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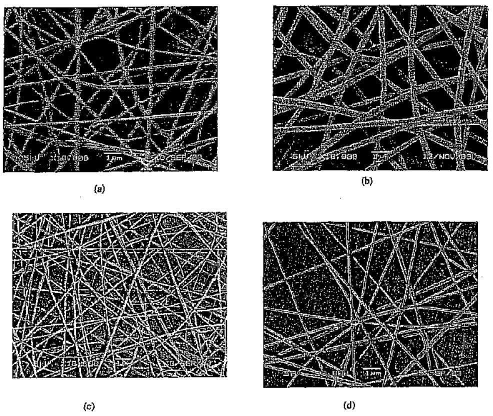
(54) Title: FIELD-RESPONSIVE SUPERPARAMAGNETIC COMPOSITE NANOFIBERS AND METHODS OF USE THEREOF



Some representative SEM images of PVA and PVA/magnetite nanofibers:
(a) PVA (7.5%), (b) PVA (7.5%) + Fe_3O_4 (0.75%), (c) PVA (7.5%) +SDS (1%), (d) PVA (7.5%) +SDS (1%) +Fe_3O_4 (0.75%)

(57) Abstract: The present invention relates to magnetic field-responsive fibers, which comprise magnetite particles and a polymeric matrix. The invention also provides methods of producing the same, in particular via electrospinning of a stably dispersed or monodispersed polymer solution, either aqueous or organic, comprising the magnetite particles, and applications thereof.

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FIELD-RESPONSIVE SUPERPARAMAGNETIC COMPOSITE NANOFIBERS AND METHODS OF USE THEREOF

FIELD OF THE INVENTION

[001] The present invention relates to field-responsive, composite nanofibers, methods of producing the same, and applications thereof. The present invention has wide application in such fields as magnetic filters, sensors, information storage, magnetic shielding, tunable composites, magnetic separation, SMART fabrics and piezomagnetic transducers.

BACKGROUND OF THE INVENTION

[002] Magnetic composite fibers, in which magnetic nanoparticles are embedded into a polymeric fiber matrix, can be expected to exhibit interesting magnetic field-dependent mechanical behavior with potential applications in a range of areas. Magnetic composite fibers, with particles of ferromagnetic materials such as iron oxide below approximately 100 nm in diameter would, in theory, no longer exhibit the cooperative phenomenon of ferromagnetism found in the bulk, due to thermal fluctuations sufficient to reorient the magnetization direction of entire particles and instead, might be superparamagnetic, exhibiting strong paramagnetic properties with large susceptibility. The relative magnitudes of the stiffness enhancement and fiber deformation by such fibers are expected to increase as the diameter of the embedding polymer fiber is reduced, and therefore, to date, production of magnetic composite nanofibers (i.e. with diameters on the order of 100 nm or less) with superparamagnetic properties, with defined mechanical properties, has not been achieved.

[003] Electrospinning is an effective method for the production of polymeric nanofibers with diameters ranging from a few nanometers to a few micrometers. This technique has attracted interest over the last decade due to potential applications for

nanofibers numerous applications. In a typical electrospinning process, a polymer solution or melt is extruded through a capillary and, in the presence of a strong electric field, deforms, resulting in ejection of a charged jet from the apex of the cone, which is accelerated toward a grounded collecting device, traveling first as a steady jet for a certain distance, and then in some instances undergoing an electrostatically driven whipping instability that bends and stretches the jet. The result of the whipping instability is a dramatic reduction in the diameter of the jet, typically by about 2 orders of magnitude, which allows for rapid solidification of the jet through solvent evaporation (for solution) or cooling (for melts). The solid fibers are deposited on an electrically grounded collecting device in the form of threads or as a non-woven fabric.

[004] The incorporation of nanoparticles into nanofibers by electrospinning a nanoparticle-filled polymer solution, however, necessitates dispersion stability of the nanoparticles in the polymer solution.

SUMMARY OF INVENTION

[005] In one embodiment, this invention provides a superparamagnetic fiber comprising magnetite particles and a polymeric matrix. In one embodiment, the fiber is a nanofiber, which in another embodiment is less than 500 nm in diameter, or in another embodiment, the nanofiber has a diameter that ranges from 10nm - 1 µm.

[006] In one embodiment, the matrix comprises polyethylene oxide, polyvinyl alcohol or a combination threof. In another embodiment, the superparamagnetic fiber is magnetic field- responsive.

[007] In another embodiment, this invention provides a field-responsive fiber comprising ferromagnetic nanoparticles and an organic polymeric matrix. According to this aspect, and in one embodiment, the fiber is a nanofiber, and in another embodiment,

has a diameter ranging from 10- 500 nm. In another embodiment, the organic polymeric matrix comprises polymethyl methacrylate.

[008] In another embodiment, according to this aspect of the invention, the nanoparticles are monodispersed within said polymeric matrix. In another embodiment, the fiber has a high saturation magnetization, ranging from 250 kA/m to 2000 kA/m. In another embodiment, the fiber has a tunable Nèel relaxation time which ranges from 2 milliseconds to 4 seconds, or in another embodiment, the tunable Nèel relaxation time is a function of nanoparticle size.

[009] In another embodiment, this invention provides a device or apparatus comprising a field-responsive or superparamagnetic fiber of this invention. In one embodiment, the device or apparatus is used as a filter or a sensor, or in another embodiment, is used for information storage, or in another embodiment, is used for magnetic imaging, or in another embodiment, is used for magnetic shielding. In another embodiment, this invention provides a fabric comprising a fiber of this invention, which in another embodiment, is a SMART fabric.

[0010] In another embodiment, this invention provides a method of producing a field-responsive fiber comprising magnetite particles and a polymeric matrix, the method comprising the step of electrospinning a polymer solution comprising magnetic nanoparticles.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Figure 1 demonstrates a DLS curve for a 2.5 wt % magnetite nanoparticle solution.

[0012] Figure 2 is a micrograph obtained by transmission electron microscopy of magnetite fluid.

[0013] Figure 3 is a plot of magnetization (M) versus magnetic field (H) for 2.5 wt % as-synthesized magnetite fluid.

[0014] Figure 4 demonstrates some representative SEM images of PEO and PEO/magnetite nanofibers: (a) PEO (1%), (b) PEO (1%) +Fe_3O_4 (3.52%), (c) PEO (2%), PEO (2%)+Fe_3O_4 (0.75%).

[0015] Figure 5 demonstrates some representative SEM images of PVA and PVA/magnetite nanofibers: (a) PVA (7.5%), (b) PVA (7.5%) + Fe_3O_4 (0.75%), (c) PVA (7.5%) +SDS (1%), (d) PVA (7.5%) +SDS (1%) +Fe_3O_4 (0.75%).

[0016] Figure 6 demonstrates TEM images of superparamagnetic nanofibers. (a) PEO nanofiber with 28 wt% magnetite nanoparticles. (b) PVA nanofiber with 8 wt % magnetite nanoparticles.

[0017] Figure 7 demonstrates magnetization curves of superparamagnetic nanofibers: (a) PEO nanofiber with (28 wt %) magnetite nanoparticles, (b) PVA nanofiber with (8 wt %) magnetite nanoparticles.

[0018] Figure 8 schematically depicts a tip-sample interaction during an indentation test.

[0019] Figure 9 demonstrates indentation curves for PVA/magnetite (8 wt %) nanofiber: (a) calibration on hard surface (mica), cantilever bending without indentation; (b) indentation curve on PVA/magnetite nanofiber, cantilever bending and indent; (c) indentation curve on PVA/magnetite after subtracting the cantilever bending.

[0020] Figure 10 demonstrates field responsive behaviors of PVA/magnetite fabric (a) without magnetic field, (b) within a low gradient of magnetic field, (c) within a high gradient of magnetic field.

[0021] Figure 11 demonstrates TEM images of magnetite nanoparticles. The nanoparticles are 8, 14 and 16 nm in size, respectively (left to right).

[0022] Figure 12 demonstrates a representative SEM image of PMMA fiber containing 37 wt% of 16 nm magnetite nanoparticles.

[0023] Figure 13 demonstrates magnetization curves of PMMA fiber containing 37 wt% of 16 nm magnetite nanoparticles.

DETAILED DESCRIPTION OF THE INVENTION

[0024] In one embodiment, this invention provides a field-responsive fiber, comprising nanoparticles and a polymeric matrix.

[0025] In one embodiment, the nanoparticles range in size from about 4 nm to about100 nm. In one embodiment, the nanoparticles are magnetic and comprise iron, oxides of iron, cobalt, oxides of cobalt, alloys of iron and cobalt, platinum, alloys of iron and platinum, alloys of cobalt and platinum, manganese oxide, alloys of manganese and iron or alloys of nickel and iron or nickel and cobalt.

[0026] In one embodiment, the nanoparticles which comprise the fibers of this invention can be synthesized by an organic route or, in another embodiment, by an aqueous route, as exemplified herein, and as will be appreciated by one skilled in the art.

[0027] In one embodiment, synthesis of the nanoparticles via an aqueous route may comprise the steps of co-precipitating metal salts at high pH (14) in the presence of a stabilizing polymer. The stabilizing polymer has carboxylic moieties, in some embodiments.

[0028] The present invention provides, in one embodiment a field-responsive, superparamagnetic fiber comprising magnetite particles and a polymer matrix. As exemplified herein, and representing some embodiments of the invention, the polymer/magnetite nanofibers exhibited superparamagnetic behavior at room temperature, and deflected in the presence of an applied magnetic field.

[0029] In one embodiment, this invention provides a superparamagnetic fiber comprising magnetite particles, which in one embodiment, refers to an iron ore that is strongly attracted by a magnet. In one embodiment "magnetite" refers to a molecule with a general formula of Fe_3O_4, which in another embodiment, possesses a Fe^{2+} to Fe^{3+} ratio of about 1:1.5 to about 1:2.5, or in another embodiment, about 1:2.

[0030] In another embodiment, the superparamagnetic nanofibers may comprise particles which are chemical equivalents of magnetite, such as, for example, and in one embodiment, $(Fe,M)OFe_2O_3$ where M may be, in one embodiment, Zn, Co, Ni, Mn, or Cr. In another embodiment, the Fe^{2+} to Fe^{3+} ratio includes any ratio that permits the formation of the superparamagnetic fibers of the present invention.

[0031] In another embodiment, the concentration of magnetite in suspsension is 2.5 wt %. In another embodiment, the concentration of magnetite in suspsension is 0.75 wt %. In another embodiment, the concentration of magnetite in suspsension is 0.75 - 50 wt %, or in another embodiment, the concentration of magnetite in suspsension is 0.75 – 2.5 wt %, or in another embodiment, the concentration of magnetite in suspsension is 0.75 – 5.0 wt %, or in another embodiment, the concentration of magnetite in suspsension is 0.75 – 10 wt %, or in another embodiment, the concentration of magnetite in suspsension is 0.75 – 15 wt %, or in another embodiment, the concentration of magnetite in suspsension is 0.75 – 20 wt %, or in another embodiment, the concentration of magnetite in suspsension is 0.75 – 25 wt %, or in another embodiment, the concentration of magnetite in suspsension is 0.75 – 30 wt %, or in another embodiment, the concentration of magnetite in suspsension is 0.75 – 35 wt %, or in another embodiment, the concentration of magnetite in suspsension is 0.75 – 40 wt %, or in another embodiment, the concentration of magnetite in suspsension is 0.75 – 50 wt %, or in another embodiment, the concentration of magnetite in suspsension is 2.5 – 10 wt %, or in another embodiment, the concentration of magnetite in suspsension is 2.5 – 20 wt %, or in another embodiment, the concentration of magnetite in suspsension is 2.5 – 25 wt %, or in another embodiment, the concentration of magnetite in suspsension is 2.5 – 30 wt %, or in another embodiment, the concentration of magnetite in suspsension is 2.5 – 40 wt %, or in another embodiment, the concentration of magnetite in suspsension is 2.5 – 50 wt %, or in another embodiment, the concentration of magnetite in suspsension is 10 – 20 wt %, or in another embodiment, the concentration of magnetite in suspsension is 10 – 30 wt %, or in another embodiment, the concentration of magnetite in suspsension is 10 – 40 wt %, or in another embodiment, the concentration of magnetite in suspsension is 10 – 50 wt %.

[0032] The superparamagnetic fibers of this invention comprise, in one embodiment, magnetite particles and a polymer matrix. In one embodiment, the polymers comprising the polymer matrix of this invention may be copolymers.

In another embodiment, the polymers may be homo- or, in another embodiment heteropolymers. In another embodiment, the polymers may be synthetic, or, in another embodiment, natural polymers. In another embodiment, the polymers may be water-soluble. In another embodiment, the polymers comprising the polymer matrix of this invention may be free radical random copolymers, or, in another embodiment, graft copolymers. In one embodiment, the polymers may comprise polysaccharides, oligosaccharides, proteins, peptides or nucleic acids. It is to be understood that any polymers, which may be utilized to produce a superparamagnetic fiber of this invention, such as, any material that may be electrospun into a fiber, including, in other embodiments, any natural or synthetic polymer, are to be considered as part of this invention.

[0033] In one embodiment, the choice of polymer utilized may be a function of the particles employed. In one embodiment, the polymer may comprise polyacrylic acid, polystyrene sulfonic acid, polyvinyl sulfonic acid, polyethylene oxide polypropylene oxide, polyvinyl alcohol, or a combination thereof.

[0034] In another embodiment, the polymer comprises a surfactant, a polyethylene glycol, a lignosulfonate, a polyacrylamide or a biopolymer. In another embodiment, the biopolymer may comprise polypeptides, cellulose and its derivatives such as hydroxyethyl cellulose and carboxymethyl cellulose, alginate, chitosan, lipid, dextan, starch, gellan gum or other polysaccharides, or a combination thereof.

[0035] In another embodiment, the polymer comprises polyethylene oxide at a concentration of 2 – 4 wt %. In another embodiment, the polymer comprises polyacrylic acid, at a concentration of 6.5 – 15 wt %. In another embodiment, the polymeric matrix may comprise poyacrylic acid and SDS. In another embodiment, the SDS or other similar ionic surfactant may be at a concentration of 0.5-10 wt %.

[0036] According to this aspect of the invention, and in another embodiment, the molecular weight of the polyacrylic acid may be 5,000 Da, or in another embodiment, 5,000 – 20,000 Da. In one embodiment, the PAA and Jeffamine are used during nanoparticle synthesis to form a "corona" on the magnetite particles that allows them to be suspended in solution and stabilizes them against aggregation. In another embodiment, magnetite particles may be similarly prepared, via methods known to one in the art, to form stable suspensions in solution.

[0037] In another embodiment, this invention provides a field-responsive fiber comprising ferromagnetic nanoparticles and an organic polymeric matrix. In another embodiment, according to this aspect of the invention, the nanoparticles are monodispersed within said polymeric matrix.

[0038] The ferromagnetic nanoparticles can exhibit a spontaneous magnetization, and may comprise Fe, Co, Ni, Gd, Dy, MnAs, MnBi, MnSb, CrO_2, $MnOFe_2O_3$, $FeOFe_2O_3$, $NiOFe_2O_3$, $CuOFe_2O_3$, $MgOFe_2O_3$, EuO, $Y_3Fe_5O_{12}$.

[0039] In one embodiment, the organic route synthesis uses organometallic precursors decomposed at a high temperature, which in one embodiment, is at a range of between about 200-400 °C, in a high boiling point organic liquid. In one embodiment, the organic liquide is a benzyl ether, or in another embodiment, a phenyl ether, or in another embodiment, octanol, or others, as will be appreciated by one skilled in the art. In one embodiment, the process is conducted in the presence of stabilizers like oleic acid and olylamine. According to this aspect of the invention, and in one embodiment, the method for preparing the nanoparticles via an organic route produces monodisperse magnetic nanoparticles.

[0040] In one embodiment, the nanoparticles thus prepared result in particles relatively small in size. In one embodiment, seed mediated growth can be used to synthesize larger nanoparticles, in which the smaller nanoparticles synthesized can be used as seeds in a subsequent synthesis of larger-sized nanoparticles.

[0041] According to this aspect, and in one embodiment, the functionalization of the nanoparticles with an organic surface coating provides nanoparticles compatible with organic solvents. In one embodiment, the organic route synthesis permits a wide range of particle compositions, including those with larger intrinsic magnetic moments, which, in another embodiment, provide a longer Néel relaxation time. This was exemplified herein, in Example 6 via SQUID test, where the remnant magnetization at zero field for the 16nm particles indicated ferromagnetic behavior, rather than the superparamagnetic behavior exhibited by the smaller particles synthesized via aqueous route.

[0042] In one embodiment, a longer Néel relaxation time allows for changes in mechanical properties under a uniform applied field at conventional rates of deformation. Due to coupling of the particle magnetic moment with the applied field, deformation of the magnetic fibers requires additional work, resulting in increased stiffness and lower strain, compared to the equivalent nonmagnetic fibers at equal deformation energy.

[0043] According to this aspect of the invention, and in one embodiment, the fiber has a high saturation magnetization, ranging from 250 kA/m to 2000 kA/m. In another embodiment, the fiber has a tunable Nèel relaxation time which ranges from 2 milliseconds to 4 seconds, or in another embodiment, the tunable Nèel relaxation time is a function of nanoparticle size.

[0044] In one embodiment, the fibers of this invention are formed from a solution whose concentration of polymer may range from 0.5-40 wt %, or in another embodiment, the concentration ranges from 2-20 wt %, or in another embodiment, the concentration ranges from 5- 15 wt %, or in another embodiment, the concentration ranges from 6.5- 15 wt %. In one embodiment, the polymer concentration will be a function of the chemistry, molecular weight, or combination thereof of the polymer and/or solvent used.

[0045] In one embodiment, the fibers of this invention are nanofibers. In one embodiment, the nanofiber is less than 500 nm in diameter. In another embodiment, the nanofiber diameter ranges from 10 nm - 1 μm. In one embodiment, the nanofiber diameter ranges from 65 - 100 nm, or, in another embodiment, the nanofiber diameter ranges from 65 - 200 nm, or, in another embodiment, the nanofiber diameter ranges from 65 - 300 nm, or, in another embodiment, the nanofiber diameter ranges from 65 - 400 nm, or, in another embodiment, the nanofiber diameter ranges from 65 - 200 nm, or, in another embodiment, the nanofiber diameter ranges from 100 - 200 nm, or, in another embodiment, the nanofiber diameter ranges from 150 - 250 nm, or, in another embodiment, the nanofiber diameter ranges from 100 - 300 nm, or, in another embodiment, the nanofiber diameter ranges from 100 - 400 nm, or, in another embodiment, the nanofiber diameter ranges from 100 - 250 nm, or, in another embodiment, the nanofiber diameter ranges from 200 - 300 nm, or, in another embodiment, the nanofiber diameter ranges from 200 - 350 nm, or, in another embodiment, the nanofiber diameter ranges from 200 - 450 nm, or, in another embodiment, the nanofiber diameter ranges from 10 - 200 nm, or, in another embodiment, the nanofiber diameter ranges from 75 - 500 nm. In another embodiment, the nanofiber diameter ranges from 10 nm - 10 μm. In another embodiment, the nanofiber has a diameter that is less than 10 nm.

[0046] In one embodiment, the magnetite nanoparticles produced via aqueous route are stably dispersed within the polymeric matrix. In one embodiment, the term "stably dispersed" or "stabilized" or "stabilization" refers to the stability of the resulting polymer solution or matrix, following their production. In one embodiment, the terms "stably dispersed" or "stabilized" or "stabilization" refer to the fact that the magnetite particles do not aggregate or "settle out" in solution, or in another embodiment, are readily dispersed, such as, via vortexing in solution. In another embodiment, the magnetite nanoparticles dispersed within the polymeric matrix are "colloidally-stable". In one embodiment, the term "colloidally-stable" refers to refer to the fact that the magnetite particles do not aggregate or "settle out" in solution, or in another embodiment, form a homogeneous solution, wherein the particles, in another embodiment, cannot be separated by ordinary filtration or centrifugation.

[0047] In one embodiment, the magnetite nanoparticles produced via organic route are monodispersed within the polymeric matrix. In one embodiment, the term "monodispersed" refers to a relative average particle size, with a coefficient of variance of less than 10.

[0048] In another embodiment, the magnetite particles do not change in their chemical composition over a particular period of time.

[0049] In another embodiment, the fibers of this invention may further comprise a targeting moiety. The term "targeting moiety", in one embodiment, refers to a specificity conferred to the moiety, which results in attachment of the moiety to a cognate partner, or, in another embodiment, an ability to specifically "target" the moiety to a desired cognate partner molecule. The targeting moiety may, in one embodiment, facilitate attachment of the the fibers, through the targeting moiety, to a molecule of interest, such as a protein or glycoprotein, in one embodiment, or, in another embodiment, to a nucleic acid of interest, or in another embodiment, to a cellular fraction of interest. Such a property may be additionally useful, in another embodiment, in application of the superparamagnetic fibers of this invention in filtration or magnetic separation.

[0050] In one embodiment, the targeting moiety enhances attachment to a molecule in low abundance, which is of interest. In another embodiment, the targeting moiety enhances attachment following supply of an energy source, such as a UV light source. In one embodiment, the targeting moiety is chemically attached to the polymers via a chemical cross-linking group, or in another embodiment, forms a stable association with a polymer, or, in another embodiment, forms an association with the polymer, yet readily dissociates following changes in solution conditions, such as, for example, salt concentration or pH.

[0051] In one embodiment, the targeting moiety may be an antibody, which specifically recognizes a molecule of interest, such as a protein or nucleic acid. In another embodiment, the antibody may specifically recognize a reporter molecule attached to a molecule of interest. In another embodiment, the targeting moiety may be an antibody fragment, Protein A, Protein G, biotin, avidin, streptavidin, a metal ion chelate, an enzyme cofactor, or a nucleic acid. In another embodiment, the targeting moiety may be a receptor, which binds to a cognate ligand of interest, or associated with a cell or molecule of interest, or in another embodiment, the targeting moiety may be a ligand which is used to "fish out" a cell via interaction with its cognate receptor.

[0052] It is to be understood that any component of interest, such as a cell, or component thereof, wherein its separation from other materials is desired, which is amenable to the present technology is to be considered as part of this invention.

[0053] The fibers of this invention are magnetic field-responsive, such as was demonstrated, for example with superparamagnetic fibers of this invention, in Example 5. In one embodiment, the superparamagnetic fiber property, or ferromagnetic property of magnetic field-responsiveness is exploited in a variety of applications, as is discussed further hereinbelow.

[0054] In one embodiment, the term "magnetic field-responsive" refers to the property of the fibers of this invention to exhibit a structural modification, in response to the application of an external magnetic field. In one embodiment, such responsiveness is completely reversible, or, in another embodiment, mostly, or in another embodiment, partly reversible. In another embodiment, magnetic field responsiveness results in a high stiffness exhibited in the fibers of this invention. In another embodiment, it results in deformation or change of shape, such as, for example, exhibited in the superparamagnetic fibers. Such changes in stiffness and/or deformation may be rate-sensitive, in another embodiment.

[0055] In one embodiment of this invention, the fibers of this invention are produced via an electrospinning technique. Preparation of superparamagnetic or ferromagnetic polymeric nanofibers via electrospinning is exemplified hereinbelow. In one embodiment, for preparation of the former, electrospinning is conducted as described herein, on colloidally-stable suspensions of magnetite nanoparticles in polyethylene oxide and polyvinyl alcohol solutions. In some instances, the magnetite nanoparticles were aligned in columns parallel to the fiber axis direction within the fiber by the electrospinning process. In another embodiment, for the preparation of the ferromagenetic nanofibers, the electrospinning is conducted on monodispersed magnetite nanoparticles of size up to 16 nm, in THF.

[0056] In one embodiment, this invention provides a method of producing a field-responsive fiber comprising magnetite particles and a polymeric matrix, the method comprising the step of electrospinning a polymer solution comprising stably dispersed superparamagnetic magnetite particles, or monodispersed magnetite particles.

[0057] In one embodiment, the method of producing a field-responsive fiber of this invention via electrospinning comprises the step of preparing desired concentrations of polymer/magnetite nanoparticle solutions, in which the nanoparticles are dispersed.

[0058] For preparation of superparamagnetic fibers of this invention, in one embodiment such dispersions are prepared by adding the desired amount of polymer solution directly to a magnetite nanoparticle aqueous solution, which may be accompanied by, in another embodiment, vigorous stirring, which may be accomplished, in another embodiment, for a period of time of at least 24 hours at room temperature.

[0059] In one embodiment, aqueous solutions of magnetite nanoparticles may be prepared as follows: aqueous solutions containing iron (III) chloride hexahydrate, iron (II) chloride tetrahydrate, and graft copolymer may be dissolved in deoxygenated water, where the graft copolymer may comprise Jeffamine and polyacrylic acid.

[0060] In one embodiment, the particles are co-precipitated in the presence of a stabilizing polymer as described hereinbabove, which, in another embodiment, attaches to the particle surfaces and confers steric stabilization to the particle dispersion in the polymer solution. In another embodiment, the magnetic fluid thus formed, comprising an aqueous solution of stably dispersed magnetite particles in polymer, may be subjected to centrifugation and/or filtration, which, in another embodiment, may serve remove excess polymer and/or salts.

[0061] For preparation of ferromagnetic fibers of this invention, in one embodiment such dispersions are prepared by by adding the desired amount of polymer solution directly to a magnetite nanoparticle organic solution, which may be accompanied by, in another embodiment, vigorous stirring, which may be accomplished, in another embodiment, for a period of time of at least 24 hours at room temperature. In one embodiment, the solution will comprise THF and DMF.

[0062] In one embodiment, electrospinning may be conducted with the aid of any suitable apparatus as will be known to one skilled in the art. In one embodiment, a parallel-plate electrospinning apparatus may be used, such as that described by Shin et al [Shin M., Hohman M.M., Brenner M.P., and Rutledge G.C., Appl. Phys. Lett. 2001; 78:1149-1151] and/or Fridrikh et al [Fridrikh S.V., Yu J. H. , Brenner M.P., and Rutledge G. C. . Phys. Rev. Lett. 2003; 90:144502].

[0063] In one embodiment, electrospinning is conducted with two 10 cm in diameter aluminum disks, arranged parallel to each other, at a distance of up to 30 cm. In one embodiment, the electrical voltage, solution flow rate and distance between the two parallel plates are adjusted to obtain a stable jet.

[0064] In one embodiment, the methods of this invention produce superparamagnetic fibers in which magnetite particles line up within the fibers in parallel to the fiber axis direction.

[0065] In one embodiment, the method employs magnetite nanoparticles dispersed as stable suspensions in PEO solutions, for producing superparamagnetic fibers. Such solutions comprising the nanoparticles will, in another embodiment, exhibit increased conductivity, such as, for example, that shown in Table 1.

[0066] In one embodiment, the methods of this invention will employ electrospinning wherein the parameters comprise a flow rate of between 0.005 to 0.5 ml/minute, or in another embodiment, 0.01 to 0.03 ml/minute. In another embodiment, the electrospinning parameters may comprise a polymer/particle solution viscosity of 0.1 to 20 (Pa•s), or more.

[0067] In one embodiment, the polymer is PVA, at a concentration ranging from 6.5 – 15 wt %, and the viscosity ranges from 0.05 – 20 (Pa•s), or more. In another embodiment, the solution further comprises SDS, which increases the viscosity. According to this aspect of the invention, and in one embodiment, a solution comprising 1 wt % SDS, exhibits a viscosity of 0.6 – 21 (Pa•s). In one embodiment, the addition of SDS increases viscosity and conductivity of the solution, however does not affect surface tension properties. In another embodiment, the inclusion of SDS in the polymer solution decreases the diameter of the fiber formed.

[0068] In another embodiment, flow rate, viscosity, concentration, or combination thereof may vary, and be any value which enables electrospinning of the solution to produce a superparamagnetic fiber, or ferromagnetic fiber of this invention.

[0069] It is to be understood that any embodiment listed herein in reference to the fibers of this invention, may characterize the fibers as obtained by the methods provided herein, and is to be considered as part of this invention.

[0070] In one embodiment, in regard to the methods of this invention producing superparamagnetic fibers of this invention, which comprise a PEO polymer, the PEO polymer used is at a concentration of between 1 % and 3 % by weight, and in another embodiment, solutions comprising the same have a conductivity of at least 1000 μS/cm.In another embodiment the solution may have a conductivity ranging <1 microSeimen/cm up to 1300 microSeimens/cm, or greater.

[0071] In another embodiment, according to this aspect of the invention, the methods of this invention emloy the use of a polymer solution comprising polyvinyl alcohol, which in another embodiment, is at a concentration of between 6.5 % and 15 % by weight, or in another embodiment, comprises SDS, which in another embodiment, exhibits a conductivity of at least 1000 μS/cm.

[0072] In another embodiment, this invention provides a device or apparatus comprising the field-responsive fibers of this invention. It is to be understood that such a device or apparatus may comprise any embodiment of any fiber of this invention.

[0073] In one embodiment, the device or apparatus is used as a filter. In one embodiment, the superparamagnetic fibers of this invention are so arranged in a matrix as to form an impermeable barrier, when not under the influence of an external magnetic field. According to this aspect of the invention, and in one embodiment, upon exposure to an external magnetic field the fibers deform in a given orientation, such that gaps are introduced within the matrix, thereby introducing permeability. In another embodiment, the filter is suited for use in magnetoseparation. According to this aspect, and in another embodiment, magnetic particles suspended in a liquid are adsorbed and separated off with use of a layer of filter medium comprising the superparamagnetic fibers of this invention. In one embodiment, application of an external magnetic field may result in deformation of the superparamagnetic fibers comprising the filter, facilitating passage of debris, and other non-desired components, while materials adhered to magnetic particles remain attached to the filter. These are some, non-limiting applications of the superparamagnetic fibers as filters, however many other applications will be appreciated by one skilled in the art, and are to be considered as embodiments of this invention.

[0074] In one embodiment, the device or apparatus is used as a sensor. In one embodiment, the sensor will take advantage of the deformation of the superparamagnetic fibers in response to an externally applied magnetic field. In one embodiment, such sensors may be utilized for remotely sensing the alternating currants (AC) in a set of substantially parallel conductors, from the magnetic fields generated by these currents in the vicinity of the conductors. It is to be understood that any application wherein detection of the presence of a magnetic field is desired, and a sensor comprising the superparamagnetic fibers of this invention may be utilized is to be considered as part of this invention. In another embodiment, as a tunable reinforcement material, the superparamagnetic fibers of this invention, or a fabric comprising the same, could be included in a composite or multilayer construction such that the composite or multilayer is made stiffer when a magnetic field is turned on, such stiffness increase being higher when the field is higher and/or when the rate of deformation is faster. In another embodiment, as a piezomagnetic transducer, deformation of the fabric may result in a measureable magnetic field to sense or actuate other components. In another embodiment, introduction of a magnetic field may result in deflection or deformation of the piezomagnetic fiber, fabric or multilayer material.

[0075] In another embodiment, the superparamagnetic fibers of this invention may be used for information storage. In one embodiment, the superparamagnetic fibers of this invention are used in a magnetic storage medium containing a magnetic material. The magnetic material may be any magnetic material, which can store data by the alignment of the directions of the spins in the material. In one aspect, the each magnetite particle within the superparamagnetic fibers of this invention may be adapted to store one bit of data.

[0076] In another embodiment, the superparamagnetic fibers of this invention may be used for magnetic imaging. In one embodiment, an image may be formed by applying an external magnetic field to selected regions of a composite medium comprising the superparamagnetic fibers of this invention. In response to the applied field, deformation of the fibers occurs, producing a latent image, which may, in another embodiment, be developed by exposure to magnetic fluid or powders. The image may be erased, in another embodiment, by removal of the magnetic field, or in another embodiment, by exposure to an AC demagnetizing field or a DC sweep magnet.

[0077] In one embodiment, the superparamagnetic fibers are used in magnetic shielding. In another embodiment, this invention provides a fabric comprising the superparamagnetic fibers.

[0078] In many situations, such as, for example, in military shelters, protection against electro-magnetic interference signals is desired. In one embodiment, shielding of electronic equipment is desired, as the equipment would malfunction if subjected to electro-magnetic waves. In another embodiment, when certain types of electronic equipment are used, it is desirable to have shielding, which prevents detection of the location from which the signals are generated. In one embodiment, such shielding may be provided by the superparamagnetic fibers of this invention.

[0079] In one embodiment, a fabric comprising the superparamagnetic fibers, or ferromagnetic fibers of this invention may be thus utilized.

[0080] In another embodiment, a fabric comprising the superparamagnetic or ferromagnetic fibers of this invention, may further comprise additional materials which do not materially affect their properties, such as, for example, pigments, antioxidants, stabilizers, surfactants, and others as will be appreciated by one skilled in the art. In one embodiment, a fabric of this invention may be a SMART fabric, in which stiffness can be controlled by use of an external magnetic field, and which absorb impact at pre-determined rates. These properties are in addition to the field-dependent deflection behavior demonstrated previously.

[0081] In one embodiment, the surface coating of nanoparticles will be compatible (for example, hydrophilic or hydrophobic) with the polymer solution in which they are electrospun (magnetic nanoparticles should disperse uniformly in the polymeric solution).

[0082] In one embodiment, the magnetic nanoparticles will have a high saturation magnetization and tunable Nèel relaxation time (with size). The magnetization of the material may vary, in some embodiments, from 250 kA/m to 2000 kA/m. The Nèel relaxation time may vary, in some embodiments, from milliseconds to seconds, depending on the size of nanoparticles.

[0083] The following examples are presented in order to more fully illustrate some embodiments of the invention. They should, in no way be construed, however, as limiting the scope of the invention.

EXAMPLES

Materials and Methods

Materials:

[0084] Poly(ethylene oxide) (PEO, Mv 2,000,000), poly(vinyl alcohol) (PVA, 87%-89% hydrolyzed, Mw: 85k-146k)and dodecyl sulfate, sodium salt (98%)(SDS) were obtained from Aldrich and used for making electrospinnable solution. Poly(acrylic acid) (PAA; 50 wt % in water, Mw = 5000), iron(III) chloride hexahydrate (97%), iron(II) chloride tetrahydrate (99%), ammonium hydroxide (28 wt% in water), dimethyl formamide (DMF) and dicyclohexylcarbodiimide (CDI) were obtained from Aldrich (Milwaukee, WI) and used for synthesizing nanoparticles. Jeffamine XTJ-234 (PEO/PPO-NH2, EO:PO = 6.1:1, Mw = 3000) is an amine-terminated random copolymer of ethylene oxide (EO) and propylene oxide (PO) repeat units with 6.1 EO units per PO unit. It was donated by Huntsman Corp. (Houston, TX) and has characteristics similar to that of pure PEO.

Preparation of nanoparticles:

[0085] The graft copolymer was prepared by reacting the Jeffamine with the carboxyls on PAA via amidation chemistry as described [Moeser G.D., K.A.R., Green W.H., Laibinis P.E., and Hatton T.A.. Ind. Eng. Chem. Res. 2002; 41:4739 -4749]. Only a small percentage (16 %) of carboxyl groups were grafted with Jeffamine since free carboxyl groups are required for chelation with surface iron atoms and stabilization of the magnetite nanoparticles.

[0086] In a typical procedure for the synthesis of the magnetite nanoparticles [Moeser, *supra*], an aqueous solution containing 2.35 g of iron (III) chloride hexahydrate, 0.86 g of iron (II) chloride tetrahydrate, and 1 g of graft copolymer was prepared by dissolving the reagents in 40 mL of deoxygenated water. Deoxygenation was achieved by bubbling with nitrogen under vigorous stirring for 30 min before reaction. The aqueous solution was heated to 80 °C, and 5 ml of 28 wt % of ammonium hydroxide was added to precipitate iron oxide in the form of magnetite. The growth of spherical nanoparticles was arrested by the polymer in the solution, which caps the magnetite nanoparticles as soon as they form and stabilizes them sterically against aggregation. The resulting mixture was then aged for 30 min at 80 °C. This procedure produces 1 g of magnetite in 40 mL of water, which is equivalent to a 2.5 wt % suspension of magnetite. The final magnetic fluid was washed in a centrifuge with an ultrafilter (Millipore, Centricon Plus 80, MWCO 100,000) to remove excess polymer and salts.

Preparations of spinning solutions:

[0087] PEO solutions ranging from 1% to 3% by weight were prepared by directly adding the PEO polymer to distilled water. The solutions were stirred vigorously for at least 24 h at room temperature in order to obtain homogeneous solutions. PVA solutions ranging from 6.5% to 15% by weight were prepared by directly adding the polymer into distilled water, with vigorous stirring for at least 3-4 hours at 70°C.

[0088] Various concentrations of PEO/magnetite nanoparticle dispersions were prepared by adding the desired amount of PEO solution directly to the nanoparticle aqueous solution prepared as described above, with vigorous stirring for at least 24h at room temperature. A range of PVA/magnetite nanoparticle suspensions was prepared similarly, and then mixed using a vortex mixer (VWR Scientific Products) for at least ten minutes before spinning, as the particle suspension was not particularly stable against aggregation and settling.

Electrospinning:

[0089] The parallel-plate electrospinning apparatus used was similar to that described by Shin et al [Appl. Phys. Lett. 2001; 78:1149-1151] and Fridrikh et al [Phys. Rev. Lett. 2003; 90:144502]. Briefly, two aluminum disks with diameters of 10 cm were arranged parallel at a distance of up to 30 cm apart. The fluid was pumped at a constant flow rate by a syringe pump (Harvard Apparatus PHD 2000) to a stainless steel capillary with inner diameter 1mm located in the center of the upper disk. An electrical potential was applied to the upper disk by a high voltage power supply (Gamma High Voltage Research ES-30P). Current was measured by a Digital multimeter (Fluke85 III) as the voltage drop across a 1.0 MW resistor between the lower disk and ground. The electrical voltage, solution flow rate and distance between the two parallel plates were adjusted to obtain a stable jet.

Measurement and Characterization of Composite Nanofibers:

[0090] Viscosity was measured on an AR2000 Rheometer (TA Instruments) at 25°C. A Kruss 10 tensiometer was used to determine surface tensions, while conductivity was measured using a Cole Parmer 19820 conductivity meter.

Dynamic Light Scattering (DLS):

[0091] Dynamic Light Scattering (DLS) was performed to determine the hydrodynamic diameters of the coated nanoparticles using a Brookhaven BI 200-

SM system at a fixed angle of 900. The autocorrelation function was fitted with an exponential curve to obtain the diffusion coefficient, which was then used to calculate the hydrodynamic diameter via the Stokes-Einstein equation.

Scanning Electron Microscopy (SEM):

[0092] Specimens for Scanning Electron Microscopy (SEM) were prepared by direct deposition of the electrospun nanofibers on an aluminum foil and sputter-coating with gold using a Desk II cold sputter/etch unit (Denton Vacuum LLC, NJ). The images of the electrospun fiber were obtained using a JEOL-6060SEM (JEOL Ltd, Japan), and the fiber diameters were determined using AnalySIS image processing software (Soft Imaging System Corp., Lakewood, USA) by measuring 20 randomly selected fibers for each sample.

Transmission Electron Microscopy (TEM):

[0093] For Transmission Electron Microscopy (TEM), a dilute magnetite nanoparticle solution was dried on a carbon grid and visualized under the JEOL JEM200 CX TEM microscope (JEOL Ltd, Japan) to estimate the core sizes of the particles. The electrospun nanofibers were directly deposited onto a copper grid for TEM analysis.

Super Conducting Quantum Interference Device (SQUID) Test:

[0094] The SQUID test was conducted using an MPMS XL magnetometer (Quantum Design Inc., San Diego) for both PVA/magnetite and PEO/magnetite nanofibers. The sample was scanned in 40-50 equal increments with an applied magnetic field ranging from approximately –0.6 Tesla to 0.6 Tesla.

Nanoindentation:

[0095] Nanoindentation experiments were performed using a Nanoscope IV, DimensionTM 3100 AFM (Digital Instrument, Santa Barbara) with a RTESP single-beam silicon probe (Digital Instrument) (fR=280-361 kHz, k=30-40 N/m). All the nanofibers were conditioned in a vacuum oven for at least two days before experiments, at room temperature for PEO and PEO/magnetite nanofibers and at 60°C for PVA and PVA/magnetite nanofibers, respectively. During these AFM indentation tests, PVA and PVA/magnetite nanofibers were treated as a group, as were the PEO and PEO/magnetite nanofibers. Within each group, the maximum indentation force, Pmax, was the same. Pmax for the PVA group was twice that for the PEO group. Within each group, mica and a flat reference sample of epoxy were indented using the same probe and parameters. The mica has an elastic modulus of ~171 GPa and Poisson ratio of ~0.3 [27-29]. The elastic modulus of the reference epoxy sample was determined independently using a Triboindenter with Berkovich-type indentation tip (Hysitron Inc., Minneapolis). For each sample, at least 20 individual force curves were obtained.

Field Responsive testing:

[0096] A rectangular strip (length x width x thickness=1.8x0.555x0.004 cm) of electrospun nonwoven mat was placed on the surface of a table, with one end fixed by tape onto the table surface. A permanent laboratory magnet with a rectangular cross-section (1.8x0.6 cm) was suspended some distance away above the mat, and the response behavior of the nonwoven mat to the laboratory magnet was recorded by a digital camera.

Example 1

Synthesis of Composite Nanofibers Containing Magnetite Nanoparticles

[0097] The size distribution of the magnetite nanoparticles was determined by DLS (Figure 1), and corresponded to an average hydrodynamic diameter of 25 nm. An analysis of TEM images of the as-synthesized magnetite nanoparticles (Figure 2) indicated an average core size, assuming a log normal distribution, of 7.5±2.9 nm. Only the magnetite cores were visible in TEM measurements, as the polymer coatings were of low contrast, and could not be discerned in these images. The difference between the average hydrodynamic diameter and core size yielded a thickness of about 9 nm for the polymer shell.

[0098] The dependence of the magnetization, M, of the magnetite fluid on the applied magnetic field in the SQUID tests is shown in Figure 3. The magnetite nanoparticle suspension exhibited superparamagnetic behavior in that there was zero remnant magnetization at zero applied field. The saturation magnetization was approximately 0.5-0.7 Tesla.

[0099] The magnetite nanoparticles were readily dispersed as stable suspensions in PEO solutions, increasing their conductivity dramatically, as shown in Table 1.

Table 1: Solution properties and electrospinning processing parameters of some representative nanofibers

Composite		Conductivity (µS/cm)	Viscosity (Pa•s)	Voltage (kV)	Flow Rate (ml/min)	Distance (cm)	Current (nA)	Fiber Diameter (nm)
PEO (2 wt%)		107.9	1.565	9.0	0.010	25	83	390±40
	Fe_3O_4 (0.75%)	1277	1.506	9.0	0.020	25	353	400±80
PVA (7.5%)		351	0.2905	29.0	0.010	25	412	170±40
	Fe_3O_4 (0.75%)	1372	0.3926	29.0	0.010	25	1534	320±40
	Fe_3O_4(0.75%)+SDS(1%)	2740	1.941	28.5	0.016	25	1050	140±30

[00100] The preferred electrospinning parameters (Table 1) were almost identical for PEO and PEO/magnetite solutions. Some representative SEM pictures of electrospun nanofibers of PEO and PEO/magnetite are shown in Figure 4. At low PEO concentration (1 wt%) in the absence of magnetite nanoparticles, the fibers adopted a bead-on-string morphology (Figure 4 (a)), while fibers with uniform diameters were obtained when 3.52 wt% magnetite nanoparticles were added to the spin solution (Figure 4(b)). At higher concentrations (2-3 wt%) of PEO, uniform fiber morphologies were obtained for both PEO and PEO/magnetite solutions with little change in fiber diameters on the addition of magnetite nanoparticles, as shown in Figures 4 (c) and (d).

[00101] The magnetite nanoparticles were easily dispersed in PVA solutions, as well, but these solutions were not as stable as in the case of PEO, and the magnetite nanoparticles settled overnight. The settling of the suspension on standing may have been due to PEO-based shells around the nanoparticles not being as compatible with the PVA in solution as they were with PEO solutions. The PVA suspensions were easily homogenized, however, using a Vortex mixer for 10 minutes immediately before electrospinning. The presence of the magnetite nanoparticles in the PVA solutions increased the conductivity of these solutions (Table 1). Again, there was little change in the preferred electrospinning processing parameters for PVA solutions when magnetite nanoparticles were added (Table 1). SEM pictures of electrospun nanofibers using PVA and PVA/magnetite solutions (Figure 5) show that the magnetite nanoparticles lead to increased fiber diameters, but that addition of SDS to the solution counteracted this effect, as SDS generally reduces the fiber diameters (Table 1). The results of a detailed study of the effect of SDS on the PVA fiber morphology are shown in Table 2.

Table 2: Effect of SDS On PVA Solution Properties and PVA Fiber Morphology

[00102] While SDS increased both the conductivity and the viscosity of the solutions significantly, it had surprisingly little effect on the surface tension. The diameters of the nanofibers were decreased by adding 1 wt% SDS to various concentrations of PVA. At the lowest PVA concentration (6.5 wt%), the fiber morphology changed from bead-on-string (with no SDS) to uniform fibers on the addition of 1 wt% SDS.

	Conductivity (S/cm)		Viscosity (Pa•s)		Surface Tension (mN/m)		Fiber Diameter (nm)	
PVA (wt%)	No SDS	SDS (1 wt%)	No SDS	SDS (1 wt%)	No SDS	SDS (1 wt%)	No SDS	SDS (1 wt%)
6.5%	329	1223	0.1187	0.6456	41.58	42.04	Beaded	96.04±17.13
8%	315	1187	0.2905	1.375	39.5	42.42	146.67±10.90	73.72±14.51
10%	449	1156	0.8931	2.954	39.23	39.5	201.01±27.85	158.19±22.43
12%	496	1194	2.019	6.822	37.24	34.1	356.96±15.96	193.98±48.14
15%	515	1230	8.372	20.64	34.61	29.71	478.9±18.37	297.03±14.74

Example 3

Electrospinning Effects On Nanofiber Characteristics

[00103] In order to further characterize PEO/magnetite and PVA/magnetite nanofibers, transmission electron microscropy was utilized to visualize the fibers (Figure 6). The weight percentages of magnetite nanoparticles within the fibers were 28%, and 8% for PEO/magnetite and PVA/magnetite nanofibers, respectively. The relatively large size of the PEO fiber and high content of nanoparticles within the fiber made it difficult to focus the TEM pictures, but the contour of the alignment of the nanoparticles into columns along the fiber axis direction was readily visible. For the PVA/magnetite fiber, the images were

clearer, and demonstrated magnetite nanoparticle alignment in columns parallel to the fiber axis direction within the fiber.

[00104] Magnetite nanoparticles can form chains in solution owing to magnetic coupling effects between particles. The number of nanoparticles, n_0, in a chain in the fluid, at zero external field, can be estimated using the following formula:

$$n_0 = [1 - \frac{2}{3}(\frac{\phi}{\lambda^3})e^{2\lambda}]^{-1} \qquad (1)$$

where, ϕ is the volume fraction of particles in the fluid, and λ is the coupling coefficient, which measures the strength of particle-particle interactions.

λ is given by

$$\lambda = \frac{\mu_0 M^2 V}{14kT} \qquad (2)$$

where, μ_0 is the permeability of free space, M is intensity of magnetization of the magnetic particles, V is the volume of the magnetic particles, k is Boltzmann's constant, and T is the absolute temperature in degrees Kelvin.

[00105] For magnetite particles 7.5 nm in diameter, $\lambda<1$ according to equation (2), which means the particle-particle interaction energy is less than the thermal energy and no chain forms in solution prior to electrospinning for any concentrations of magnetite particles. Thus the column alignment of magnetite nanoparticles within the fiber observed in Figure 6(b) was a result of the electrospinning process itself. Possible causes for this alignment may have been hydrodynamics in the capillary, steady jet, or whipping jet regions, or induction by the local electric field.

[00106] Super Conducting Quantum Interference Device (SQUID) magnetization curves for both 28 % PEO/magnetite and 8 % PVA/magnetite nanofibers demonstrated the superparamagnetic behavior of the fibers at room temperature (Figure 7). At low temperature (5K), both systems were characterized by a narrow hysteresis and a small remnant magnetization at zero field. These can be explained by considering the magnetic relaxation of the nanoparticles. For 7.5 nm diameter particles, Neel relaxation dominates the Brownian rotation mechanism. The Neel relaxation time varies exponentially with inverse temperature. For example, at 300 K the Neel relaxation time for magnetite particles 8 nm in diameter in kerosene carrier is approximately 10^{-9} s, and increases to approximately 13 s at 5K. At low temperature, when the applied field reached zero, the dipole moments of some nanoparticles were still polarized, and therefore a small remnant magnetization was observed. The superparamagnetic behavior of the nanofibers at room temperature may be useful, in some embodiments of this invention, for applications in which alternating nonuniform fields are needed, as this would reduce the dissipative energy in a device comprising the nanofibers.

Example 4

Structural Characterization of the Composite Nanofibers Comprising Magnetite Nanoparticles

[00107] The elastic modulus of the fibers was evaluated using an AFM indentation technique according to the following formula [Vanlandingham M.R., et al., J. Adhesion 1997; 64: 31-57; Sneddon J. N., Int. J. Engng. Sci. 1965; 3: 47-56; Pharr G.M., et al., J. Mater. Res. 1992; 7: 613-617; Vanlandingham M.R., et al., Composites Part A1999; 30:75-83; Drechsler D., et al., Appl. Phys. A 1998; 66: S825-S829]:

$$S = \left.\frac{dP}{d\Delta Z_i}\right|_{P_{max}} = 2E^*\left(\frac{A}{\pi}\right)^{\frac{1}{2}} \qquad (3)$$

[00108] Here, S was the slope of the unloading curve at P_{max}, P was the applied load, A was the contact area, ΔZ_i is the indentation depth, and E* was the effective Young's modulus of the contact as defined by

$$\frac{1}{E^*} = \frac{1-\nu_s^2}{E_s} + \frac{1-\nu_t^2}{E_t} \qquad (4)$$

[00109] In equation (4), E_s and E_t were the elastic moduli, and ν_σ and ν_τ the Poisson ratios of the sample and the tip, respectively. A diamond tip was used, with asymmetric pyramidal geometry; indent size was characterized by the lateral distance from the apex to the base of the triangular impression [Vanlandingham, *supra*]. E_t and ν_τ were assumed to be 130 GPa and 0.2, respectively, corresponding to the bulk values of diamond [Kracke B., Damaschke B. ,Appl. Phys. Lett. 2000; 77:361-363; Vanlandingham M. R. , et al., J. Mater. Sci. Lett. 1997; 16:117-119; Klapperich C. , et al. J. Tribology 2001; 123: 624-631]. The nanofibers were indented in the radial direction. A schematic depiction of the tip-sample interaction during the indentation test is shown in Figure 8. The method was applicable here, in view of the fact that the diameters of the fibers (>150 nm) were much larger than the diameters of the contact area (<10 nm).

[00110] The results of the indentation tests for PVA/magnetite nanofiber are shown in Figure 9. Mica was also indented to evaluate the bending of the AFM cantilever, which was then subtracted from the raw PVA/magnetite data to determine fiber properties. In these indentation tests, the slopes of the top portions of the unloading curves were used to evaluate the modulus of each sample.

[00111] Assuming the tip geometry is the same for all the indentations, the relative changes in indent size was sufficient to relate contact areas; here, the apex to base distance was equated to a contact radius, r. The Poisson ratio, ν, was assumed to be the same for all fibers within each group. The ratio of modulus of different samples within each group was then evaluated using the formula:

$$\frac{(dP / d\Delta Z_i)|_{P_{\max}1}}{(dP / d\Delta Z_i)|_{P_{\max}2}} = \frac{r_1 E_1}{r_2 E_2} \qquad (5)$$

[00112] Table 3 provides the indentation data obtained for the nanofibers.

Table 3: Nanoindentation data of the nanofibers.

	PVA[1]	PVA+Fe_3O_4[1]	PEO[2]	PEO+ Fe_3O_4[2]	Epoxy[1]	Epoxy[2]
ΔZ_i (nm)	12.33±4.46	14 55±2.67	9.36±1 41	5 92±0.68	22.14±1 42	10.92±0.35
ΔZ_t (nm)	80 04±5 05	51.23±4 46	170.32±15.65	194.24±14 40	67.83±1.42	38.94±1.87
Modulus (GPa)	4 8 ±1.73	4 1 ±0.75	0.66 ±0.10	1.04 ±0 12	1.52±0.12*	1.52±0 12*

1: Trigger setpoint of deflection signal of the cantilever is 1.2 V.
2: Trigger setpoint of delfection signal of the cantilever is 0.6V.
*: The modulus is determined independently by a triboindenter using a Berkovich tip.

[00113] ΔZ_i represented the total displacement recovered from $P=P_{max}$ to $P=0$. ΔZ_t represented the total indentation depth, which measures the penetration of the tip into the sample surface, including both the inelastic and elastic deformation of the material. The moduli were obtained by comparing values obtained with reference epoxy sample within each group, using equation (5). The modulus of the reference epoxy sample was determined to be 1.52 GPa using a Triboindenter. The indent size, r, was found to be 40nm for the PEO and PEO/magnetite nanofibers, 10nm for PVA and PVA/magnetite nanofibers, 20nm

and 10nm for reference epoxy samples under conditions used to test the PVA group and PEO group, respectively.

[00114] As shown in Table 3, after including magnetite nanoparticles (8 wt%) within PVA nanofibers, ΔZ_i was statistically the same, and ΔZ_t decreased. This indicates that the modulus of the PVA nanofibers was maintained and the inelastic deformation was decreased due to the reinforcement effect of magnetite nanoparticles.

[00115] After including (28 wt%) magnetite nanoparticles within the PEO fiber, ΔZ_i decreased, but ΔZ_t increased showing that the modulus of PEO nanofibers was increased due to the reinforcement effect of magnetite nanoparticles. One indication of the increase in inelastic deformation of the PEO/magnetite nanofibers was that the short chains of polymeric shell around the nanoparticles may have been detrimental to the mechanical properties of the nanofibers, and overwhelmed the effect of magnetite reinforcements as the concentration of the magnetite nanoparticles within the fibers increased from 8 wt% to 28 wt% .

[00116] The superparamagnetic fibers exhibited mechanical properties comparable to those of the polymer matrix, and were not brittle. Though the fibers were ceramic, and therefore expected to be very brittle, and unlikely to deform at all, much less to as large a strain as produced int the superparamagnetic fibers.

Example 5

Composite Nanofibers Comprising Magnetite Nanoparticles Are Superparamagnetic

[00117] SQUID tests demonstrated that the magnetite nanoparticles within the nanofibers were easily magnetized by an external magnetic field, and that the dipole moments of the nanoparticles were readily polarized in the direction of the external magnetic field.

[00118] Since a magnetic dipole experiences a torque force in a uniform magnetic field and a translational force in a magnetic field gradient, it was thought that the composite nanofibers containing magnetite particles in an external magnetic field gradient, may be deformed by the translational forces experienced by the embedded nanoparticles (Figure 10). In response to an electric field provided by a small laboratory magnet, a strip of PVA/magnetite nonwoven mat exhibited field-responsive behavior.

[00119] In this example, one end of the nonwoven mat was fastened onto the surface of a table, while the other end was free to move. In the absence of the magnetic field, the nonwoven mat lay flat on the surface of the table (Figure 10a). When the magnet was placed above the nonwoven mat, the fabric was deflected by the translational forces in the direction of increasing magnetic field as shown in Figure 10b. As the magnet was brought closer to the fabric, the greater magnetic field gradients experienced by the nonwoven mat induced larger translational forces on the magnetite nanoparticles, causing a greater deflection of the free end of the mat towards the magnet (Figure 10c). The PEO/magnetite nonwoven mat showed similar response behavior to the laboratory magnet as the PVA/magnetite nonwoven mat. Thus, both superparamagnetic fabrics produced by the electrospinning techniques exemplified herein, exhibited field-responsive behavior.

[00120] Superparamagnetic polymer nanofibers ranging in diameter from 140 to 400 nm obtained via the electrospinning of polymer-stabilized magnetite nanoparticle suspensions in PEO and PVA solutions exhibited nanoparticle line up within the fibers in columns parallel to the fiber axis direction. Both sets of fibers were superparamagnetic at room temperature, and responded to an externally-applied magnetic field by deflecting in the direction of increasing field gradient, with nanoindentation tests showing magnetite nanoparticle reinforcement of the mechanical properties of nanofibers.

Example 6

Composite Nanofibers Comprising Organic-Soluble Polymers

Materials and Methods

Reagents

[00121] Iron(III) acetylacetonate (97%), Benzyl ether (99%), 1-2 hexadecanediol (97%), ethanol, oleic acid (90%) and oleylamine (70%) were purchased from Sigma Aldrich and used as received.

Synthesis of seeds

[00122] 2 mmol of Iron (III) acetylacetonate, 10 mmol of 1-2 hexadecanediol, 6mmol of oleic acid and 6 mmol of oleylamine and 20 ml of benzyl ether were mixed in a 3 neck flask and were stirred continuously under a blanket of nitrogen. The temperature was ramped up slowly to 200 °C (2.5 °C /min) and the mixture was kept at this temperature for 2 hrs. Finally the mixture was refluxed at 300 °C for 1 hr. The resulting black mixture was cooled down to room temperature and ethanol was added followed by centrifugation at 7000g to separate out magnetite. The centrifuged product was re-suspended in hexane and was used for seed mediated growth.

Synthesis of bigger nanoparticles

[00123] 2 mmol of Iron(III) acetylacetonate, 10 mmol of 1-2 hexadecanediol, 2mmol of oleic acid and 2 mmol of oleylamine , 20 ml of benzyl ether and 80 mg of seeds in 4 ml of hexane were mixed in a 3 neck flask and stirred continuously under a blanket of nitrogen. The mixture was kept at 100 °C for 30 mins and at 200 °C for 1h. Finally the mixture was refluxed at 300 °C for 30 mins. The magnetite was recovered using the procedure outlined above. The resulting magnetite nanoparticles can then be used as seeds for subsequent synthesis. In this manner stable nanoparticles up to 16 nm were synthesized.

Electrospinning

[00124] First, PMMA was directly added into DMF solvent to make 7.5 wt% solution. PMMA was directly added into THF suspension containing 3.7 wt% of Fe_3O_4. Mixing the two solutions prepared above at a ratio of 3:1, 1 7.5 wt % PMMA solution containing 2.78 wt % Fe_3O_4 in a mixture of THF and DMF (3:1) was prepared for electrospinning. A parallel-plate electrospinning apparatus was used in this research and has been described elsewhere by Shin et al [Appl. Phys. Lett. 78, 1149-1151 (2001)] and Fridrikh et al [Phys. Rev. Lett. 90:144502 (2003)].

Measurement and characterization

[00125] The images of the electrospun fiber were obtained using a JEOL-6060SEM (JEOL Ltd, Japan), and the fiber diameters were determined using AnalySIS image processing software (Soft Imaging System Corp., Lakewood, USA) by measuring 20 randomly selected fibers for each sample. Transmission Electron Microscopy (TEM) was performed on the JEOL JEM200 CX TEM microscope (JEOL Ltd, Japan).The Superconducting Quantum Interference Device (SQUID) test was conducted using an MPMS XL magnetometer (Quantum Design Inc., San Diego) for PMMA/magnetite nanofibers.

Results

[00126] In order to determine whether nanoparticles could be prepared via an organic route, synthesis using organic solvents was undertaken. The TEM micrographs of magnetite nanoparticles of different diameters synthesized by the organic route are shown in Figure 11. The TEM micrographs confirmed the seed mediated growth. It was difficult to re-suspend bigger nanoparticles in hexane (>14 nm), possibly due to higher magnetic interaction between the bigger nanoparticles. Nanoparticles were sonicated to get a suspension in THF. The sonication tended to disturb the alignment, thereby aiding in dispersion. The shape of the nanoparticles changed from spherical to cubical shape with increased particle size, perhaps attributable to a different amount of surfactants adsorbing on different faces of the growing crystal.

[00127] Electrospinning of the PMMA/16 nm magnetite nanoparticle dispersion in THF was not possible as the jet dried too fast at the capillary tip. The jet became stable, however, following the addition of a 33% in volume of DMF in THF dispersion, and a uniform fiber was obtained.

[00128] The preferred processing parameters were 17.5 kV for applied electrical potential, 0.05 ml/min for flow rate, and 25 cm for the plate-to-plate distance. The current measured was 72.5 nA and the diameter of the fiber was around 1.53±0.34 μm. A representative SEM picture of the electrospun PMMA fiber containing 16nm magnetite nanoparticles is shown in Figure 12.

[00129] A SQUID magnetization curve for PMMA fiber containing 37% by weight of 16 nm magnetite particles is shown in Figure 13. At room temperature, a small hysteresis and a small remnant magnetization at zero field are observed.

This is in contrast to the superparamagnetic behavior observed for the magnetic fibers containing 7.5 nm magnetite nanoparticles, shown above. These can be explained by considering the magnetic relaxation of the nanoparticles. For the particles within the fiber, only the Néel relaxation mechanism is operative, since the nanoparticles can not rotate through a Brownian mechanism within the fiber matrix. 16 nm magnetite nanoparticles have a longer Néel relation time than 7.5 nm magnetite nanoparticles. At room temperature, when the applied field reached zero, the dipole moments of the 16 nm nanoparticles were still partially aligned while those of the 7.5 nm nanoparticles were completely relaxed, and therefore a small remnant magnetization was observed for fibers containing 16nm nanoparticles, but not for containing 7.5 nm nanoparticles.

[00130] In this example, textiles comprised of magnetic fibers containing 16 nm magnetite nanoparticles have been produced by electrospinning. The organic synthesis route for nanoparticles employed here complements the aqueous synthesis route above, and provides for functionalization of the nanoparticles with an organic surface coating that is compatible with organic solvents. The resulting particles can therefore be dispersed in either aqueous or organic solutions, respectively. The range of polymers that can be electrospun with magnetic particles to form field-responsive fibers is thus expanded to include both organic-soluble and water-soluble polymers.

[00131] The organic route synthesis, in contrast to the aqueous route presented above also permits a wider range of particle compositions, includes those with larger intrinsic magnetic moments. The larger particles produced via organic route result in a longer Néel relaxation time, as demonstrated by the SQUID test, where the remnant magnetization at zero field for the 16nm particles indicated ferromagnetic behavior, rather than the superparamagnetic behavior exhibited by the smaller particles obtained via aqueous synthesis.

[00132] The longer Néel relaxation time provides materials, which exhibit changes in mechanical properties under a uniform applied field at conventional rates of deformation. Due to coupling of the particle magnetic moment with the applied field, deformation of the magnetic fibers requires additional work, resulting in increased stiffness and lower strain, compared to the equivalent nonmagnetic fiber at equal deformation energy.

What is claimed is:

1. A superparamagnetic fiber comprising magnetite particles and a polymeric matrix.

2. The superparamagnetic fiber of claim 1, wherein said fiber is a nanofiber.

3. The superparamagnetic fiber of claim 2, wherein said nanofiber is less than 500 nm in diameter.

4. The superparamagnetic fiber of claim 2, wherein said nanofiber diameter ranges from 10 nm - 1 μm.

5. The superparamagnetic fiber of claim 1, wherein said matrix comprises polyethylene oxide, polyvinyl alcohol or a combination thereof.

6. The superparamagnetic fiber of claim 1, wherein said polymeric matrix comprises a polysaccharide, an oligosaccharide, a surfactant, a polyethylene glycol, a lignosulfonate, a polyacrylamide, a polypropylene oxide, a cellulose derivative a polyacrylic acid or a combination thereof.

7. The superparamagnetic fiber of claim 1, wherein said polymeric matrix comprises any polymer that can be electrospun from solution.

8. The superparamagnetic fiber of claim 1, wherein said superparamagnetic fiber is magnetic field- responsive.

9. The superparamagnetic fiber of claim 1, wherein said magnetite nanoparticles are stably dispersed within said polymeric matrix.

10. A device or apparatus comprising the superparamagnetic fiber of claim 1.

11. The device or apparatus of claim 10, wherein said device or apparatus is used as a filter or a sensor.

12. The device or apparatus of claim 10, wherein said device or apparatus is used for information storage.

13. The device or apparatus of claim 10, wherein said device or apparatus is used for magnetic imaging.

14. The device or apparatus of claim 10, wherein said device or apparatus is used for magnetic shielding.

15. The device or apparatus of claim 10, wherein said device or apparatus is used as a tunable mechanical reinforcement component in a composite

16. The device or apparatus of claim 10, wherein said device or apparatus is used as a piezomagnetic transducer

17. A fabric comprising the superparamagnetic fiber of claim 1, wherein said fabric may be woven or nonwoven.

18. A field-responsive fiber comprising ferromagnetic nanoparticles and an organic polymeric matrix.

19. The fiber of claim 18, wherein said fiber is a nanofiber.

20. The fiber of claim 19, wherein said nanofiber has a diameter ranging from 10- 500 nm.

21. The fiber of claim 18, wherein said matrix comprises polymethyl methacrylate.

22. The fiber of claim 18, wherein said nanoparticles are monodispersed within said polymeric matrix.

23. The fiber of claim 18, wherein said fiber has a high saturation magnetization, ranging from 250 kA/m to 2000 kA/m.

24. The fiber of claim 18, wherein said fiber has a tunable Nèel relaxation time which ranges from 2 milliseconds to 4 seconds.

25. The fiber of claim 24, wherein said tunable Nèel relaxation time is a function of nanoparticle size.

26. A device, apparatus or fabric comprising the fiber of claim 18.

27. A method of producing a field-responsive fiber comprising magnetite particles and a polymeric matrix, the method comprising the step of electrospinning a polymer solution comprising magnetic nanoarticles.

28. The method of claim 27, wherein said field-responsive fiber is a nanofiber.

29. The method of claim 27, wherein said nanofiber is less than 500 nm in diameter.

30. The method of claim 29, wherein said nanofiber diameter ranges from 10 nm - 1 μm.

31. The method of claim 27, wherein said field-responsive fiber is superparamagnetic.

32. The method of claim 31, wherein said polymer solution comprises polyethylene oxide.

33. The method of claim 32, wherein said polyethylene oxide is at a concentration of between 1 % and 3 % by weight.

34. The method of claim 33, wherein said polymer solution has a conductivity of between 0.1 and 10000 μS/cm.

35. The method of claim 31, wherein said polymer solution comprises polyvinyl alcohol.

36. The method of claim 35, wherein said polyvinyl alcohol is at a concentration of between 6.5 % and 15 % by weight.

37. The method of claim 31, wherein said polymer solution comprises SDS.

38. The method of claim 31, wherein said polymer solution comprises a polysaccharide, an oligosaccharide, a surfactant, a polyethylene glycol, a lignosulfonate, a polyacrylamide, a polypropylene oxide, a cellulose derivative a polyacrylic acid or a combination thereof.

39. The method of claim 31, wherein said polymer solution is an aqueous solution.

40. The method of claim 27, wherein said field-responsive fiber is ferromagnetic.

41. The method of claim 40, wherein said matrix comprises polymethyl methacrylate.

42. The method of claim 40, wherein said nanoparticles are monodispersed within said polymeric matrix.

43. The method of claim 40, wherein said fiber has a high saturation magnetization, ranging from 250 kA/m to 2000 kA/m.

44. The method of claim 40, wherein said fiber has a tunable Nèel relaxation time which ranges from 2 milliseconds to 4 seconds.

45. The method of claim 44, wherein said tunable Nèel relaxation time is a function of nanoparticle size.

46. The method of claim 40, wherein said polymer solution is an organic solution.

47. The method of claim 27, wherein said polymer solution comprises any polymer that can be electrospun from solution.

48. A superparamagnetic fiber produced by the method of claim 27.

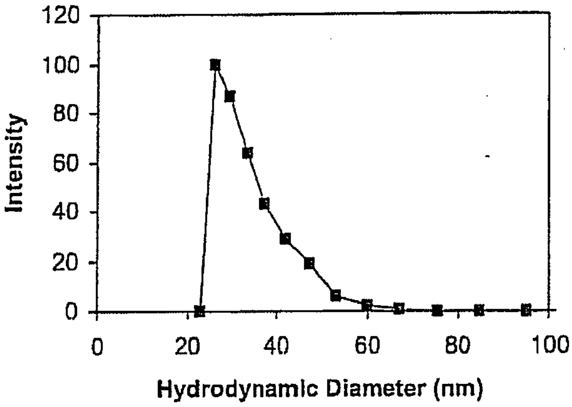


Figure 1: Intensity versus hydrodynamic diameter from the DLS curve for the 2.5 wt% magnetite nanoparticle solution. Exponential sampling model was used to obtain a diameter distribution from the DLS data.

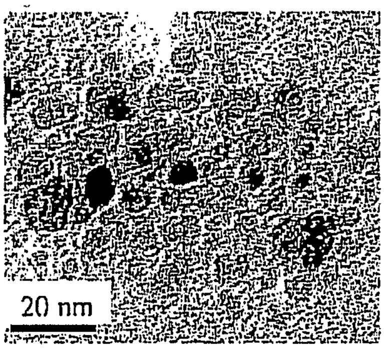


Figure 2: TEM image of the magnetite fluid.

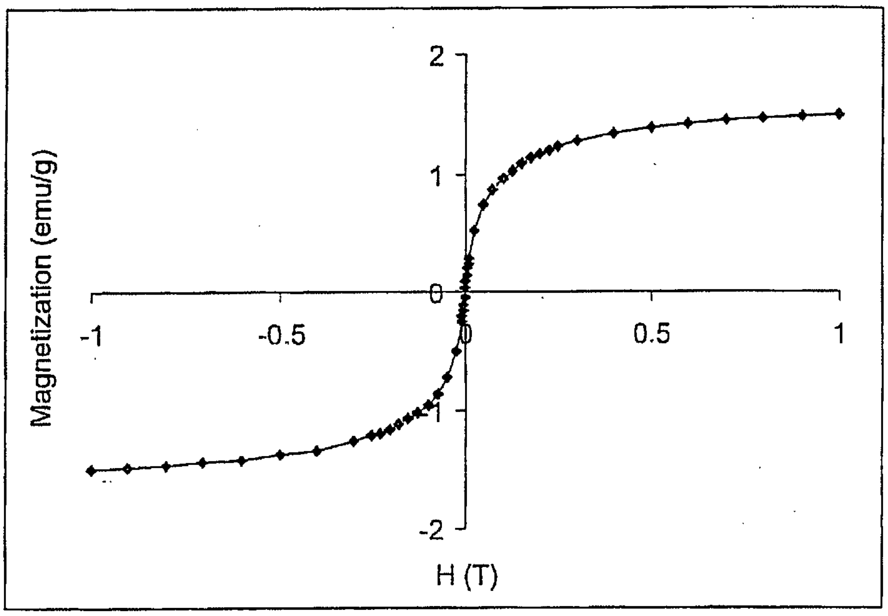
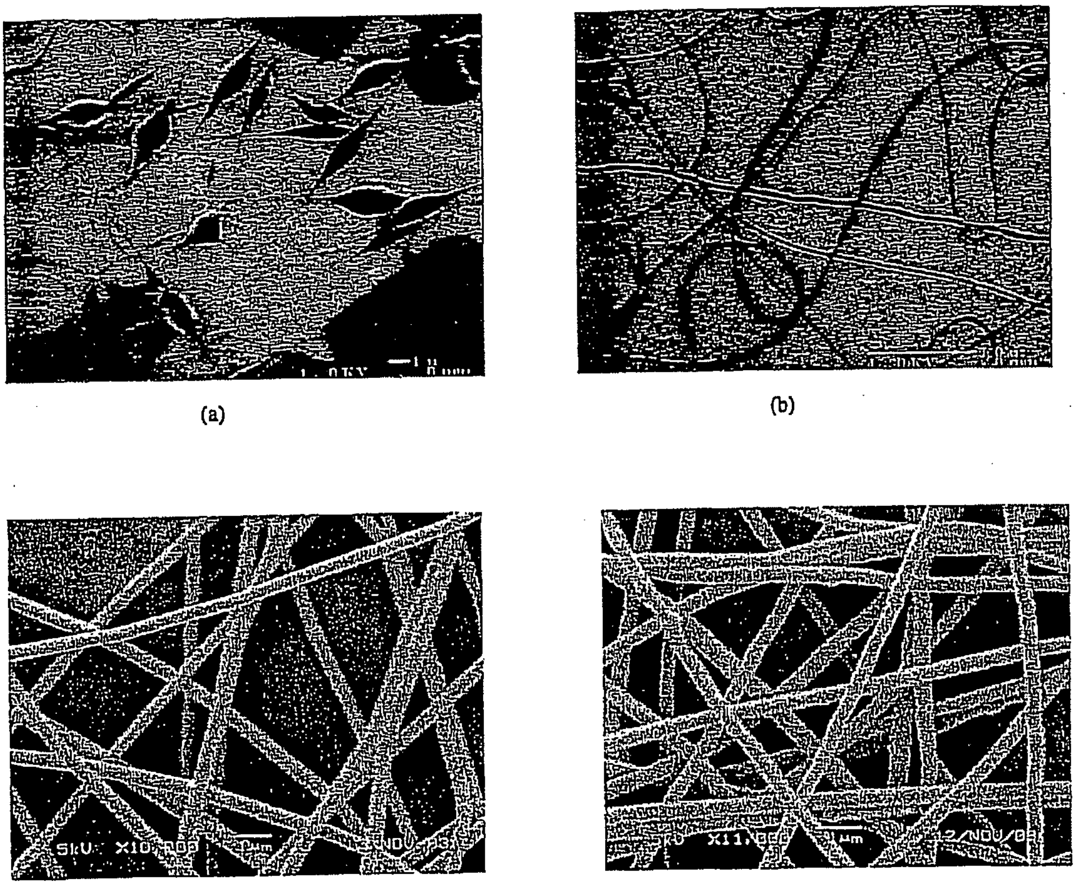


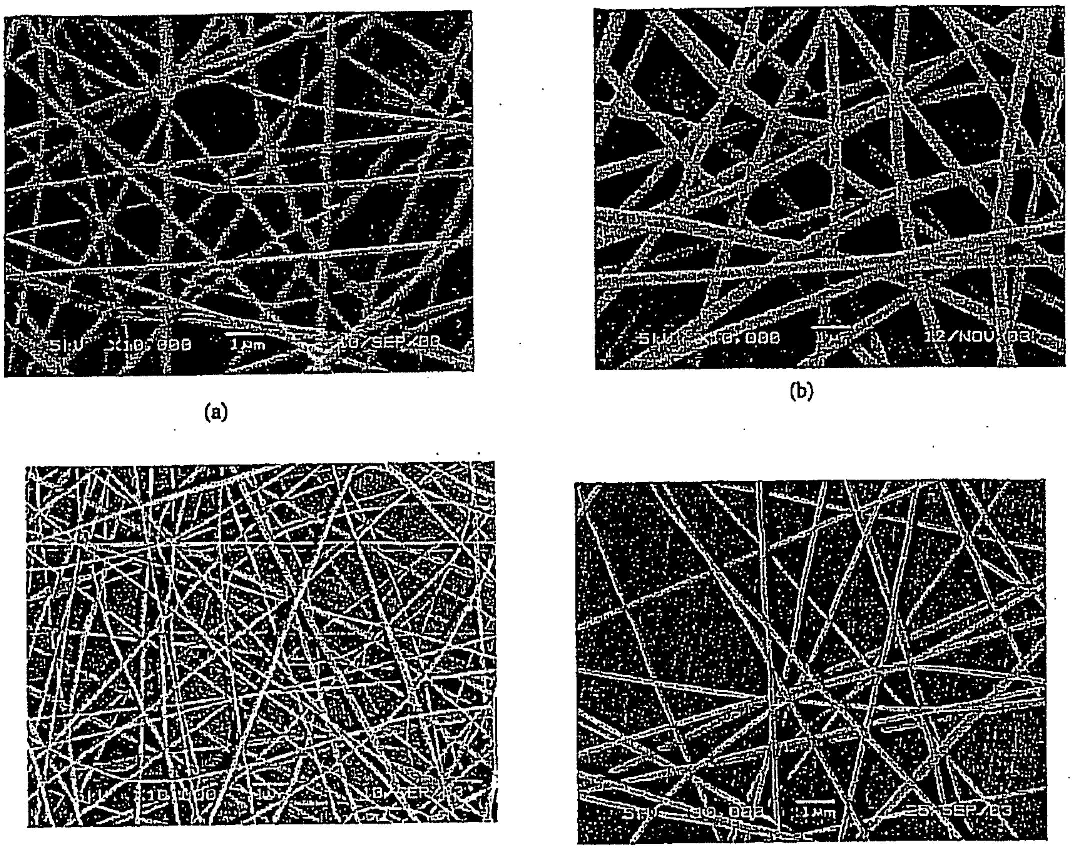
Figure 3: Magnetization (M) versus magnetic field (H) for the 2.5 wt% as-synthesized magnetite fluid.



(a) (b)

(c) (d)

Figure 4: Some representative SEM images of PEO and PEO/magnetite nanofibers: (a) PEO (1%), (b) PEO (1%) +Fe_3O_4 (3.52%), (c) PEO (2%), PEO (2%)+Fe_3O_4 (0.75%).



(a) (b)

(c) (d)

Figure 5: Some representative SEM images of PVA and PVA/magnetite nanofibers:
(a) PVA (7.5%), (b) PVA (7.5%) + Fe_3O_4 (0.75%), (c) PVA (7.5%) +SDS (1%),
(d) PVA (7.5%) +SDS (1%) +Fe_3O_4 (0.75%)

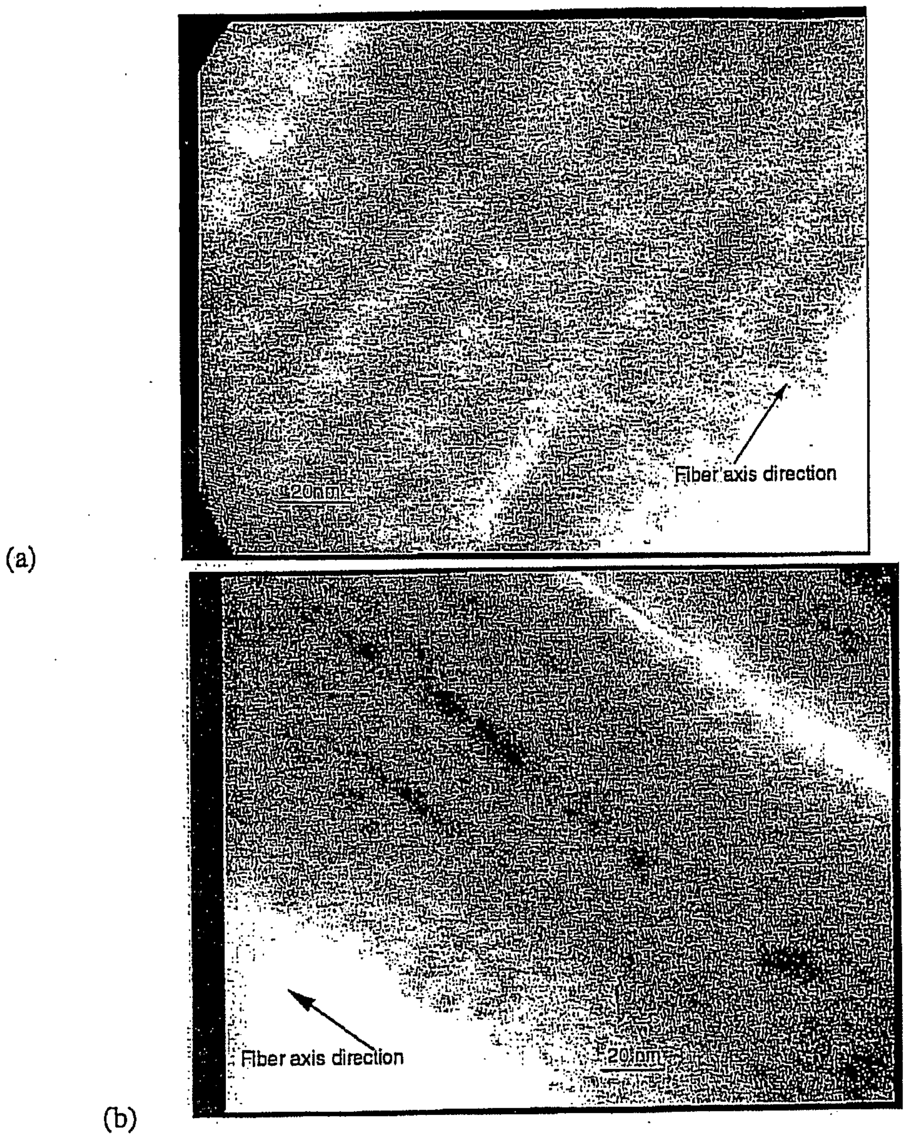
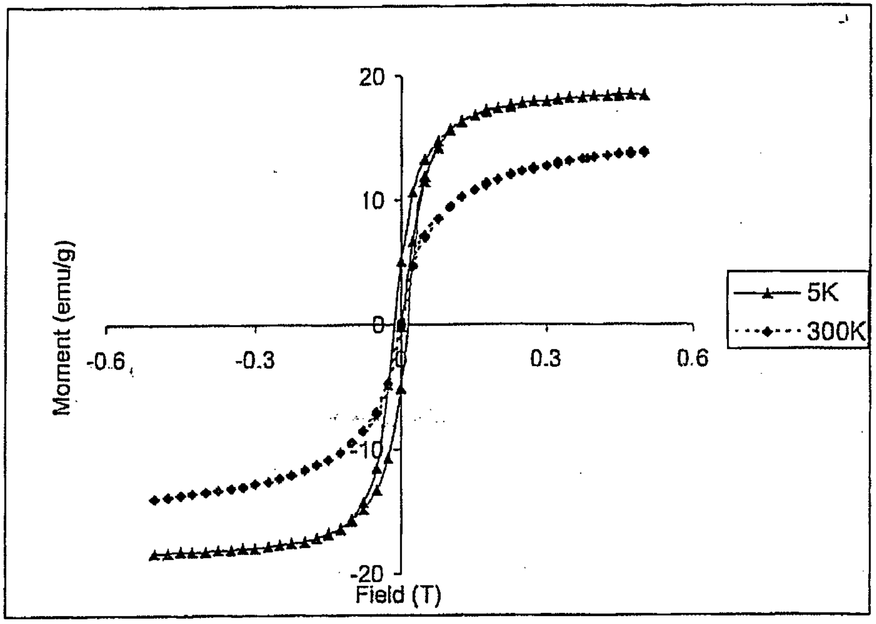
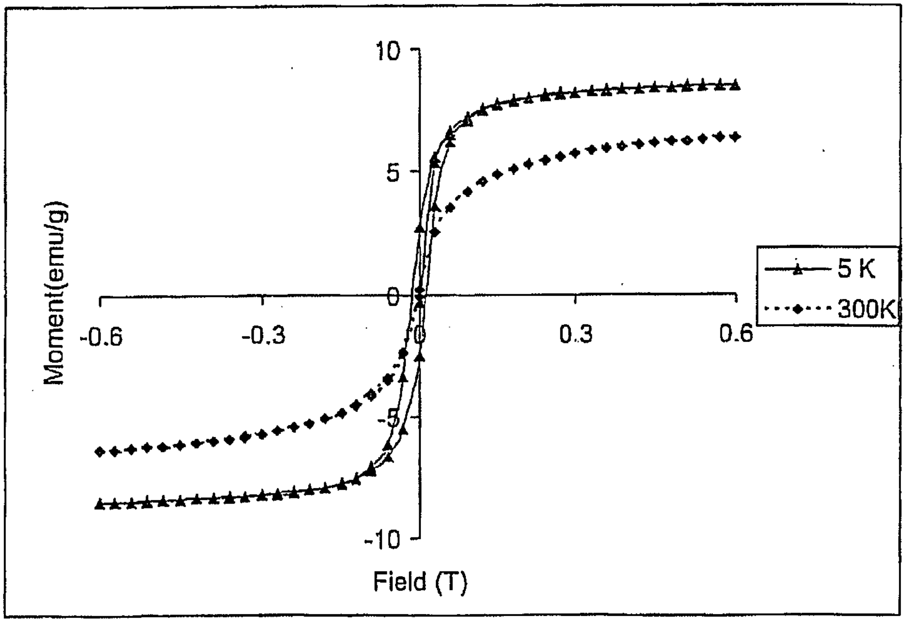


Figure 6: TEM images of ferromagnetic nanofibers. (a) PEO nanofiber with 28wt% magnetite nanoparticles. (b) PVA nanofiber with 8wt % magnetite nanoparticles.



(a)



(b)

Figure 7: Magnetization curves of ferromagnetic nanofibers: (a) PEO nanofiber with (28 wt%) magnetite nanoparticles, (b) PVA nanofiber with (8 wt %) magnetite nanoparticles.

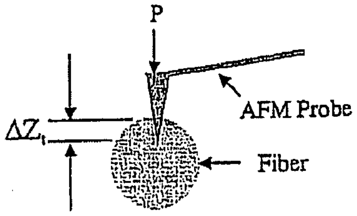
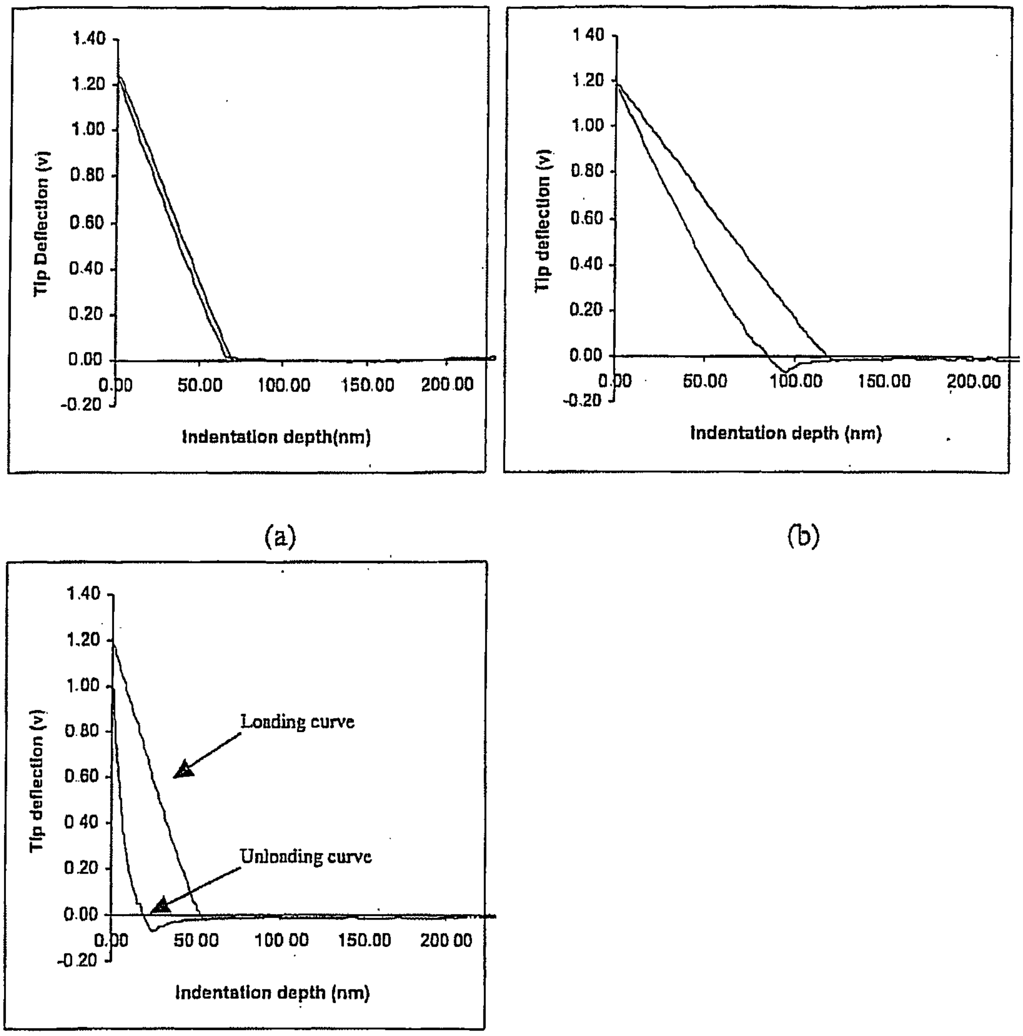


Figure 8: A schematic of tip-sample interaction during the indentation test.

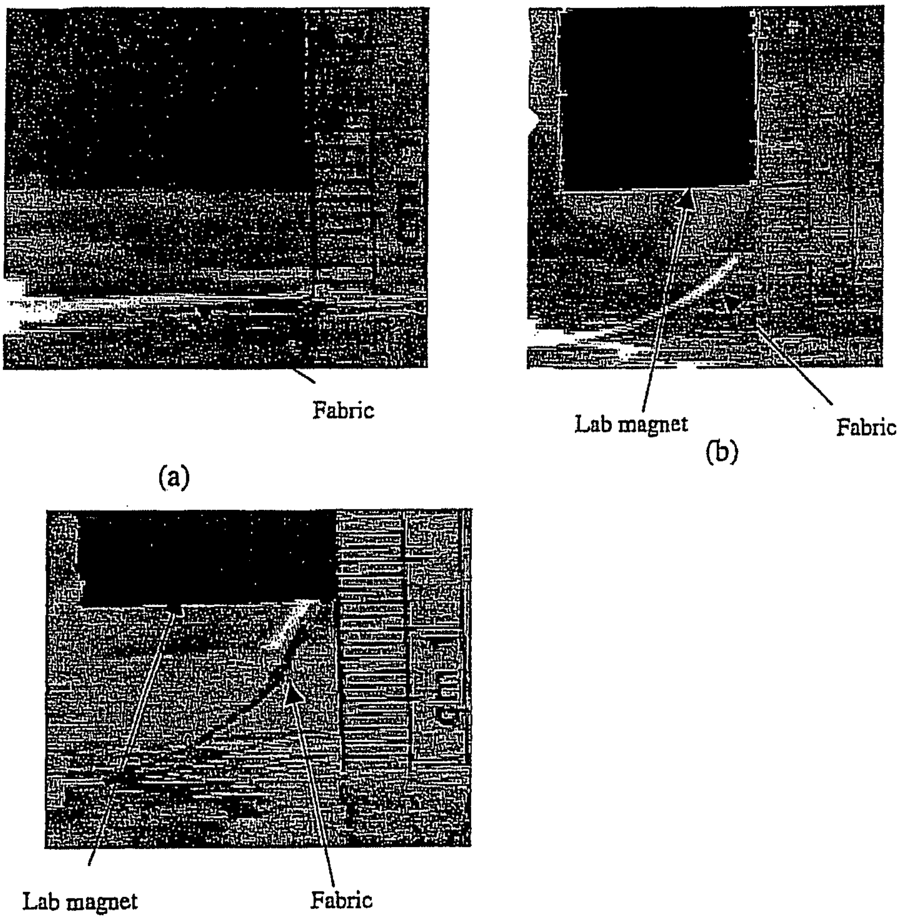


(a)

(b)

(c)

Figure 9: Indentation curves for PVA/magnetite(8 wt%) nanofiber: (a) calibration on hard surface (mica), cantilever bending without indentation; (b) indentation curve on PVA/magnetite nanofiber, cantilever bending and indent; (c) indentation curve on PVA/magnetite after subtracting the cantilever bending.



(a)

(b)

(c)

Figure 10: Field responsive behaviors of PVA/magnetite fabric (a) without magnetic field, (b) within low gradient of magnetic field, (c) within high gradient of magnetic field

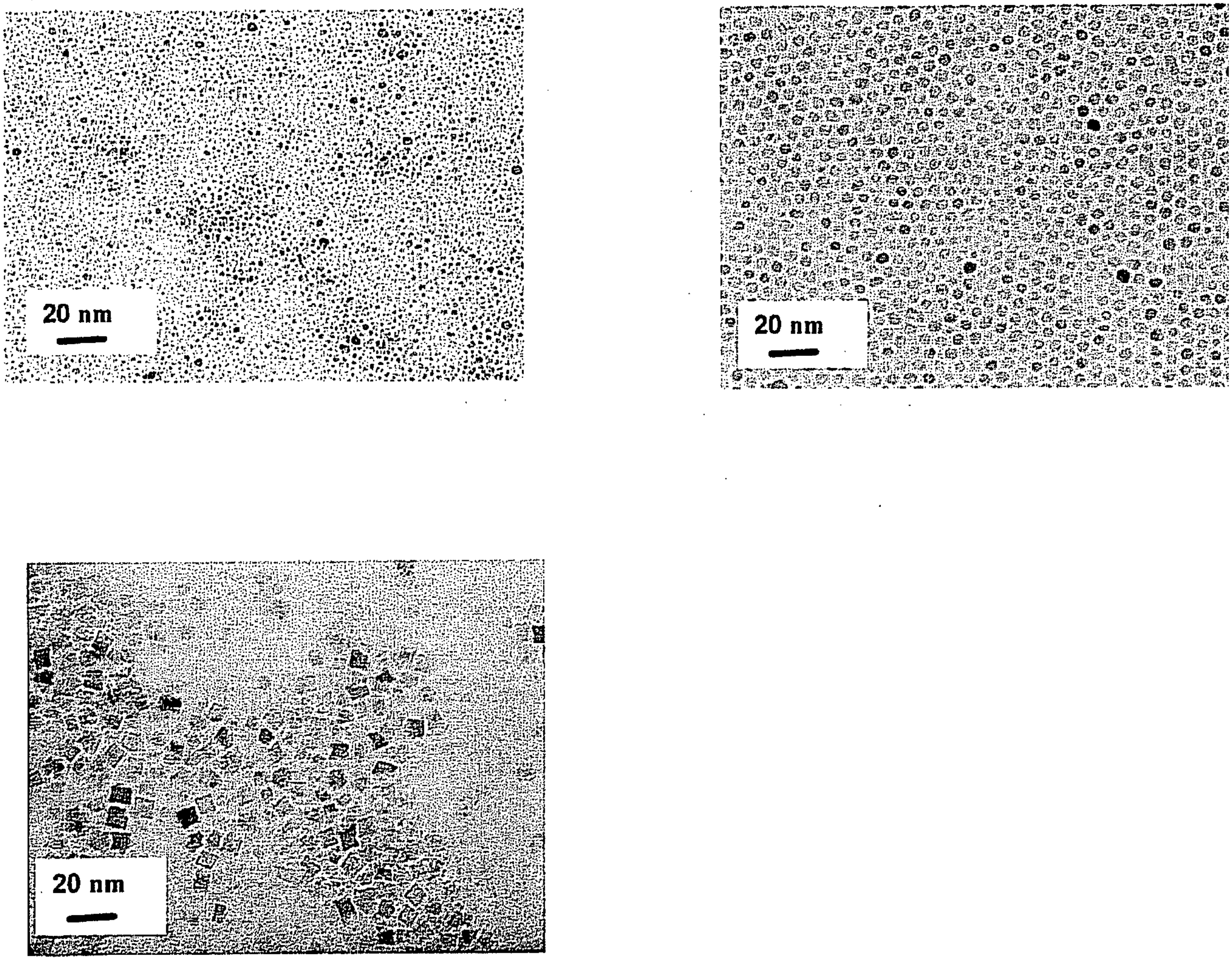


Figure 11

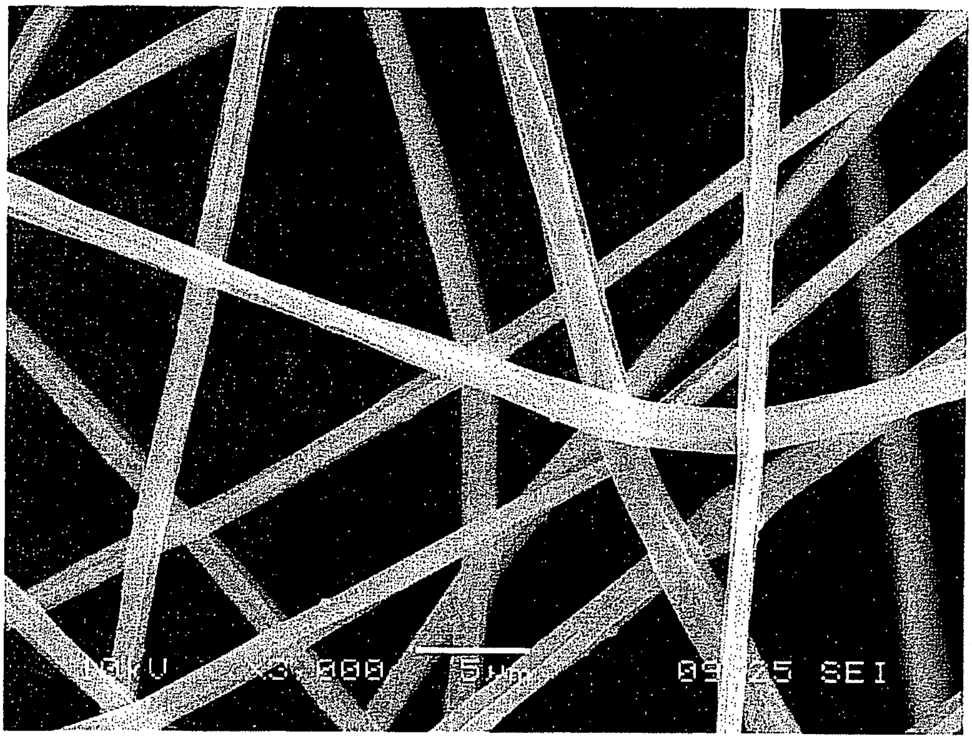


Figure 12

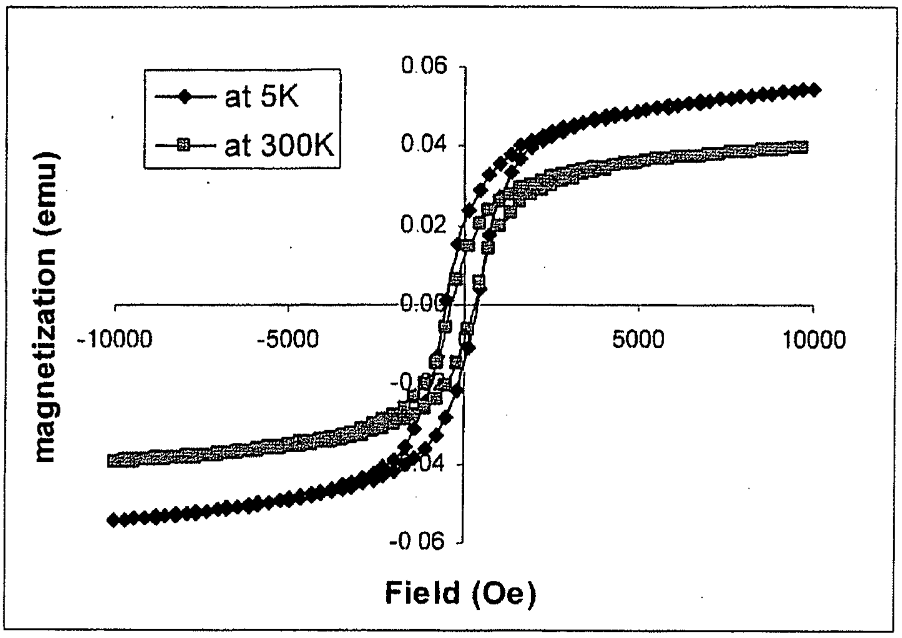

at 5K
at 300K
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
-10000
-5000
5000
10000
magnetization (emu)
Field (Oe)

Figure 13