photo of the collector's tin foil used for deposition.

A 0.05ml/min flow rate was insured by the syringe pump for 5 minutes.

In our setup, the linearly oscillating collector allows for subsequent deposition of PVA electrospun and ferrofluid. Fig. 4ab shows typical SEM images of the subsequent deposition of fiber into the ferrofluid. The nanofibers are caught in-between layers of ferric oxide by subsequent electrospraying. Nevertheless, there are regions (Fig. 3 – the whitish region C particularly) where nanofibers are predominant. Fig. 4b shows nanocraks of the brittle deposited ferric oxide layer due to bending of the tin foil colector used for imaging.



(a) (b)

Fig. 4 Typical deposition layer: SEM images of concurrent electrospraying and electrospinning using a linearly oscillating collector

There is spatial variation of the electrospun and electrospray content (Fig 3 - regions A, B, and C) which can be controled by changing the physical parameters of the process such as frequency and amplitude of the oscillations, distance between nozzles, nozzle size, or applied voltage. Content concentration is apparent on the collector.

III. Conclusion

New magnetic nanomaterials were produced using concurrent electrospinning of PVA solutions and electrospraying of ferric oxide based ferrofluid. The methods allow for great customization of the material structure and inherently of its properties. The SEM image shows the ferric oxide microparticles attached to the scaffold-like structure of PVA nanofibers. A new linearly oscillating collector is reported in the concurrent electrospraying and electrospinning. The linearly oscillating collector may allow for designing materials with structure not achievable with the usually employed rotating cylinder or disk collectors.

IV. Acknowledgments

The authors are thankful to Justin Patus and Joshua Apenowich for their lab work. Help with the setup from Ryan Ellis, Danielle Citro, Bruce Zellar, and Fred Scoles is also acknowledged. Moreover, discussions with and support received from Dr. Zych were beneficial to this study.

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