Ferritin-Based Hybrid Nanofibers with Magnetic Properties

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ABSTRACT

We report for the first time that polymeric nanofibers containing ferritin, which are known as multifunctional biomolecular nanoparticles, have superparamagnetic properties at room temperature because of the ferritin incorporated in their polymeric matrix. We have confirmed that the ferritin nanoparticles were well dispersed in the polymeric nanofibers without any marked aggregation. The blocking temperature of a nanofibrous mat containing ferritin was about 12 K, and the zero-field-cooled and 200-Oe field-cooled curves bifurcated at a temperature of about 20 K. The magnetization curve as a function of applied magnetic field demonstrates that the hybrid nanofibrous mats had superparamagnetic properties at room temperature.

Keywords: ferritin, nanofiber, electrospinning, magnetic property.

1 INTRODUCTION

There has been intense interest in polymeric nanocomposites using nanoparticles, nanowires, and nanotubes, because nanocomposites possess improved physical properties compared with the unmodified polymer [1–3]. In particular, a mixture of polymers and nanoparticles can form flexible nanocomposites that exhibit advantageous electrical, magnetic, or mechanical properties [1,4,5]. In this work, we incorporated a ferritin biomolecule into a poly(vinyl alcohol) (PVA) matrix employing electrospinning to fabricate biocompatible hybrid nanofibers with magnetic properties.

Ferritin, an iron storage protein, has intrinsic advantages, such as its structural stability and uniform nanosize, as well as its electrochemical, electrical, and magnetic properties [6–11]. In addition, ferritin has a protein shell consisting of peptide chains containing functional groups that can form direct chemical interactions with a polymeric matrix [6,12]. Recently, Shin and coworkers reported that ferritin well dispersed into a PVA matrix plays an important role as a reinforcing nanomaterial for enhancing the elastic modulus of PVA nanofibers [1].

Electrospinning is a good technique for fabricating one-dimensional composite nanostructures with a uniform shape from a polymeric blend solution in addition to pure polymeric nanofibers because of its simplicity and versatility [13–15]. Electrospinning can be used to control the diameter of a nanofiber from tens of nanometers to below ten nanometers by adjusting the process parameters, such as the applied voltage, the flow rate of the solution, and the concentration of the solution [16].

2 EXPERIMENTAL

Ferritin (Type I from horse spleen) samples dissolved to a concentration of 76 mg/mL in a 0.15 M NaCl solution were purchased from Sigma Chemicals (USA). The poly(vinyl alcohol) (PVA, $M_w \approx$ 124,000–186,000) and ethyl alcohol (denatured, HPLC grade) used were obtained from Aldrich Chemicals (USA).

To prepare a 7.5wt% PVA/ferritin solution in a water and ethyl alcohol mixture, PVA was dissolved in water, and then stirred for 1.5 h at 90 °C, before being allowed to cool to 30 °C. Then, small amount of ethyl alcohol/water was added to the solution, which was then stirred for 3 h at room temperature.

To fabricate PVA/ferritin nanofibers employing electrospinning, the PVA/ferritin solution was loaded into a plastic syringe equipped with a stainless steel needle. The polymer solutions were fed at a flow rate of 8 μL/min using a syringe pump (KD Scientific, USA) located in a horizontal mount. A voltage of 10 kV was applied between the syringe needle and the grounded electrodes using a high-voltage power supply (Nano Technics, Korea). The syringe needle acted as an anode, and an aluminum electrode acted as a cathode. The distance between the syringe needle and the aluminum electrode was 20 cm.

The morphology of the nanofibers was characterized using scanning electron microscopy (SEM, Hitachi (Japan), Model S4700, accelerating voltage = 15 kV) and transmission electron microscopy (TEM; Philips (Netherlands), Model CN30, accelerating voltage = 300 kV). The magnetic properties of the PVA/ferritin nanofibrous mats were measured using a superconducting quantum interference device (SQUID).

3 RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show an SEM image of the PVA/ferritin nanofibers and a TEM image of a single PVA/ferritin nanofiber, respectively. From Figure 1(a), we confirmed that continuous and uniform PVA/ferritin nanofibers were fabricated from the PVA/ferritin solution employing electrospinning. The average diameter of PVA/ferritin nanofibers randomly deposited on an aluminum electrode was about 250 nm. From Figure 1(b), we also confirmed that the ferritin nanoparticles were well dispersed in the PVA matrix without any marked aggregation during electrospinning. Because the average core size of ferritin measured was 6 nm with a standard deviation of < 1 nm, the ferritin consisted of a uniform single magnetic domain and could be a state of uniform magnetization at any given field [17]. Therefore, the magnetization behavior of ferritin nanoparticles above a blocking temperature would be identical to that of superparamagnetism, except that extremely large susceptibilities are involved [18].

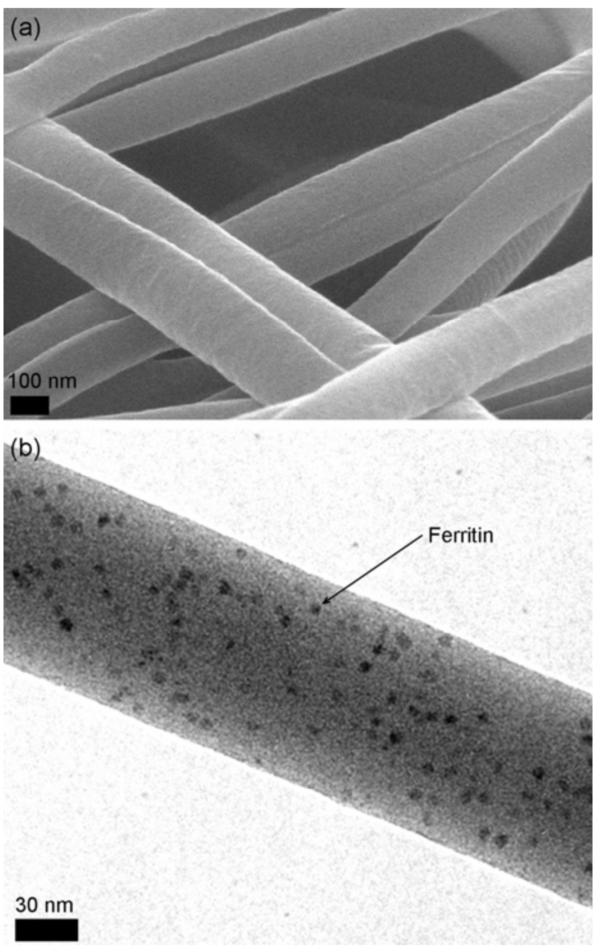

Figure 1. (a) An SEM image showing PVA/ferritin nanofibers, and (b) a TEM image showing ferritin nanoparticles incorporated into the PVA matrix.

Figure 2(a) shows the temperature dependence of the magnetization of a PVA/ferritin nanofibrous mat in an applied field of 0 and 200 Oe. The inset shows the blocking temperature occurring around 12 K and the bifurcation temperature occurring around 20 K. Figure 2(b) shows the field dependence of the magnetization of a PVA/ferritin nanofibrous mat at various temperatures. Both the induced magnetization curves as a function of temperature and the magnetization curves as a function of applied magnetic field at various temperatures of PVA/ferritin nanofibers are similar to those of ferritin nanoparticles reported in the literature [19,20]. This means that the magnetic properties of ferritin incorporated into a PVA matrix do not change during either the mixing or electrospinning processes. In Figure 2(b), the magnetization curve as a function of applied magnetic field demonstrates that the PVA/ferritin nanofibrous mats had superparamagnetic properties at room temperature. That is, although a distinct magnetic hysteresis was observed at 2 K, as shown in the inset of Figure 2(b), the magnetic hysteresis disappeared as the temperature increased.

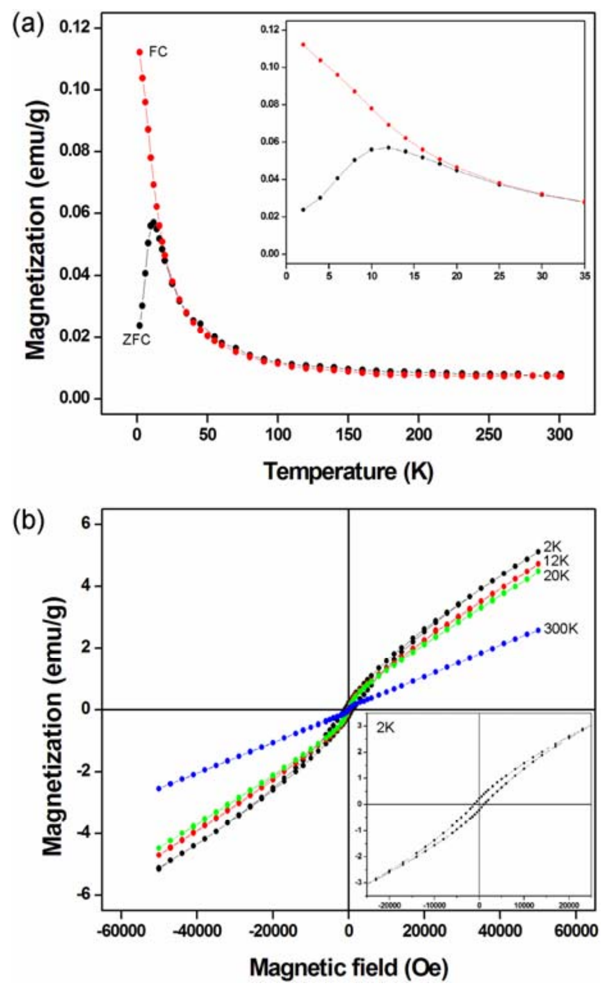

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Figure 2. (a) Temperature dependence of the magnetization of a PVA/ferritin nanofibrous mat in an applied field of 0 and 200 Oe. The inset shows the blocking temperature occurring around 12 K and the bifurcation temperature occurring around 20 K. (b) Field dependence of the magnetization of a PVA/ferritin nanofibrous mat at the indicated temperature. The inset shows the distinct magnetic hysteresis of the sample at 2 K.

4 CONCULSIONS

We have fabricated hybrid nanofibers containing homogeneously dispersed ferritin nanoparticles. It was confirmed that the PVA/ferritin nanofibers have superparamagnetic properties at room temperature. Moreover, the hybrid nanofibrous mat became a water-swellable nanofibrous hydrogel after a methanol treatment [21]. Therefore, if they are implanted into the body, hybrid nanofibrous hydrogels can be detected noninvasively using a magnetic resonance imaging (MRI) system because of the superparamagnetic property of ferritin.

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