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Production of Smooth and Pure Nickel Metal Nanofibers by the Electrospinning Technique: Nanofibers Possess Splendid Magnetic Properties

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In the present study, smooth, unceasing, hydrogen-free, and pure nickel metal nanofibers have been synthesized using the electrospinning technique. A sol–gel consisting of nickel acetate tetrahydrate and poly(vinyl alcohol) has been electrospun, and the obtained nanofiber mats were vacuously dried and then calcined in argon atmosphere at 700 °C. The invoked physiochemical characterization instruments assured formation of pure nickel nanofibers with an average diameter of 120 nm after the calcination process. The electrospun nickel nanofibers have revealed unique magnetic properties, with much enhanced coercivities relative to bulk materials. The outstanding features of this approach to get one-dimensional magnetic nanostructure are its simplicity, effectiveness, safety, and ease of assembly.

1. Introduction

Due to the privileged magnetic and electrical properties of the transition metal nanoparticles such as Fe, Co, and Ni, they have been given much attention to be utilized in various applications such as electronic, optical, and mechanic devices, magnetic recording media, catalysis, superconductors, ferrofluids, magnetic refrigeration systems, and contrast enhancement in magnetic resonance imaging carriers for drug and targeting.1–7 Much literature has been reported confirming that the magnetic properties of those materials are highly dependent on the particle shape.8–12 1D magnetic nanomaterials are expected to have interesting properties, as the geometrical dimensions of the material become comparable to key magnetic length scales, such as the exchange length or the domain wall width.13,14 Some authors have introduced synthetic methodologies to prepare 1D magnetic nanostructures including template-assisted electro-deposition,15–20 metallization of DNA,21,22 nanolithography,23 organometallic precursors decomposed in solution,24 catalyzed high-temperature growth via the vapor–liquid–solid (VLS) mechanism,25,26 solvothermal synthesis,27 and direct electrochemical precipitation.28 Surface area to volume ratio is the essential parameter in the magnetic properties. Consequently, magnetic nanowires have been extensively exploited for their utilization in high-density magnetic recording, spintronic devices, magnetic sensors, and magnetic composites.29–31 Some attempts have been done in this field; for instance nanoscale magnetic logic junctions have recently been fabricated with ferromagnetic nanowires as building blocks,32 and magneto-optical switches have been prepared using suspensions of ferromagnetic nanowires.33

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Among the 1D nanoshapes, nanofibers have considerable importance due to the high surface area to volume ratio characteristic. Therefore, nanofibers are the best candidate for nanodevices and nanomembranes. Some techniques have been utilized to produce the nanofibers; for instance: electrochemical deposition,34,35 template-assisted,36–38 self-assembly,39–41 interfacial polymerization,42,43 seeding approach,44 and electrospinning.45 Electrospinning is the most popular technique utilized in production of functional nanofibers due to its simplicity, low cost, and high yield.46 Metal base nanofibers are produced by electrospinning of a sol–gel composed of a metal precursor and accordant polymer. The electrospinning process has been exploited to synthesize Co, Cu, Fe, and Ni nanofibers by calcination of the electrospun metal precursor/polymer nanofiber mats in hydrogen atmosphere.47–49 However, this strategy does have some imperfections in the case of nickel: the produced nickel nanofibers will be polluted by hydrogen50 which affects the magnetic properties of the nanofibers and consequently the operating efficiency in the nanodevices. Moreover, for the hydrogen atmosphere process, besides the safety requirements in a case of high production yield, the surface morphology of the obtained nanofibers was not satisfactory.

In the present study, we have synthesized hydrogen-free and unblemished nickel nanofibers by using the electrospinning technique. A sol–gel consisting of nickel acetate tetrahydrate and poly(vinyl alcohol) was electrospun. After vacuum drying of the obtained nanofiber mats, calcination in argon atmosphere was achieved. The final nanofibers obtained were analyzed for structural and morphological properties. A possible growth mechanism is discussed based on the observations. The results assured that the final product is pure nickel metal nanofibers. The produced nanofibers have revealed admirable magnetic properties.

2. Experimental Details

2.1. Materials. Nickel(II) acetate tetrahydrate (NiAc, 98%) and poly(vinyl alcohol) (PVA, molecular weight (MW) = 65000 g/mol) were obtained from Showa Co., Japan, and Aldrich Co.,
USA, respectively. These materials were utilized without any further treatments. Distilled water was used as solvent.

2.2. Experimental Work. Sol−gel was prepared by mixing 20 wt % of aqueous NiAc solution and 10 wt % of PVA aqueous solution in a weight ratio of 1:3. The mixture was vigorously stirred at 50 °C for 5 h. The obtained solution was placed in a plastic capillary. A copper pin connected to a high-voltage generator was inserted in the solution, and the solution was kept in the capillary by adjusting the inclination angle. A ground iron drum covered by a polyethylene sheet was serving as a counter-electrode. A voltage of 20 kV was applied to this solution. The formed nanofiber mats were initially dried for 24 h at 80 °C under vacuum and then calcined at 700 °C for 5 h in an argon atmosphere with a heating rate of 2.3 °C/min. Actually, to keep the evolved gas in the reaction media, the argon gas flow rate was very small.

2.3. Characterization. Surface morphology was studied by a scanning electron microscope (SEM, JEOL JSM-5900, Japan) and a field-emission scanning electron microscope (FESEM, Hitachi S-7400, Japan) equipped with an energy dispersive X-ray (EDX). Information about the phase and crystallinity was obtained by using a Rigaku X-ray diffractometer (XRD, Rigaku, Japan) with Cu Kα (λ = 1.540 Å) radiation over the Bragg angle ranging from 30 to 90°. The high-resolution image and selected area electron diffraction patterns were obtained with a transmission electron microscope (TEM, JEOL JEM-2010, Japan) operated at 200 kV. Thermal properties have been studied by the thermal gravimetric analyzer (TGA, Pyris1, PerkinElmer Inc., USA). Magnetic properties of the nanofibers were evaluated using commercial superconducting quantum interface device (SQUID) magnetometry. The nanofibers were weighed and then filled into capsules in an inert gas environment. After this, the capsules were sealed with paraffin wax to prevent the nanofibers from air oxidation.

3. Results and Discussion

Figures 1A and 1B demonstrate low and high magnification SEM images for NiAc/PVA nanofiber mats. (C) and (D) are the SEM images for the nanofibers obtained after calcination. FE SEM micrographs for the calcined nanofibers are demonstrated in (E) and (F) images.

Figure 1. SEM and FE SEM images for the NiAc/PVA nanofibers and the obtained nanofibers after calcination in Ar atmosphere: (A) and (B) represent low and high magnification SEM images for NiAc/PVA nanofiber mats. (C) and (D) are the SEM images for the nanofibers obtained after calcination. FE SEM micrographs for the calcined nanofibers are demonstrated in (E) and (F) images.

Figure 2. XRD results for the synthesized nanofibers. (111), (200), (220), and (311) represent pure nickel metal main crystal planes.
respectively. As shown in these figures, the obtained nanofibers are relatively smooth. Calcination of the nanofiber mats enhanced the nanofiber morphology as shown in Figures 1C and 1D which reveal low and high magnifications of SEM images of the calcined nanofibers. The produced nanofibers are smooth, circular, and uncensored ones. FE SEM micrographs (Figure 1E and 1F) indicate that the surface of the obtained nanofibers is not crimped as the nanofibers produced in hydrogen atmosphere.\textsuperscript{47-49}

The typical XRD pattern of the calcined powder is presented in Figure 2, where the standard peaks of the nickel are observed. The strong diffraction peaks at 2\theta values of 44.45, 51.85, 76.45, and 92.95° corresponding to (111), (200), (220), and (311) crystal planes indicate the formation of cubic crystalline nickel (JCDPS, card no 04-0850). No other peaks can be observed in the spectra which indicate that the sample is free from nickel oxide or any other crystalline materials. Moreover, according to the thermal properties of PVA, we can guarantee that the sample is free from this polymer.\textsuperscript{51}

To understand the atomic composition of calcined powder, EDX analysis was carried out which confirmed that the obtained nickel metal had a zero oxidation state, and the nanofibers do not have any oxide form. The corresponding spectrum is presented as Figure 3. This clearly supports the XRD results (Figure 2) and simultaneously affirms formation of pure nickel metal nanofibers.

Figure 4 shows the high-resolution TEM (HRTEM) image of the calcined nanofibers, where the distance between the two adjacent planes almost matches that of the standard value of pure nickel metal. The inset shows the SAED pattern where the atoms are seen arranged uniformly. There are no dislocations or imperfections observed in the lattice planes which indicate good crystallinity of the synthesized nanofibers.

Thermal decomposition of metal acetate compounds in an inert atmosphere has been studied by some authors.\textsuperscript{52-54} Juan et al.\textsuperscript{53} have reported in detail thermal decomposition of NiAc in an inert gas atmosphere. In that work, the authors have proved that the NiAc molecule decomposes in an abnormal strategy as a function of temperatures producing many gases including some reducing ones (see ref 53 for more details). Therefore, pure nickel metal can be obtained from the thermal decomposition of NiAc in an inert gas atmosphere. Pure nickel was synthesized in many steps. Initially, nickel carbonate was synthesized then decomposed into the oxide form which was reduced by the obtained reducing gases to produce pure nickel metal. The corresponding changes in the phase were supported by thermogravimetric studies. Phase changes had been construed by...
peaks in the first derivative of the TGA curve. Formation of pure nickel was explained by the following equations

\[
\text{Ni(CH}_3\text{COO)}_2 \cdot 4\text{H}_2\text{O} \rightarrow 0.86\text{Ni(CH}_3\text{COO)}_2 \cdot 0.14\text{Ni(OH)}_2 + 0.28\text{CH}_3\text{COOH} + 3.72\text{H}_2\text{O} \quad (1)
\]

\[
0.86\text{Ni(CH}_3\text{COO)}_2 \cdot 0.14\text{Ni(OH)}_2 \rightarrow \text{NiCO}_3 + \text{NiO} + \text{CH}_3\text{COCH}_3 + 2\text{H}_2\text{O} \quad (2)
\]

\[
\text{NiCO}_3 \rightarrow \text{NiO} + \text{CO}_2 \quad (3)
\]

\[
\text{NiO} + \text{CO} \rightarrow \text{Ni} + \text{CO}_2 \quad (4)
\]

Carbon monoxide in eq 4 comes from decomposition of the resultant acetic acid in the first equation. Figure 5A shows the thermogravimetric curve of the NiAc/PVA nanofiber mats in argon atmosphere along with the first derivative curve, which depicts various peaks at different temperatures. The peak at \(\sim 50^\circ\text{C}\) indicates evaporation of moisture from the sample. A strong and sharp peak at \(\sim 240^\circ\text{C}\) demonstrates the decomposition of PVA.\(^{51}\) There are two obvious peaks at \(\sim 370^\circ\text{C}\) and \(\sim 585^\circ\text{C}\). According to the previous intensive study, the first peak demonstrates decomposition of NiAc (eqs 1 and 2). Taking into consideration that the utilized physiochemical characterizations have affirmed formation of pure nickel, the second peak can be explained as formation of nickel oxide and reduction of this oxide to nickel (eqs 3 and 4). The broadness of the last two peaks draws attention to the fact that more than one phase formation occurs within these wide temperature ranges. Moreover, there is no change in the weight after these peaks.

It is well-known that the polymeric material thermal degradation depends upon the calcination atmosphere. Figure 5B demonstrates the TGA result of NiAc/PVA nanofiber mats in oxygen atmosphere. As shown in this figure, the weight of the sample became fixed at lower temperature (\(\sim 350^\circ\text{C}\)) than in the case of argon atmosphere (\(\sim 650^\circ\text{C}\); Figure 5A). Also, the degradation rate is higher than in the case of argon. Moreover, there is a distinct difference between the amounts of the inorganic residual materials in both cases: the residuals represent 15 and 25.4% in the cases of argon and oxygen atmospheres, respectively. Taking into consideration that the residuals in the case of calcination in the oxygen atmosphere is nickel oxide (NiO),\(^{55}\) one can say that this observation supports the XRD data and simultaneously affirms formation of pure nickel due to calcination in the argon atmosphere. To ensure that the obtained nickel is free from the polymer, we have achieved TGA in the oxygen atmosphere for a sample obtained after calcination in the argon atmosphere. The results are demonstrated in Figure 5B. As shown in this curve, there is no weight change observed at the degradation temperature range of the polymer. A slight decrease in the weight is seen starting at \(\sim 350^\circ\text{C}\). According to the obtained TGA results of NiAc/PVA in the same curve and the thermal properties of PVA,\(^{51}\) we can say PVA cannot exist at \(350^\circ\text{C}\). Moreover, according to the detailed pervious study about the calcination behavior of NiAc in the argon atmosphere,\(^{51}\) we cannot expect the presence of NiAc in the sample. Therefore, this trivial decrease in the weight might be due to decomposition of a trace amount of impurities in the sample or instrumental error. This decrease in weight can be neglected since it represents almost 2% of the total sample weight.

The magnetic properties of the produced nickel nanofibers have been studied. Figure 6 shows the hysteresis loops at 5 and 300 K. It can be observed the nickel nanofibers reveal typical ferromagnetic behavior. The ferromagnetism of Ni nanofibers is clearly shown by coercivity (\(H_c\)), saturation magnetizations (\(M_s\)), remanent magnetization (\(M_r\)), and saturation field (\(H_s\)) listed in Table 1. A higher coercivity is a key factor for information storage although real devices also require intensive studies on magnetization interaction, local magnetization reversal characterization, and other important issues. The first column in Table 1 shows the coercivity of the Ni nanofibers obtained due to calcination in Ar atmosphere, calcination in H\(_2\) atmosphere, and the bulk material. As shown in this table, the synthesized magnetic metallic nanofibers exhibit great enhanced coercivities at room temperature, which is about 100 times the

**TABLE 1: Magnetic Parameters of the Synthesized Nickel Nanofibers Compared with the Bulk Material and Nickel Nanofibers Prepared in Hydrogen Atmosphere**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>at 5 K</th>
<th>(H_s^{57})</th>
<th>at 30 K</th>
<th>(H_s^{57})</th>
<th>Bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coercivity, (H_c) (Oe)</td>
<td>391</td>
<td>228</td>
<td>70</td>
<td>124</td>
<td>0.7(^{56})</td>
</tr>
<tr>
<td>Saturation Magnetization, (M_s) (emu/g)</td>
<td>29.22</td>
<td>27.76</td>
<td>26.75</td>
<td>24.8</td>
<td>58.6(^{58})</td>
</tr>
<tr>
<td>Remanent Magnetization, (M_r) (emu/g)</td>
<td>12</td>
<td>12.88</td>
<td>3.6</td>
<td>12.2</td>
<td>—</td>
</tr>
<tr>
<td>Saturation Field, (H_s) (emu/g)</td>
<td>8000</td>
<td>5000</td>
<td>6000</td>
<td>1500</td>
<td>—</td>
</tr>
</tbody>
</table>
magnitude of bulk material. The coercivity at room temperature is 70 Oe, while it is 0.7 Oe for the bulk material. Moreover, at 5 K the synthesized nanofibers do have higher coercivity compared with the nanofibers prepared in calcination in hydrogen atmosphere. In general, the larger coercivity for Ni nanofibers produced in Ar or H$_2$ atmosphere at low temperature for the nanofibers may be explained by considering the reduced influence of thermal fluctuation on the rotation of magnetic dipoles. As a result, an increased amount of energy (or higher magnetic field strength) was required to change the magnetization direction of these aligned dipoles, and a larger coercivity of the nanofibers can be observed.

The room-temperature saturation magnetization $M_s$ of Ni nanofibers obtained in Ar atmosphere is 26.76 emu/g which is about half of the value of corresponding bulk metals (58.57 emu/g$^{58}$) and a little higher than the value of corresponding Ni nanofibers produced by calcination in H$_2$ atmosphere (24.75 emu/g$^{57}$). Nanostructures usually have saturation magnetization lower than that for bulk materials.$^{59-61}$ A logic explanation of that can be drawn as: the high surface area enhances oxidation of the surface of magnetic nanofibers, which may create a magnetically dead layer. Moreover, the large specific area and the imperfection of the crystalline structure at the surface may also lead to a significant decrease in the nanofiber saturation magnetization.$^{57}$ At 5 K, there was little increase in the saturation magnetization for both of the prepared Ni nanofibers and the ones obtained in the hydrogen atmosphere as shown in Table 1; however, the prepared nanofibers possess slightly higher $M_s$. The higher $M_s$ may be attributed to a strong increase in the local surface anisotropy at 5 K with surface spins frozen along the easy axis. When the applied fields are high enough, the surface anisotropy is overcome, and the surface spins tend to align along the field direction, which results in a higher $M_s$ value. The remaining magnetic parameters are demonstrated in Table 1; columns 3 and 4. As shown in this table, calcination in the Ar atmosphere intensively enhanced the saturation magnetization at room temperature and 5 K. While there was no observed effect on remanent magnetization ($M_r$) especially at 5 K, however, in a case of room temperature, the prepared nanofibers do have low $M_r$. Nevertheless, such novel magnetic nanofibers are of potential interest for high-density information storage application. Additionally, because the magnetic coercivities of the nanofibers are outstanding and the proposed method is safe and highly efficient, bulk amounts of the synthesized Ni nanofibers could be used for manufacturing flexible magnets after blending different loads with polymers.

**Conclusion**

Calcination of electrospun nanofiber mats consisting of nickel acetate tetrahydrate and poly(vinyl alcohol) in an argon atmosphere completely eliminates the polymer and decomposes the metal salt into pure nickel. The final nickel metal possesses distinct nanofibrous morphology. The proposed strategy strongly enhanced the magnetic properties of the nickel metal; hence, the obtained nanofibers have novel magnetic properties. Producing hydrogen-free nanofibers, safety, and high-yield characteristics give the proposed strategy the opportunity to be exploited to produce other transition metal nanofibers.

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**Supporting Information Available:** The standard experimental setup and a photograph for the utilized electrospinning experiment. This material is available free of charge via the Internet at http://pubs.acs.org.

**References and Notes**


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