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Preparation of NiZn-ferrite nanofibers by electrospinning for DNA separation

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ABSTRACT

We present the synthesis, magnetic and UV spectrometry of NiZn-ferrite nanofiber. The single phase of spinel ferrite was obtained at 600 °C. The NiZn-ferrite fibers fabricated by an electrospinning process were formed as a polygonal grain growth with firing temperature in fiber matrix. It appeared that the saturation magnetization (M_S) of NiZn-ferrite nanofiber was dependent on Ni/Zn molar ratio which is similar to that of the inverse spinel ferrites. The NiZn-ferrite fibers showed good DNA adsorption efficiency that can be modified and utilized for DNA separation with magnetic nanofiber as a novel material in clinical applications.

Although electrospinning techniques have been generally used for the fabrication of polymer nanofibers, they are now also used for the preparation of ceramic nanofibers including composite materials [1–7]. The possibility of extending this process to ceramic materials has started in nanostructure research for new applications. One reason for this increasing interest in electrospinning stems from the fact that it is a relatively inexpensive technique to make nanofibers. With the expansion of electrospinning from polymers to composites and to ceramics, applications expand to the preparation of nanostructured materials. Their typical properties of having a high surface-to-volume ratio make them useful for potential applications such as nanoelectronic devices, sensors, solar cells, photonics, and multiferroic materials [6], molecular sieves [8], high-temperature insulation [9], catalysis [10], biomedical separation, and microwave absorbers.

Recently, a few popular processes to produce ceramic nanofiber and inorganic-polymer composite fiber as well as polymer fiber have been reported [11]. In general, ceramic nanofibers are prepared by the electrospinning of ceramic precursors in the presence of polymers followed by calcination. Careful preparation of the precursors is essential to electrospun ceramic systems. Several parameters such as solvent volatility, viscosity, surface tension, conductivity, and applied voltage need to be controlled. Electrospinning methods usually adopt the cone-jet principle to manufacture ultra-thin fibers. For this purpose, the electrospinning solution must have a high polymer concentration, high enough to cause entanglement with low viscosity to allow motion induced by the electric field. To prevent the solvent from collapsing into droplets before it evaporates, the surface tension of the solution must be low. Morphological change of electrospun fibers before calcinating can be strongly dependent upon the distance between nozzle needle and collector in various applied electrical field, flow rate, and ambient environment like temperature and humidity. The increase of needle-to-collector distance or decrease in the electrical field may result in reduced bead density, regardless of the polymer solution concentration [12].

The chemical synthesis of spinel ferrite-based particulates may represent an important step towards the engineering of typical magnetic carriers. Bio-separation is a crucial phenomenon for the success of several biological processes. Magnetic separation of cells or bio-molecules is more effectively done by adsorption/desorption from the modified particles of spinel iron oxides. The synthesis parameters on the morphological and magnetic properties of spinel iron oxide are strongly dependent on the reaction conditions. A novel technology for DNA separation using the new magnetic materials can be promising for enhancing the efficiency of the bio-separation process. Classical methods for DNA/RNA isolation are either column-based techniques or include precipitation and centrifugation steps having the disadvantage of being time consuming, difficult to automate or not useful for down-scaling to small sample volumes [13].

Effective cell separation is a primary and most important process for many clinical immunological applications using the magnetic oxide compounds. The selection of magnetic particles based on shape, size, and microstructures will significantly affect the final result of separation. Work presented here describes a new challenging process for efficient and direct DNA separation with functionalized NiZn-ferrite fibers.

Magnetic separation is an emerging technology that uses magnetism for the efficient separation of micrometer-sized

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magnetic carriers from chemical or biological suspensions. Magnetic separation has many advantages compared to other techniques used for bio-separation or purification and is generally done with iron oxide nanoparticles as magnetic carriers. Now, to make magnetic ceramic nanofibers might be another way of gaining a large surface area and appropriate nanostructure for the application of DNA separation.

The spinel ferrite MFe_2O_4 (M = Ni, Zn) nanofibers were synthesized by an electrospinnng process in this study. Raw materials used were iron (III) chloride ($FeCl_3$), nickel acetate tetrahydrate ($C_4H_6O_4Ni \cdot 4H_2O$) and zinc acetate dehydrate ($C_4H_6O_4Zn \cdot 4H_2O$). The aqueous metal salt/polymer solution was prepared with polyvinyl pyrrolidone (PVP) in DMF (*N*,*N*-dimethylformamide) and metal salts under stirring at room temperature. The applied electric field and spurting rate for spinning conditions were 10 kV, 2 ml/h, respectively. The obtained fibers were calcined at 600 °C for 3 h and annealed at 900 °C in air. By tuning the viscosity of batch solution before electrospinning, we were able to control the microstructure of NiZn-ferrite fiber in the range 70–200 nm at 770 cp. The multiple individual grain size in a ferrite fiber was about 10–15 nm. The properties of those NiZn-ferrite fibers as magnetic carrier were determined from X-ray diffraction, electron microscopy, thermal analysis, and magnetic measurement. The DNA adsorption efficiency yields compared to magnetite nanoparticle showed about 50% for UV-light wavelength, which can be modified and utilized for DNA separation with magnetic nanofiber in clinical applications.

Prior to electrospinning, the viscosities of batch solutions were measured with the viscometer. The crystalline phases were idendified by X-ray diffraction (XRD); and the morphology of the NiZn-ferrite nanofiber were observed by FE-SEM. Reaction processes during the calcinations were studied by thermal analysis (TG–DTA) in the temperature range of 20–900 °C to determine calcination temperatures. Magnetic measurements were carried out at room temperature using VSM.

Fig. 1 shows the results of microstructure of electrospun polymer and viscosity with polymer (PVP) content to optimize the experimental conditions of raw materials for fabrication of NiZn-ferrite fiber. The morphology and diameter of electrospun fibers are dependent on a number of processing parameters that include the type of polymer in solution, the operational conditions of electrospinning unit [14]. As shown in Fig. 1a–d, we can obtain the various electrospun PVP fibers prepared with PVP content and the

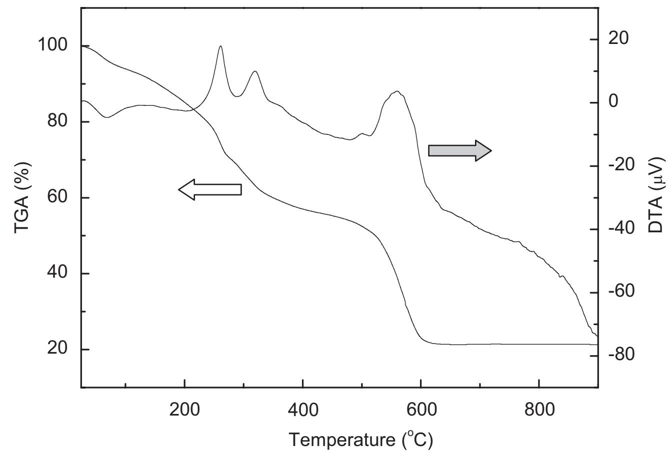

Fig. 2. Thermal analysis (TG–DTA) curves of metal salts/PVP solution.

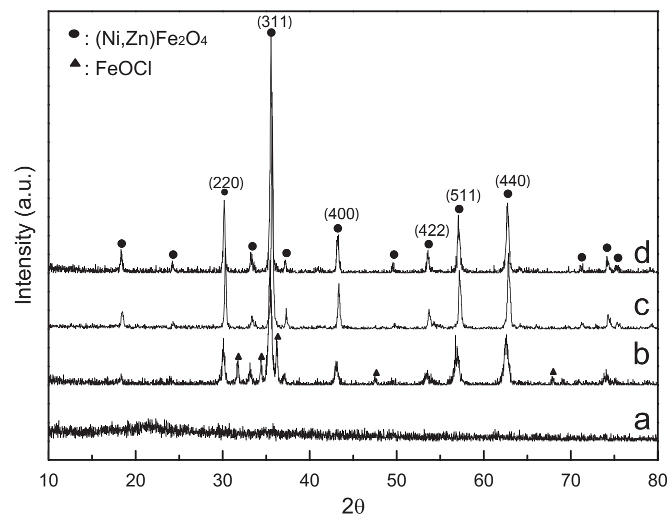

Fig. 3. XRD patterns of NiZn-ferrite ($Ni_{0.4}Zn_{0.6}Fe_2O_4$) nanofibers fabricated at various firing temperatures. (a) As electrospun, (b) calcined at 400 °C, (c) calcined at 600 °C, and (d) calcined at 600 °C and annealed at 900 °C, respectively.

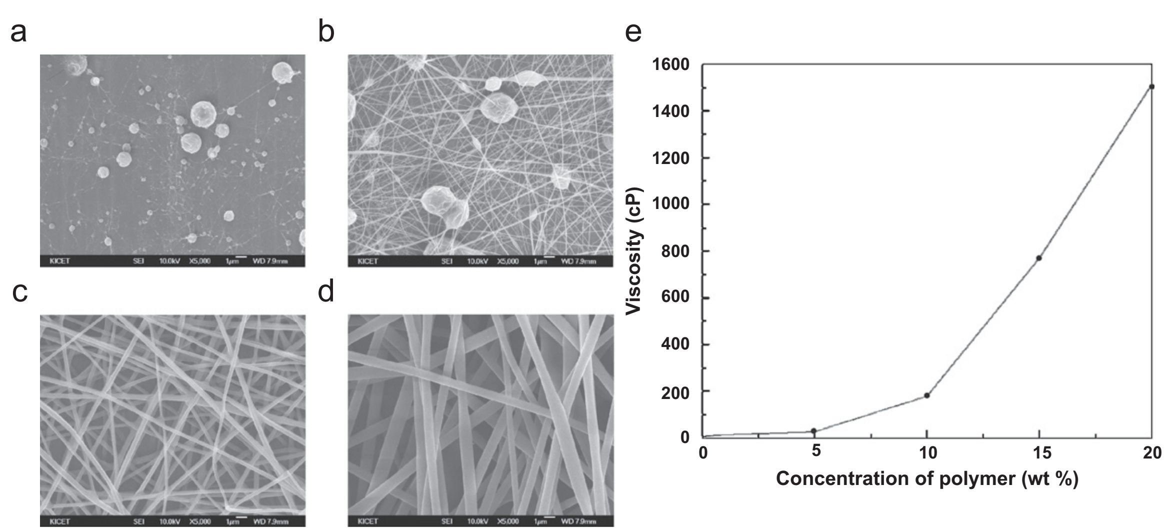

Fig. 1. Various electrospinning conditions for PVP fiber made from (a) 5 wt% (27 cP), (b) 10% (180 cP), (c) 15% (770 cP), (d) 20% (1,515 cP) of the polymer, and (e) the viscosity at 2.3 cm^{-1} shear rate increases with higher PVP concentration.

fiber diameter. The formation of beads in electrospun fibers in Fig. 1a and b can be affected by the solution properties as viscosity, surface tension, and the density of net charges carried by the liquid jet [15]. It can be clearly presented that the viscosity of solution was dramatically increased at a proper concentration of polymer. The batch solution of sol precursor was affected the viscosity which was resulted in change of ferrite fiber diameter. The viscosity for high performance of fiber by electrospinning was obtained in the range 300–700 cP at a shear rate of $2.3\,s^{-1}$. In order to obtain a normal electrospun fiber (Fig. 1c and d), the PVP content should be over 15% in batch solution.

Fig. 2 shows the characteristic thermal analysis (TGA and DTA) curves of the batch solution of metal salts with PVP. Between 200 and 300 °C, weight loss and an exothermic DTA peak in TGA were observed because of the decomposition of PVP which yields to an increasing viscosity. A further weight loss in TGA and exothermic DTA peaks at around 500–600 °C is consistent with the burning-out of metal salts (Fe-chloride, Ni-acetate, Zn-acetate). An exothermic DTA peak at about 550 °C indicates the onset in crystallization of spinel structure of NiZn-ferrite fiber. The XRD patterns of NiZn-ferrite fibers are presented in Fig. 3. The unreacted FeOCl phase appeared at 400 °C (Fig. 3b). NiZn-ferrite fibers, thus, can be obtained at over 600 °C with single phase of spinel structure with good crystallinity. The molar ratio (Ni:Zn) of NiZn ferrite was selected as 0.4:0.6 ($Ni_{0.4}Zn_{0.6}Fe_2O_4$) due to its high saturation magnetization (Fig. 4). NiZn-ferrite fibers obtained at various calcination temperatures show ferromagnetic behavior [16]. It also appeared that the saturation magnetization (M_S) of NiZn-ferrite nanofiber was dependent on the Ni/Zn molar ratio as is typically found in inverse spinel ferrites [17].

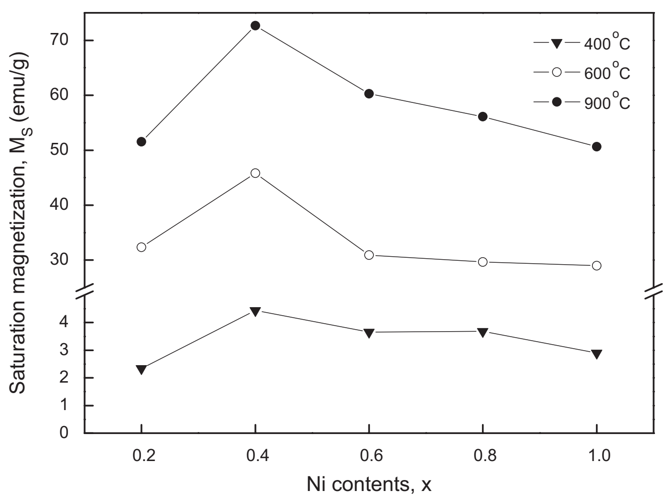

Fig. 4. Saturation magnetization (M_S) of $Ni_xZn_{1-x}Fe_2O_4$ nanofibers with Ni content at various firing temperature.

The NiZn-ferrite ($Ni_{0.4}Zn_{0.6}Fe_2O_4$) fibers fabricated by electrospinning process were also characterized by scanning electron microscope. Fig. 5 shows the microstructures of NiZn-ferrite ($Ni_{0.4}Zn_{0.6}Fe_2O_4$) nanofibers calcined at various calcination temperatures. SEM images of NiZn-ferrite nanofiber in Fig. 5a–c shows the multiple grains as a polygonal grain growth with firing temperature in matrix. The bubble-shaped individual grain in NiZn-ferrite fiber (Fig. 5a) was identified as an unreacted phase of FeOCl by EDS analysis (Fig. 5d). At 600 °C, no residual chloride of PVP was detected anymore (Fig. 5e) and pure NiZn-ferrite fiber obtained with a continuous structure.

Magnetic separation is an emerging technology that uses magnetism for the efficient separation of nano-sized para- and ferromagnetic particulate media from chemical or biological suspensions [18]. The basic technology of using magnetic separation techniques to purify biological compounds (nucleic acids, proteins, etc.) and cells is interesting due to advantages over other techniques used for the same processes. The efficiency of magnetic separation is well suited for large-scale purification using small particles of 0.05–0.1 μm in diameter. The increasing application of magnetic carriers in biochemical or molecular biology processing has many advantages compared to other nonmagnetic separation.

Table 1 shows the variation of UV-light absorbance with adsorption time measured by UV/VIS spectrophotometer for characterization of DNA separation using NiZn-ferrite ($Ni_{0.4}Zn_{0.6}Fe_2O_4$)

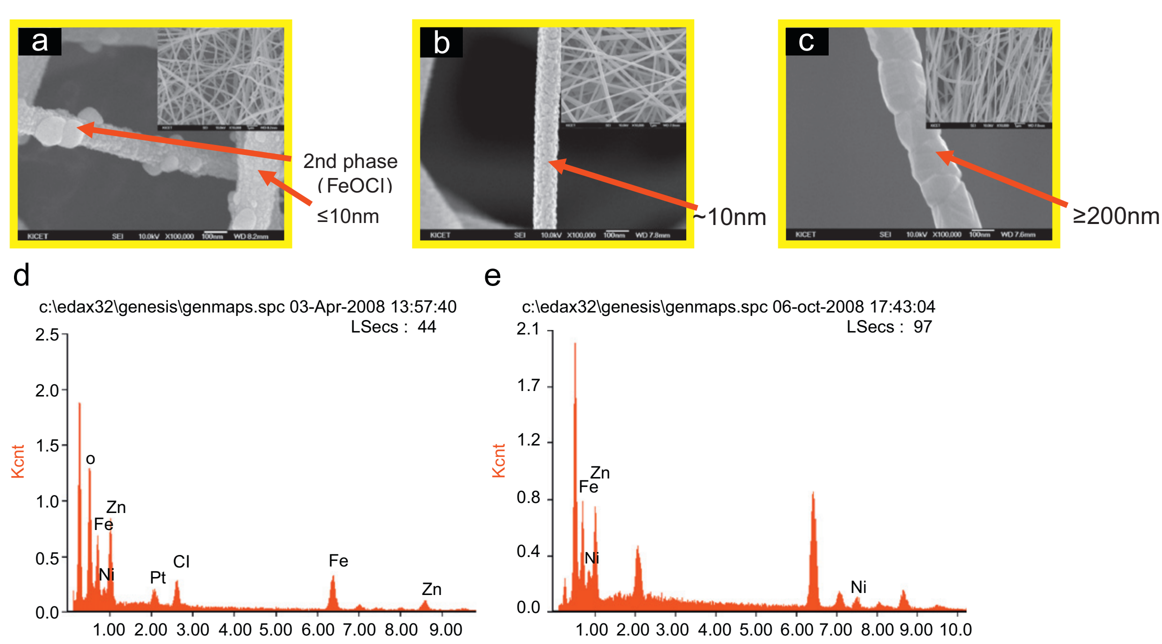

Fig. 5. SEM images of various NiZn-ferrite ($Ni_{0.4}Zn_{0.6}Fe_2O_4$) nanofibers (a) calcined at 400 °C, (b) calcined at 600 °C, and (c) calcined at 600 °C and annealed at 900 °C. The EDS analysis peaks of some of the nanofibers are shown in (d) calcined at 400 °C and (e) calcined at 600 °C.

Table 1
Characterization of DNA separation using NiZn ferrite ($Ni_{0.4}Zn_{0.6}Fe_2O_4$) nanofibers.

Adsorption time (h)	UV-light absorbance	
	DNA only	NiZn ferrite fiber added
2	0.53	**0.31**
4	0.53	**0.28**
6	0.59	**0.32**

nanofiber. NiZn-ferrite fibers thus clearly adsorb DNA, and NiZn-ferrite nanofibers can be used like other magnetic carriers for DNA separation. Different incubation times do not produce significantly different DNA adsorptions (Table 1). The magnetic fiber can also be suitable for the purification with relatively high DNA adsorption efficiency, which can be modified and utilized for DNA separation with magnetic nanofiber as a novel material in clinical applications. The bio-compatibility of NiZn-ferrite nanofiber with a large surface area and the application to the DNA separation give promising experimental data for the further development of DNA purification procedures. The fabrication of NiZn-ferrite nanofiber is presented as a preliminary work for new techniques of the magnetic separation, and further modification will be undertaken in a next step to make this method a successful DNA separation with functionalized magnetic nanofibers that can be utilized in clinical diagnoses and biomolecular recognition.

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