MULTIFUNCTIONAL NANOPARTICLES REINFORCED NANOFIBERS BY ELECTROSPINNING

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Abstract

Nanomaterials in various geometry such as quantum-dots, carbon nanotubes and nanoclays have been used effectively as coating and fillers for many products to achieve nanoscale effects. In order to amplify the nanoscale effect and provide a means to carry the nanoscale effect to macrostructures, the nanoparticles are incorporated in ultrafine fibers to form nanocomposite fibrils. This was carried out by a co-electrospinning process wherein nanocomposite fibrils were spun from a spinning dope consisting of a mixture of nanoparticles and polymer solution. The multiphase fibrils and fibrillar assemblies not only manifests the nanoscale effects inherent to the individual nanocomponents but also provides a means to facilitate processing and translation of the nanoscale effects to macroscopic structures. In this study the processing, structure and properties of nanocomposite fibrils consisting of nanofillers are discussed.

1. Introduction

Nanotechnology is the field of science dealing with the synthesis, characterization and application of nanoscale materials. The concept of nanotechnology was famously described by Richard Feynman in 1960 in a talk “There’s plenty of room at the bottom” which is considered the first talk on nanotechnology [1]. These nanoscale materials can be synthesized though various paths including template, vapor grown, lithography and electrospinning [2, 3]. Nanomaterials tend to behave differently from bulk materials due to their size and quantum confinement effect in optical, electrical and magnetic behavior of materials. This becomes more evident at the size smaller than 100 nm. One of the unique features of nanomaterial is the enormous surface area to volume ratio as compared to the bulk material. This can make materials more chemically reactive and affect their strength and/or electrical properties.

In order to facilitate the translation of nanoscale effect to macrostructures, creating nanocomposite has been one of the effective methods to utilize the unique properties of nanoscale materials. Among various techniques of fabricating polymer-nanoparticles nanocomposite systems, creating fibrous structure can provide several advantages over the conventional particles imbedded films or coatings of films. In particular the formation of nanofibers by the electrospinning technique has been proved to be simple and effective methods to fabricated ultrafine composite fibers.

Electrospinning is a simple process that can produce nanometers to micrometers polymer fibers from polymer melt or solution using an electric field. As illustrated in Fig 1, ultrafine fibers can be produced by applying high voltage to polymer solution reservoir. When electric potential is applied to melt or solution of polymer, the charged polymer liquid forms a cone shape droplet at the tip of the spinneret nozzle.

When an electrostatic force is sufficient enough to overcome the surface tension of the liquid droplet, the tip of the droplet elongates in the form of a jet and pulled towards a grounded collection plate. This charged jet attenuates by undergoing a series of whipping motions in the instability region of the spinning line. While, traveling to the target, the solvent evaporates leaving solidified ultrafine fibers on the collection plate [4, 5]. Optical microscope image of the electrospun fibers on human hair and the expected surface area per unit

volume as a function of fiber diameter are also illustrated in Fig 1. The expected surface area increases exponentially as diameter of fibers decreases assuming square packing of fibers. The increment of surface area not only increase reactive surface area but also can greatly enhance sensitivity of fibers to external environment even in simple diffusion. These characteristics make finer fiber more attractive in optical and electrical application.

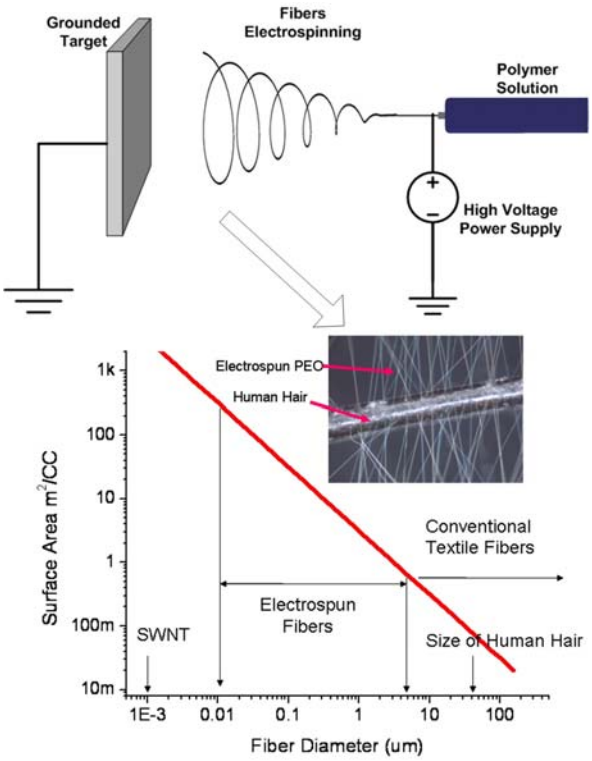

Fig 1. Schematics of electrospinning process and expected surface area of fibrous structure at given volume

The diameter and morphology of fibers produced by electrospinning can be controlled by varying solution concentration, molecular weight of polymer, tip-to-collection plate distance, electrostatic field strength, and the geometry of the grounded target. Larger diameters of fibers are produced from higher concentration or higher molecular weight of polymer solution whereas lower concentration or lower molecular weight solutions results in finer fibers as well as a tendency to form beads. The longer the spinning distance of the spinneret from the target allow more time for the solvent to evaporate thereby creating more favorable condition for the production of finer fibers [6, 7]. It has been observed that oriented fibers or yarns can be collected by changing the target geometry and by changing the fiber collection mechanism [8]. Various synthetic and natural polymers including conductive polymers, biodegradable polymers, silkworm silk and genetically engineered spider silk have been successfully spun into ultrafine fibers [9, 10].

Among various available nanomaterials in 0-D, 1-D, and 2-D geometry, magnetic nanoparticles, quantum dots, photo catalytic nanoparticles and carbon nanotubes are excellent examples of nanoparticles that can be incorporated into electrospinning process to fabricate composites fibers with interesting functions. Iron oxide nanoparticles can be used for biomedical applications, electromagnetic interference shielding, catalyst and sensors [11]. Quantum dots such as CdS, CdSe and ZnS can be used in semiconductive devices, biological labeling and optical switches [12, 13]. TiO_2 particle has been known for its strong photo catalytic properties for filtration and antibacterial applications [14]. Carbon nanotubes has brought a great attention for its superb mechanical and electrical properties [15]. Creating nanocomposite fibers through the electrospinning process using nanosize particles has been previously explored and successfully demonstrated. Previous work of carbon nanotubes (CNT) nanocomposite fabrication by Ko 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 [15].

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. In this paper we report our work on the processing, structure and properties of quantum dot (CdS) filled fluorescence nanofibers and magnetic nanoparticles (Fe_3O_4) filled nanofibers produced by co-electrospinning.

2 Experiments and Results

2.1 Fluorescence Nanofibers

Quantum dots (QDs) are semiconductor nanocrystals with diameters ranging typically from 2 to 10 nm. When excited by sufficiently high energy, electrons of semiconductor in the valence band can overcome the band gap and jump into the conduction band. Being unstable at the high energy state, the electrons recombine with the holes in valence band, releasing energy by emitting photons. Typically QDs can be excited by UV light and emit visible light. Due to the quantum confinement effect, QDs exhibit distinctive and controllable photoluminescence properties by controlling band gap which can be tailored by material selection and varying the particle size. Both organometallic and aqueous synthesis methods have been developed to produce various QDs with excellent properties [16].

The advantages of QDs over the traditional fluorescent molecules include tunable fluorescence colors, controllable excitation along with narrow emission spectra, high intensity of emission, good photostability, and long fluorescence lifetime. This enables QDs to be used as powerful imaging and tracking tools in various biological and medical applications. By immobilizing an antibody on their surface, QDs can bind selectively to a particular antigen and may be used to locate the cells selectively [17]. QDs can also be used as chemical sensor, which respond selectively to physiologically important metal cations, such as Zn^{2+}, Cu^{2+}, and detect the explosive 2,4,6-trinitrotoluene (TNT) in aqueous environments[18]. Depending on the synthesis method QDs exist as particles dispersed in aqueous or organic solvents. Dried QD powders can be obtained from these solutions according to application needs.

To fabricate fluorescence composite nanofibers quantum dots from cadmium sulphide (CdS) were prepared using an environmentally friendly and low-cost synthesis procedure [19]. Unlike traditional organometallic method this procedure has an advantage of utilizing one step reaction of simple inorganic precursors. An aqueous solution of CdS QDs was prepared in water by the reaction between cadmium nitrate [$Cd(NO_3)_2$] and sodium sulfide [Na_2S] with 3-mercaptopropionic acid [MPA] as the capping molecules. The resultant clear aqueous QDs suspension remains stable for more than 12 months at 4^{o}C away from light.

Electrospinning dopes were prepared by dissolving 5% Polyethylene oxide (PEO, Mw 600,000, purchased from Sigma) by weight into various concentrations of aqueous CdS solution by magnetically stirring for 24 hours. The prepareded PEO-CdS spinning dopes were then transferred to a glass syringe containing 18-gauge needle and was electrospun. 5% PEO was electrospun with 1.6 mM, 6.4 mM and 12.8 mM concentrations of aqueous CdS. A spinning distance of 15 cm and voltage of 15 kV were found to be optimum conditions for the formation of continuous and uniform nanofibers free of beads or droplets.

TEM has been used to confirm the presence of CdS nanoparticles in the fibers. TEM images of the PEO-1.6 mM CdS electrospun fibers and as-prepared CdS solution are shown in Fig 2. Fig 2a shows the presence of the CDs in the PEO fibers and CdS particles obtained from aqueous solution is shown in Fig 2b. The synthesized particle sizes were measured around 5~6 nm in diameter. Localized CdS particle aggregations were observed in some part of fibers and well distribution of particles as well.

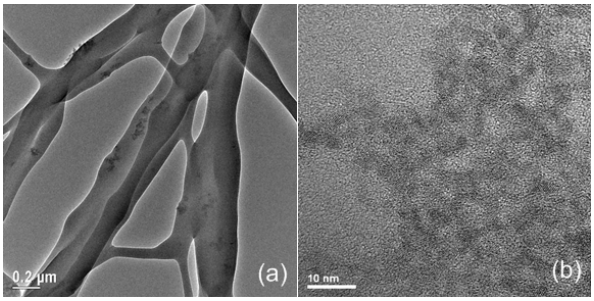

Fig 2. TEM of CdS particles and electrospun CdS-PEO fiber

The average fiber diameter obtained from 5 wt% PEO-water solution without CdS particle was 290 nm. The average diameter of the fibers with different combinations of CdS solution concentration were 271 nm, 226 nm and 225 nm for the 5 wt % of PEO dissolved in 1.6 mM, 6.4 mM and 12.8 mM of CdS solution respectively. Fig 3 shows the fiber morphology and diameter distribution of various nanocomposite structures. Fiber diameter tends to decrease as CdS concentration increases. It has been known that electrical properties of solution and electrical field strength applied to solution during the electrospinning play an important role in the fiber forming. It is believed that the inclusion of CdS particles alters the electrical properties of the solution thus cause the decrease of fiber diameter. However validity of this theory needs to be confirmed in the future with the consideration of

multiple parameters such as conductivity, dielectric permittivity, solution surface tension, solution viscosity…etc.

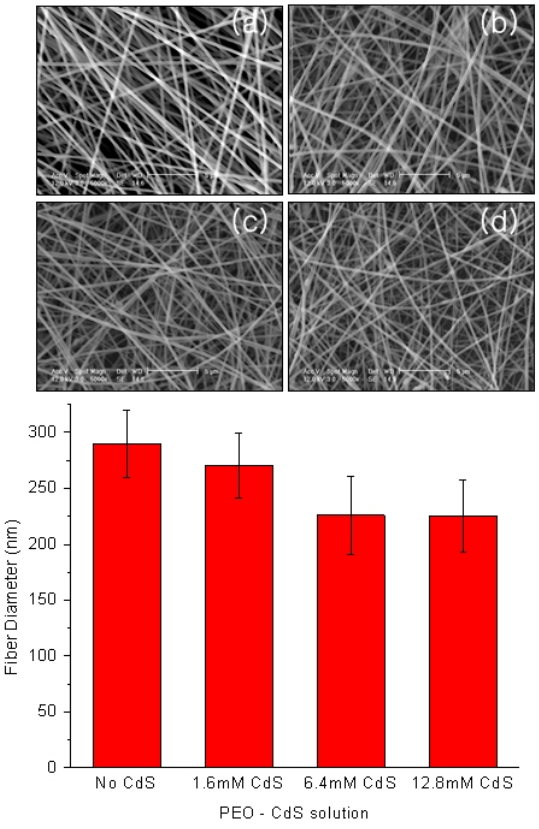

Fig 3. ESEM of fibers and average fiber diameter (a) 5 wt% PEO in water (b) 5 wt% PEO in 1.6 mM CdS, (c) 5 wt% PEO in 6.4 mM CdS, (d) 5 wt% PEO in 12.8 mM CdS

In Fig 4, Photoluminescence(PL) of the CdS-PEO solution and electrospun fibers were measured using a QM-4/2005 spectrofluorometer (Photon Technology International, Birmingham, NJ) with excitation and emission slit width of 2 nm. The photoluminescence spectra showed that lower concentration of as-received CdS had relatively higher emission intensity. This is believed to be in part due to higher concentration of excess MPA and other ions in CdS suspension produced during the synthesis of in the higher concentration of CdS solution. Also, higher concentration might promote the formation of CdS clusters trapping the charge carriers in the interfacial states and preventing the electron-hole recombination. The neighboring clusters might absorb the emission by another particle thereby reducing the PL intensity.

As shown in figures, the pure PEO-water solution did not show fluorescence property. However when 5 wt % of PEO was mixed with the various concentration of CdS, the peaks were observed at emission wavelength of 580 nm, 570 nm and 543 nm from 1.6 mM, 6.4 mM and 12.8 mM solutions respectively. It was found that the addition of PEO did not have effect on the emission wavelength although it tends to reduce the emission intensity of the solution. The peaks of emission wavelength of electrospun fibers were observed at 529 nm, 541 nm and 534 nm from the PEO-CdS composite fibers of 1.6 mM and 6.4 mM and 12.8 mM respectively.

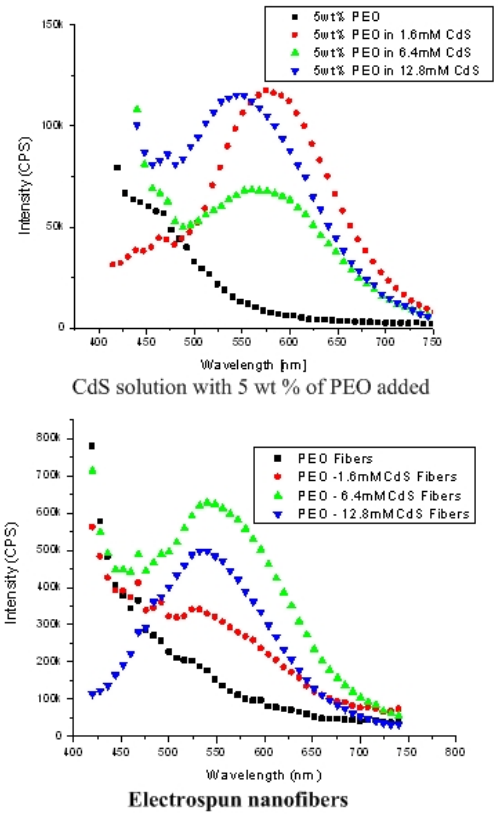

Fig 4. Photoluminescence of CdS-PEO solution and electrospun fiber

As the lowest concentration of CdS solution showed the highest emission intensity, there was the least effect of PEO which appears around 475nm from 1.6 mM CdS – PEO solution. However this PEO overlapping effect in PL trend disappeared

when CdS-PEO was electrospun into nanofiber. At lower CdS concentration, the emission of PEO exists until 475nm. PL of CdS began to dominate above 475nm. Higher CdS content fiber showed less interference from PEO. Trace of PEO was negligible on electrospun fibers from 12.8 mM CdS solution. This suggests that high concentration of CdS in fiber is more desirable to have higher intensity of fluorescence from composite fiber and more effective in overcoming optical properties of polymer. However further optimization of CdS solution is required to clarify this phenomena.

The optical microscopy and naked eye examination under UV lamp of electrospun nanofibers proved that the fluorescence properties of CdS are intact and one can use this technique for variety of applications. The electrospun fibers were processed into yarns then were woven as shown in Fig 5. A woven fabric consisting of PEO and PEO-CdS yarns was utilized to demonstrate the optical difference under naked eye. When this fabric was examined under a UV lamp, PEO-CdS composite yarns appeared distinctively yellowish in color while pure PEO yarns did not show any fluorescence. This could not be differentiated between yarns having PEO from the PEO-CdS composite yarns under normal light.

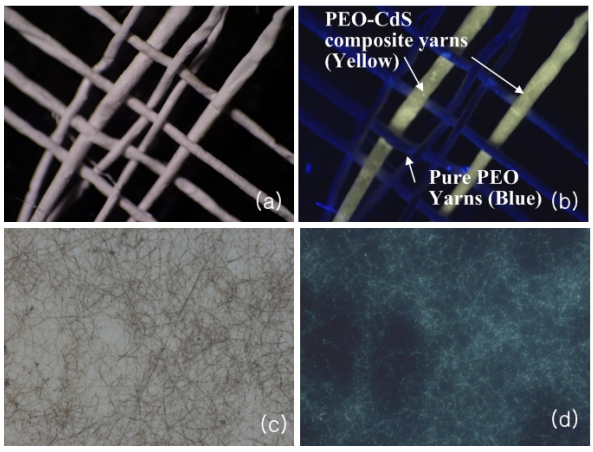

Fig 5. Naked eye views of hand woven nanofibrous yarns containing mixture of PEO and PEO-CdS composite fibers and fluorescence microscopy. (a) woven structure under normal light (b) woven structure under UV light. (c) Regular optical microscope and (d) Fluorecscence microscope image

2.2 Magnetic Nanofibers

Magnetite (Fe_3O_4) is well known magnetic material for its ferromagnetic properties. This ferromagnetism is induced by the magnetic moment due to electron spin. In ferromagnetic materials, coupling interactions of neighboring atoms aligns atomic dipole with one another resulting in the permanent magnet without external electrical field or magnetic field. For some solid materials, inherent magnetic moments are randomly oriented in the absence of external magnetic field but they align with external magnetic field which is called paramagnetism. Natural ferromagnetic material loses its atoms ordering at high temperature and shows paramagnetic behavior due to thermal energy. The family of magnetic nanoparticles can be synthesized through various chemical routes such as arc discharging or chemical precipitation [11].

When the diameters of ferromagnetic particles approach 100 nm or lower the ferromagnetic particles exhibit paramagnetic properties at room temperature. This phenomenon is referred to as superparamagnetic property. In magnetic storage industry this thermal limit became a great challenge in fabricating high density storage devices [20]. Typically these superparamegnetc particles exhibit a great susceptibility to external field making it suitable for various applications [21]. Magnetic nanoparticle fiber composite is a also good example of functional nanocomposite structure that with wide area of applications such as EMI shielding, biomedical and sensors [22, 23].

In this study, 20 wt% of PVDF-TeFE was dissolved into a mixture of Dimethylformadide and 2-Butane. 5 wt% and 10 wt% of dispersed 20~30nm Fe_3O_4 nanoparticles (purchased from Nanostructured & Amorphous Materials, Inc) were blended into the polymer solution for co-electrospinning. Various process parameters such as solution concentration, distance between target and nozzle and the effect of different types of solvent were evaluated in order to optimize the electrospinning process. The morphology, mechanical properties and the electrical property of nanocomposite were characterized.

The diameter of electrospun fibers without magnetic particles was about 620 nm from 20 wt% of the solution. When Fe_3O_4 nanoparticles were added the average fiber diameters noticeably decreased to 515 nm and 370 nm for 5 % and 10 % by weight of loading and showed wide variation of fiber diameter as shown in Fig 6. This is also believed to be due to the changes in electrical

properties and solution viscosity of the electrospinning dope. However further research is needed in order to confirm the cause of fiber diameter decrease.

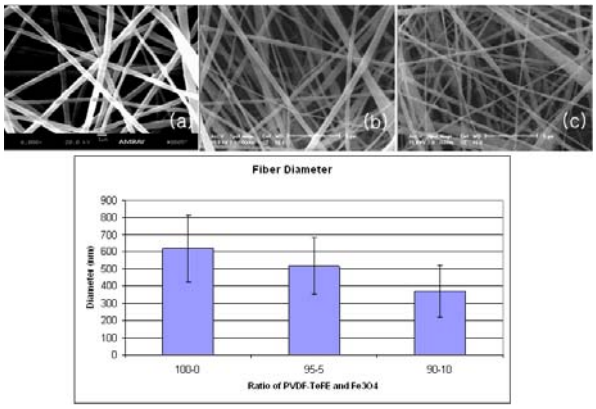

Fig 6. SEM of electrospun fibers from (a)20 wt% PVDF-TeFE solution (b) 20 wt% PVDF-TeFE with 5wt% Fe3O4, (c) 20 wt% PVDF-TeFE with 10wt% Fe3O4

The magnetic properties of PVDF-TeFE and PVDF-TeFE/Fe_3O_4 composites were measured using a SQUID (Superconducting Quantum Interference Devices) magnetometer (Quantum Design, MPMS2). The applied external field was from -25K to 25K Oe (Oersted) at the temperature of 10K and 300K. The measured magnetic moment (emu) of samples loaded with 5 wt % and 10 wt % of Fe_3O_4 were plotted in Fig 7. Paramagnetic properties were observed from Fe_3O_4 loaded PVDF-TeFE composite fibers while pure PVDF-TeFE showed typical diamagnetic property. Although bulk Fe_3O_4 is know for its strong ferromagnetic properties and it has been widely used for its permanent magnetism, as expected, composite fibers containing 20~30 nm Fe_3O_4 particles exhibited superparamagnetic properties due to the size of particles. Extremely high susceptibility to external magnetic field was shown regardless of particle contents in the composite fibers. Magnetic moment tended to be saturated at 10K Oe and completely saturated about 20K Oe. At low temperature, both samples showed slightly higher magnetic moment than that of room temperature. Weak magnetization was observed from all samples under the magnetic field at 10K. When 5 wt % Fe_3O_4 was added, the magnetic moment was half of 10 wt % Fe_3O_4 sample. This linear behavior was observed from all temperatures.

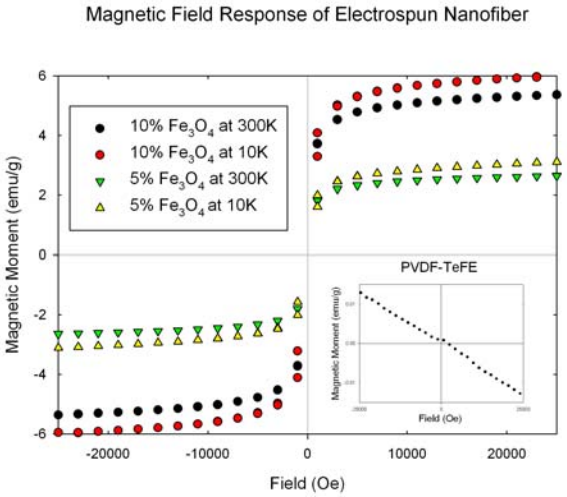

Fig 7. Magnetic moment of iron oxide nanopartcles embedded nanofiber

This strong filed responsive behavior of electrospun magnetic composite mats to external magnetic filed was demonstrated in Fig 8. 2 cm strip of 5 wt% Fe_3O_4 loaded PVDF-TeFE was fixed at one end and the other end was allowed move freely. When the composite fiber mat was exposed to external magnetic field induced by a simple lab magnet, the flexible mat was deformed toward the magnet as magnet moved closer to the composite fiber bundle. It was showed that the sample was flexible and field responsive.

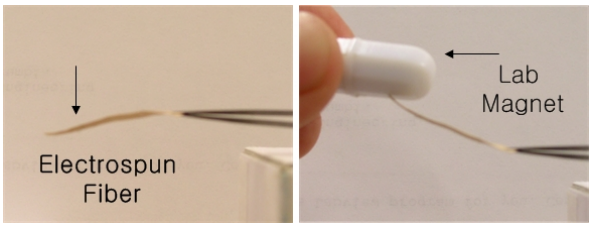

Fig 8. Response of Electrospun Composite Fiber to External Magnetic Field

3. Conclusion

In this study, quantum dot and magnetic nanoparticle suspensions have been successfully incorporated into PEO and PVDF-TeFE solutions to fabricate ultrafine composite fibers by the co-electrospinning process. It was demonstrated that quantum dot particles were intimately blended in the less than 300 nm PEO fibers without sacrificing

their molecular structure and optical properties. The photoluminescence spectra were repeatedly observed for the solution kept in room temperature for 3 months. The solutions showed outstanding stability of fluorescence spectra for the entire one year duration. The fabricated fibers also showed strong fluorescent properties over several months without photobleaching at room temperature. It has been demonstrated that uniform fibers can be fabricated with smaller fiber diameter when particles were added. As shown in TEM of CdS-PEO fibers, localized particle agglomeration was observed. Proper surface treatment of particles would contribute to separate the particles to enhance the properties of composite fibers.

Magnetic particle embedded PVDF-TeFE fibers showed strong superparamagnetic properties with high sensitivity to applied external magnetic field. The magnetization behavior of composite fibers agreed with previously explored properties of magnetic particles suggesting the electrospinning process did not alter the properties of Fe_3O_4 particles. Inclusion of particles resulted in significant fiber diameter decrease. The fabricated magnetic composite fibers exhibited extremely high sensitivity to applied field. Its magnetic properties were easily modified by simply controlling the amount of the particles in the fiber at room temperature as well as low temperature.

A new class of composite nanofibers was demonstrated with unique properties tailorable by the inclusion of a few types of nanoparticles. It is of interest to note that after the electrospinning, there is no need for further processing was necessary to functionalize the electrospun fibers.

Nonwoven mats of particle embedded electrospun fiber exhibit extreme flexibility and high surface area to volume ratio due to its fine fiber diameter with great mechanical stability. Success in the development of composite nanofibers by the co-electrospinning showed a new pathway to connect nanoscale effect to macro structure performance. Combining these geometrical advantages with functional material characteristics it can provide wide area of application such as optical/biological sensors, scaffolds for tissue engineering, biological labeling, anti-counterfeiting, multi-functional textile and damage detection for composite structures.

4. References

[1] Feynman RP. "There's Plenty of Room at the Bottom: An invitation to enter a new field of physics". *CALTECH Engineering and Science* 1960;23(5):22-36.

[2] Cao G. "*Nanostructures and Nanomaterials* ": World Scientific Publishing Company, 2004.

[3] Gogotsi Y. "*Nanomaterials Handbook*": CRC, 2006.

[4] Baumgarten PK. "Electrostatic Spinning of Acrylic Microfibers". *Journal of Collid and Interface Sciences* 1971;36(1):71-79.

[5] Doshi J and Reneker DH. "Electrospinning process and applications of electrospun fibers". *Journal of Electrostatics* 1995;35(2-3):151.

[6] Darrell HR and Iksoo C. "Nanometre diameter fibres of polymer, produced by electrospinning". *Nanotechnology* 1996;7(3):216.

[7] Fong H, Chun I, and Reneker DH. "Beaded nanofibers formed during electrospinning". *Polymer* 1999;40(16):4585.

[8] Sundaray B, Subramanian V, Natarajan TS, Xiang R-Z, Chang C-C, and Fann W-S. "Electrospinning of continuous aligned polymer fibers". *Applied Physics Letters* 2004;84(7):1222.

[9] Norris ID, Shaker MM, Ko FK, and MacDiarmid AG. "Electrostatic fabrication of ultrafine conducting fibers: polyaniline/polyethylene oxide blends". *Synthetic Metals* 2000;114(2):109.

[10] Sukigara S, Gandhi M, Ayutsede J, Micklus M, and Ko F. "Regeneration of Bombyx mori silk by electrospinning. Part 1: processing parameters and geometric properties". *Polymer* 2003;44(19):5721-5727.

[11] Lee J, Isobe T, and Senna M. "Preparation of ultrafine Fe3O4 particles by precipitation in the presence of PVA at high pH". *JOURNAL OF COLLOID AND INTERFACE SCIENCE* 1996;177(2):490-494.

[12] Qi L, Cölfen H, and Antonietti M. "Synthesis and Characterization of CdS Nanoparticles Stabilized by Double-Hydrophilic Block Copolymers". *Nano Letters* 2001;1(2):61-65.

[13] Murray CB, Kagan CR, and Bawendi MG. "SYNTHESIS AND CHARACTERIZATION OF MONODISPERSE NANOCRYSTALS AND CLOSE-PACKED NANOCRYSTAL ASSEMBLIES". *Annual Review of Materials Science* 2000;30(1):545-610.

[14] Trapalis CC, Keivanidis P, Kordas G, Zaharescu M, Crisan M, Szatvanyi A, and Gartner M. "TiO2(Fe^{3+}) nanostructured thin films with antibacterial properties". *Thin Solid Films* 2003;433(1-2):186-190.

[15] Ko FK, Gogotsi Y, Ali A, Naguib N, Ye H, Yang GL, Li C, and Willis P. "Electrospinning of Continuous Carbon Nanotube-Filled Nanofiber Yarns". *Advanced Materials* 2003;15(14):1161-1165.

[16] Brus LE. "Electron--electron and electron-hole interactions in small semiconductor crystallites: The size dependence of the lowest excited electronic state". *The Journal of Chemical Physics* 1984;80(9):4403-4409.

[17] Chan WCW, Maxwell DJ, Gao X, Bailey RE, Han M, and Nie S. "Luminescent quantum dots for multiplexed biological detection and imaging". *Current Opinion in Biotechnology* 2002;13(1):40.

[18] Chen Y and Rosenzweig Z. "Luminescent CdS Quantum Dots as Selective Ion Probes". *Anal. Chem.* 2002;74(19):5132-5138.

[19] Shih W-H, Shih WY, Li H, and Schillo MC;. "Synthesis of water soluble nanocrystalline quantum dots and uses thereof ". *US Patent* 2006;20060078490.

[20] Weller D and Moser A. "Thermal effect limits in ultrahigh-density magnetic recording". *Magnetics, IEEE Transactions on* 1999;35(6):4423-4439.

[21] Wang M, Singh H, Hatton TA, and Rutledge GC. "Field-responsive superparamagnetic composite nanofibers by electrospinning". *Polymer* 2004;45(16):5505-5514.

[22] Tan ST, Wendorff JH, Pietzonka C, Hong Z, Gui J, and Wang Q. "Biocompatible and Biodegradable Polymer Nanofibers Displaying Superparamagnetic Properties". *ChemPhysChem* 2005;6(8):1461-1465.

[23] Mornet S, Vasseur S, Grasset F, and Duguet E. "Magnetic nanoparticle design for medical diagnosis and therapy". *Journal of Materials Chemistry* 2004(14):2161-2175.