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Synthesis and characterization of magnetic diphasic $\text{ZnFe}_2\text{O}_4 / \gamma\text{-Fe}_2\text{O}_3$ electrospun fibers

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Abstract

Magnetic nanofibers of $\text{ZnFe}_2\text{O}_4 / \gamma\text{-Fe}_2\text{O}_3$ composite were synthesized by electrospinning from a sol-gel solution containing a molar ratio Fe/Zn of 3. The effects of the calcination temperature on the phase composition, particle size and magnetic properties have been investigated. Zinc ferrite fibers were obtained by calcinating the electrospun fibers in air from 300 °C to 800 °C and characterized by thermogravimetric analyses, Fourier transformed infrared spectroscopy, x-ray photoemission spectroscopy, x-ray diffraction, vibration sample magnetometry and magnetic force microscopy. The resulting fibers, with diameters ranging from 90 to 150 nm, were ferrimagnetic with high saturation magnetization as compared to bulk. Increasing the calcination temperature resulted in an increase in particle size and saturation magnetization. The observed increase in saturation magnetization was most likely due to the formation and growth of $\text{ZnFe}_2\text{O}_4 / \gamma\text{-Fe}_2\text{O}_3$ diphasic crystals. The highest saturation magnetization (45 emu/g) was obtained for fibers calcined at 800 °C.

Keywords

Zinc Ferrite; Magnetic Fibers; Electrospinning; Poly(vinyl) alcohol; Calcination

1. Introduction

Nanostructures of ferrites are of interest due to their mechanical hardness, chemical stability, electric, magnetic, and optical properties that enable them to be considered as promising materials for sensing and catalysis applications, amongst others [1-6]. Particularly, cubic spinel ZnFe_2O_4 has been the focus of intensive research because of its tunable magnetic properties at the nanoscale. In the normal zinc ferrite, Zn^{2+} ions occupy tetrahedrally coordinated A-sites while Fe^{3+} ions are located at octahedral B-sites. This particular

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arrangement causes the material to be antiferromagnetic at temperatures below the Néel Temperature ($T_N = 10.5$ K) and paramagnetic at room temperature. Despite of the expected magnetic behavior in this normal ferrite, large magnetization at room temperature has been measured for nanocrystalline powders and thin films [7]. This particular magnetic behavior is partially attributed to changes in the distribution of Zn^{2+} and Fe^{3+} ions at the A and B sites in the spinel lattice. The degree of deviation from the normal spinel (inversion degree) has been found to be affected by the annealing temperature during the formation of $ZnFe_2O_4$ nanocrystals. In addition to this atomic re-arrangement, the formation of $ZnFe_2O_4$ is generally accompanied by the segregation of secondary phases, such as cubic γ - Fe_2O_3 (maghemite), which is structurally stable at the nanoscale [8]. Indeed, when the zinc ferrite nanocrystals are synthesized from solutions with molar ratio $Fe/Zn > 2$ the co-existence of γ - Fe_2O_3 became evident [9, 10]. Recent studies by Bo et al. have found that excess Fe suppressed the coarsening of $ZnFe_2O_4$ grains favoring instead the formation of $ZnFe_2O_4/\gamma$ - Fe_2O_3 composite nanostructure [11]. Upon further heat treatment, this γ - Fe_2O_3 phase transforms to rhombohedral hematite, α - Fe_2O_3 , which is magnetically weak at room temperature [12]. Accordingly, the magnetic properties of ferrite nanostructures will strongly depend on the synthesis approach, structure and phase composition [13-15].

High saturation magnetization has also been observed in $ZnFe_2O_4$ thin films. For example, Tanaka et al. [16] deposited polycrystalline thin films of $ZnFe_2O_4$ (average crystallite size 10 nm) by radio frequency sputtering that exhibited ferrimagnetic behavior at room temperature with a saturation magnetization of 32 emu/g. This magnetic response was attributed to the random distribution of Fe^{3+} species in the ferrite lattice caused by the sputtering deposition process. Similarly, Sultan et al. reported a maximum magnetization of 42 emu/g for $ZnFe_2O_4$ thin films deposited by rf-sputtering in a pure oxygen environment [17].

Nanostructures of $ZnFe_2O_4$ have been successfully obtained by several methods, including nanowires with the use of templates [18], nanorods using precursors in solution phase [19] and nanofibers produced by electrospinning [20]. The electrospinning deposition technique allows for the formation of long fibers with nanometric diameters and a chemical composition that can be tailored to enhance a desired property. On the above basis, the present study proposes a method for synthesizing $ZnFe_2O_4/\gamma$ - Fe_2O_3 composite nanostructures with tailored morphological and magnetic properties. The enhanced magnetic properties will increase the response of the nanofibers to external magnetic fields which is desirable in many potential applications [21].

Nanofibers and nanoribbons of this composite were produced from an electrospun metal-Poly(vinyl) alcohol (PVA) precursor solution (Fe/Zn mole ratio of 3) and subsequent heat treatment to develop the ferrite structure while keeping the fiber shape. The effects of calcination temperature on the structure, composition, crystallite size and magnetic properties were investigated and discussed. The composite nanostructures were characterized by differential thermal analyses (TGA/DTA), Fourier transformed IR spectroscopy (FT-IR), x-ray photoemission spectroscopy (XPS), scanning electron microscopy (SEM), x-ray diffraction (XRD), vibrating sample magnetometry (VSM), and magnetic force microscopy (MFM).

2. Experimental

2.1 Fibers synthesis

Ferric (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, 98%, Aldrich Chemical Co.) and zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, 99.99%, Aldrich Chemical Co.) were used as precursors salts. Poly (vinyl) alcohol (PVA, $M_w = 85,000$ -146,000 g/mol) was purchased

from Aldrich Chemical. Distilled water was used as solvent. A precursor solution was prepared by dissolving 0.006 mol (2.5 g) iron nitrate nonahydrate and 0.002 mol (0.4 g) zinc acetate dihydrate in an aqueous solution containing PVA (10-15 % w/w) and subsequent stirring for 8 h at room temperature conditions. Electrospun fibers were collected using an applied voltage of 20 kV and a flow rate of 0.35 ml/h. The syringe tip-collector distance was 20 cm. Collected samples were dried at 95 °C for 12 h and calcined in air for 2 h in the temperature range between 300 °C and 800 °C.

2.2 Sample characterization

The thermal decomposition paths of the precursors were monitored by thermogravimetric-differential thermal analyses (Mettler Toledo, SDTA 851) for a scanning rate of 5 °C/min. Fourier transformed Infrared spectroscopy analysis, using KBr pellets, was carried out in the range of 400-4000 cm⁻¹. The morphological features of the fibers were investigated using a scanning electron microscope (Jeol 6360 SEM) while the fibers diameters were determined using image processing software. X-ray diffraction (SIEMENS D500) was performed using CuK_α radiation ($\lambda = 1.54056 \text{ \AA}$) at 40kV and 35mA. The size of coherently diffracting domains were calculated from Scherrer formula, $D = 0.94\lambda / (\beta \cos \theta)$, where λ is the x-ray wavelength, θ the diffracting angle of the (311) planes of ZnFe₂O₄, and β is the half maximum breadth. The magnetic properties were measured at room temperature by using a vibrating sample magnetometer (Lake Shore 736, model 3474-140). Magnetization curves were recorded up to applied field values of ± 20 kOe. The shape and distribution of magnetic domains were visualized by magnetic force microscopy (CP-II, Veeco).

3. Results and Discussion

The thermal decomposition behavior of zinc ferrite/PVA composite fibers (10 % w/w) is shown in Figure 1. The TGA plot shows that most of the mass loss occurs at temperatures below 550 °C. This mass loss would be caused by the thermal decomposition of PVA, CH₃COO from zinc acetate, and molecular and coordinated H₂O, from FeOOH. As observed in the DTA curve, there is an endothermic peak below 300 °C corresponding to the loss of absorbed water, decomposition of zinc acetate and ferrite nitrate and the pyrolysis of PVA by the dehydration of the polymer side chains [22]. The exothermic peak observed around 370 °C has been related to a second PVA degradation step which is dominated by chain-scission reactions along the main chain [23]. Further adsorption peaks are assigned to the continuous decomposition of the zinc acetate and ferric nitrate. For temperatures higher than 650 °C the TGA curve did not show any further mass loss, indicating the completion of the thermal decomposition reactions, i.e. oxides formation.

IR transmittance spectra of as deposited and heat treated fibers were recorded from 400 to 4000 cm⁻¹ and shown in Figure 2. The bands at 3460 cm⁻¹, 1640 cm⁻¹ and 1422 cm⁻¹ can be assigned to OH symmetric and antisymmetric stretching, OH bending, and CH₂ bending, respectively, which are characteristic of PVA [24]. The intensity of these bands decreased at higher temperatures which is consistent with the thermal decomposition of the polymer. The tetrahedral and octahedral Fe-O stretching band at 416 cm⁻¹ and 570 cm⁻¹ were also observed in all heat treated samples. These absorption bands became wider owing to the crystallization and growth of ZnFe₂O₄/γ-Fe₂O₃ spinels as the fibers are calcined at increasingly higher temperatures.

XPS measurements were performed for fibers calcined at 700 °C to investigate their surface chemical composition. As Figure 3a shows the Fe 2P core levels are split into Fe 2P_{1/2} and Fe 2P_{3/2} with a binding energy of 711.3 eV and 724.7 eV respectively. Two shake-up satellite lines at 718.8 eV and 733.4 eV, characteristic of Fe³⁺, were also observed. Deconvolution was applied to 2p_{3/2} and 2p_{1/2} peaks and satellites. The profile shapes and

peaks positions are indicative of the presence of Fe^{3+} cations as expected for ZnFe_2O_4 [25, 26]. In turn, the absence of Fe^{2+} peaks suggests that impurities such as Fe_3O_4 , FeCO_3 or FeO would not be included. For the case of Zn species, (Figure 3b), a single peak was observed at 1022 eV that corresponds to Zn $2\text{P}_{3/2}$. This is a typical value for the oxidation state of Zn^{2+} in the compound.

Electrospun precursor fibers were produced from solutions containing 10, 13 and 15 % w/w PVA concentration. SEM images of Figure 4 show the morphologies of the electrospun fibers, prepared at these PVA concentrations, before and after thermal treatment. The as-deposited fibers exhibited average diameter of 250 ± 60 nm, 330 ± 80 nm and 370 ± 110 nm, respectively. As seen in Figure 4F, some fibers become discontinuous owing to the shrinking in size and decomposition of the polymer after calcinations at 500 °C. Also, the corresponding average fiber diameter decreases to 120 ± 30 nm, 130 ± 30 nm and 120 ± 20 nm, respectively. It is known that for certain electrospinning conditions and precursor properties, e.g. low viscosity, fibers tend to retain some solvent and remain soft at arrival on the substrate. These soft fibers acquire a flat shape and resemble ribbons as evidenced by the SEM images of Figure 4C and 4F.

The x-ray diffractograms of calcined samples are presented in Figure 5. For samples calcined from 300 °C to 700 °C, the diffraction peaks can be assigned to a spinel crystal structure. Since the peaks corresponding to spinels zinc ferrite (Franklinite, JCPDS card # 33-0664) and cubic $\gamma\text{-Fe}_2\text{O}_3$ (Maghemite, JCPDS card # 39-1346) are too close to each other to be resolved, the presence of both phases can not be ruled out from these measurements. Indeed, recent studies have identified $\gamma\text{-Fe}_2\text{O}_3$ as one of the first phases that form at low temperature calcination of amorphous Zn-Fe gel powders [27]. In our case, both phases are expected to form as a result of the excess Fe (Fe/Zn mole ratio of 3) in the electrospinning solution. Broad peaks with low intensity are observed for samples produced at low temperature treatment that is indicative of short-range ordering in small crystal sizes. As the calcination temperature increases, peaks become sharper and intense evidencing the growth of the $\text{ZnFe}_2\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$ crystals. High intensity sharp peaks are obtained for samples heated at 700 °C (Figure 5c) owing to the full crystallization of the material and complete degradation of PVA which TG/DTA analysis indicates occurs at about 650 °C.

It is known that cubic spinel $\gamma\text{-Fe}_2\text{O}_3$ is a metastable phase and undergoes an irreversible transformation to $\alpha\text{-Fe}_2\text{O}_3$ which has a rhombohedral structure. This polymorphic transformation takes place at about 400 °C in bulk materials and between 350 °C and 600 °C in nanoparticles depending on their previous history [12]. It has also been found that at the nanometer scale Fe_2O_3 is amorphous up to a size of 5 nm, while the $\gamma\text{-Fe}_2\text{O}_3$ phase is stable up to 30 nm. For larger sizes the stable phase becomes $\alpha\text{-Fe}_2\text{O}_3$ [28]. Thus, growth of the $\gamma\text{-Fe}_2\text{O}_3$ crystal becomes indispensable for the formation of hematite, $\alpha\text{-Fe}_2\text{O}_3$. Since these $\gamma\text{-Fe}_2\text{O}_3$ particles coexist with zinc ferrite, an increase in the diphasic particle size should precede the formation of hematite. It is clearly observed in Figure 5 that $\alpha\text{-Fe}_2\text{O}_3$ is not detected by XRD in samples calcined from 300 °C to 700 °C. At 800 °C, Figure 5d, high intensity sharp peaks corresponding to hematite appear. From these observations and the likelihood of formation of $\gamma\text{-Fe}_2\text{O}_3$ at lower temperatures due to the excess iron, it is inferred that the $\gamma/\alpha\text{-Fe}_2\text{O}_3$ transition started to take place somewhere between 700 °C and 800 °C.

The relative intensities of the diffraction peaks of ZnFe_2O_4 and $\alpha\text{-Fe}_2\text{O}_3$ correspond to that of the standard powder diffraction suggesting that crystal growth developed without a preferred orientation. A calculation of the percent of $\alpha\text{-Fe}_2\text{O}_3$ in the fibers from x-ray peak intensities is not possible due to the expected overlapping of peaks corresponding to spinels ZnFe_2O_4 and $\gamma\text{-Fe}_2\text{O}_3$. A maximum mass percentage of $\alpha\text{-Fe}_2\text{O}_3$ can be estimated if we assume that stoichiometric spinel ZnFe_2O_4 has fully formed and all excess Fe ions, when

subtracting the component of ZnFe_2O_4 from the initial molar ratio, are segregated as $\alpha\text{-Fe}_2\text{O}_3$. If there is no loss of material then the maximum mass percentage of $\alpha\text{-Fe}_2\text{O}_3$ would be about 25%.

The room temperature MH loops of the produced fiber are shown in Figure 6a. The lack of saturation in the MH profiles, for samples calcined from 300 °C to 700 °C, could be indicative of superparamagnetic behavior. Large saturation magnetizations are obtained as compared to bulk ZnFe_2O_4 ($M_s = 1.3$ emu/g) even for the sample calcined at 300 °C ($M_s = 11.48$ emu/g). It is well known that if the ZnFe_2O_4 particle size decreases below 10 nm then its magnetization increases as result of the increase in degree of inverted spinel. In the case of the proposed $\text{ZnFe}_2\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$ nanocrystals, high magnetization can be attributed to both, the inversion in Fe cation occupancy in spinel ZnFe_2O_4 and the contribution from $\gamma\text{-Fe}_2\text{O}_3$ since this phase is expected to form after heat treatment. When nanostructures of ZnFe_2O_4 and $\gamma\text{-Fe}_2\text{O}_3$ coexist, there is an increase in the magnetization because both phases are ferromagnetic or superparamagnetic at room temperature [29]. Bulk $\gamma\text{-Fe}_2\text{O}_3$ has a saturation magnetization of 76 emu/g [30].

The saturation magnetization (M_s) of the fibers increases with calcination temperature, as shown in Figure 6b. For temperatures between 300 °C and 600 °C the particle sizes are below 30 nm, the predicted maximum size for stable $\gamma\text{-Fe}_2\text{O}_3$, and the increase in magnetization is attributed to the growth of the $\text{ZnFe}_2\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$ crystals. At 700 °C the particles have grown up to an average size of 41 nm, more than double the size at 600 °C which suggest the coalescence of individual grains through an intergrain diffusional process. This $\text{ZnFe}_2\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$ crystal size is large enough that the transformation of $\gamma\text{-Fe}_2\text{O}_3$ to $\alpha\text{-Fe}_2\text{O}_3$ might be possible even though it is not observed in XRD. Also, the transformation of maghemite to $\alpha\text{-Fe}_2\text{O}_3$ supposes a decrease in magnetization given that in bulk this phase is a weak canted ferromagnet. For example, Mitra et al. found that nanocrystalline $\alpha\text{-Fe}_2\text{O}_3$ with sizes ranging from 100 nm to 600 nm showed very weak ferromagnetic behavior at room temperature and a saturation magnetization of about 0.5 emu/g [31]. Similar decrease in magnetization due to the formation of $\alpha\text{-Fe}_2\text{O}_3$ phase has been observed by Suzuki et al. in ferrite thin films [32].

At 800 °C, the average particle size has increased to 100 nm and the amount of $\alpha\text{-Fe}_2\text{O}_3$ is considerable as indicated by the high intensity sharp peaks corresponding to this phase in XRD, however, the saturation magnetization is observed to increase drastically to about 45 emu/g. The highest magnetization in these fibers should have been achieved when part or all of the available Fe reacts to give the maximum amount of $\gamma\text{-Fe}_2\text{O}_3$. Further heat treatment that transforms part or all of the $\gamma\text{-Fe}_2\text{O}_3$ into the $\alpha\text{-Fe}_2\text{O}_3$ phase should, therefore, decrease the saturation magnetization. Indeed, after calcinating at 900 °C, the saturation magnetization drops to less than 1 emu/g (not shown). These results suggest that even larger saturation magnetization can be obtained for temperatures between 700 °C and 800 °C. In this temperature range most of the $\text{ZnFe}_2\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$ crystals should have grown to a size where $\gamma\text{-Fe}_2\text{O}_3$ is no longer stable and starts to transform to $\alpha\text{-Fe}_2\text{O}_3$. Since the fibers are composed of a distribution of particle sizes it can be expected that while some particles are still growing, and consequently increasing magnetization, others might be transforming to the $\alpha\text{-Fe}_2\text{O}_3$ phase which decreases magnetization. Thus, a detailed study of phase composition and magnetization in this temperature range is needed to obtain a maximum magnetization value. It should be noticed that even with the enhanced generation of $\alpha\text{-Fe}_2\text{O}_3$ at 800 °C, the saturation magnetization is high as compared to bulk values for a 75/25 w/w mixture of $\text{ZnFe}_2\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$, which would only yield 20 emu/g. A contribution to the total magnetization from the inversion in Fe cation occupancy in spinel ZnFe_2O_4 can account for such difference.

The viscosity of the solution used for electrospinning should also influence the evolution of particle size and morphology as predicted by the Einstein-Stokes theorem, $D = \kappa T / 6\pi\eta r$, where the diffusion coefficient (D) of a solute of radius (r) in a solvent is inversely proportional to the viscosity of the solution (η) at a given temperature (T) of the solvent [31]. For high viscosity, the rate of diffusion is slow and nucleation occurs to form larger aggregates. Increasing viscosity, by changing the amount of polymer in solution, produces an increase in saturation magnetization as shown in Figure 6c. If we assume that at this temperature the α -Fe₂O₃ phase has not formed, then magnetization is dominated by the size of the ZnFe₂O₄/γ-Fe₂O₃ particle. Further studies on the effects of the viscosity in precursors PVA solutions are underway.

The MFM/AFM images of a $200 \times 200 \text{ nm}^2$ area of a typical fiber calcined at 500 °C are presented in Figure 7. Figure 7A shows the magnetic domains while Figure 7B shows a topographic image of the same area. We observe magnetic domains with shapes and sizes similar to the topographical grains. The average diameter of the grains is 20 nm which is larger than the particle sizes as obtained by x-ray diffraction. Therefore, the grains are composed of several crystalline ZnFe₂O₄/γ-Fe₂O₃ particles which will contribute to the total magnetization of the domains. The grains also have a noticeable elongation along the fiber direction. A possible cause for this asymmetric grain growth is that the atomic diffusion coefficients are different along different directions in the fiber. During electrospinning the fiber stretches under the electric field and the polymer chains align along the stretching direction increasing crosslinking. Asymmetric atomic diffusion can result from differences in atomic movement along the polymer chains compared to movement perpendicular to the chain. This elongated grain morphology can enhance the magnetic properties of the fibers since theory predicts that a system containing magnetic dipoles that are arranged into a linear chain will exhibit increase coercivity [33]. For example, it has been observed that the dipole-dipole interactions between grains play a dominant role in the magnetization process in doped zinc ferrite nanofibers [34]. Under this interaction, the magnetic dipoles tend to line up along the same axis and differences in the coercive field have been observed between fibers and powders of the same material. This effect has only been observed at low temperatures because at high temperature the influence of thermal fluctuations on the rotation of the magnetic dipoles dominates the dipole-dipole interaction and the enhancement vanishes [35].

A structural model for the formation of the ZnFe₂O₄/γ-Fe₂O₃ diphase nanostructure was proposed by Bo et al. [11] where the ZnFe₂O₄ nanocrystals will start to form from the Zn and Fe ionic species randomly distributed in the suspension after heat treatment at temperatures as low as 200 °C. Excess Fe will simultaneously crystallize to form pockets of γ-Fe₂O₃ that surround the ZnFe₂O₄ nanocrystals forming the diphase nanostructures. Upon further heat treatment these ZnFe₂O₄/γ-Fe₂O₃ crystals will grow until the size of the γ pockets are no longer stable and transform into the kinetically stable α-Fe₂O₃ phase. A model for the γ/α-Fe₂O₃ phase transition in nanoparticles is given by Belin et al. [12] in analogy with the phase transition in the alumina γ/α-Al₂O₃ system. In this germination-growth model, the α-Fe₂O₃ germ nucleates on the surface of the γ-Fe₂O₃ particle and grows continuously until reaching the size of the original γ-Fe₂O₃ particle. It is expected that this phase transformation is conditioned by factors such as intergranular diffusion, surface area and critical size of the system. Our observations on the evolution of particle size and magnetization with heat treatment are in agreement with these models.

4. Conclusion

Nanofibers composed of ZnFe₂O₄/γ-Fe₂O₃ composite were successfully prepared by electrospinning from a sol-gel solution containing a molar ratio Fe/Zn of 3. The resulting

fibers, with diameters ranging from 90 to 150 nm, were ferrimagnetic with high saturation magnetization as compared to bulk. Calcinating in air from 300 °C to 700 °C results in an increase in particle size as well as magnetization most likely due to the formation and growth of the diphase. Further increase in calcination temperature produces a γ -Fe₂O₃ / α -Fe₂O₃ phase transformation with the corresponding decrease in magnetization. The highest saturation magnetization (45 emu/g) was obtained for fibers calcined at 800 °C. A higher magnetization is predicted for fibers calcined at a temperature between 700 °C and 800 °C when the maximum amount of γ -Fe₂O₃ is obtained. The fibers show magnetic domains of similar size and shape as the grains. The grains are elongated along the fiber direction which can lead to an enhancement of the magnetic properties of the fibers at low temperatures.

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Fig. 1.
TGA-DTA of zinc ferrite/PVA composite fibers.

Fig. 2. FT-IR spectra of ZnFe₂O₄/PVA fibers; (A) as deposited and calcined at (B) 300 °C, (C) 400 °C, and (D) 700 °C.

Fig. 3. XPS spectra of $\text{ZnFe}_2\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$ fibers calcined at 700 °C (a) Fe 2p spectra, (b) Zn 2p spectra.

Fig. 4. SEM images of ZnFe_2O_4 -PVA composite fibers at different solution concentrations, as deposited; (a) 10%, (b) 13%, (c) 15% w and after calcined at 500 °C in air for 2 h; (d) 10%, (e) 13%, and (f) 15% w/w.

Fig. 5. XRD of zinc ferrite-PVA fibers calcined at (a) 300 °C, (b) 500 °C, (c) 700 °C, (d) 800 °C. Also peak positions are indicated for Franklinite (ZnFe_2O_4 , card #22-1012), Maghemite ($\gamma\text{-Fe}_2\text{O}_3$, card # 39-1346) and Hematite ($\alpha\text{-Fe}_2\text{O}_3$, card # 33-0664).

Fig. 6.

(a) Magnetization curves for ZnFe₂O₄-PVA samples calcined at different temperatures. (b) Saturation magnetization and particle size as a function of calcination temperature (c) Magnetization curves of fibers calcined at 500°C with polymer concentrations of 10, 13 and 15 % w/w.

Fig. 7. MFM/AFM images of a typical nanofiber surface of $200 \times 200 \text{ nm}^2$. (A) MFM of fiber calcined at 500°C and (B) Topographic image of same area.