Electrodeposited magnetic nanowires: arrays, field-induced assembly, and surface functionalization

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Abstract

Electrodeposition into nanoporous templates provides a means of fabricating large quantities of magnetic nanowires with diameters in the range 5 nm–10 \( \mu \)m, and lengths up to 60 \( \mu \)m. Several recent developments in nanoporous templates and Ni nanowires are described. Templates formed by \( \alpha \)-particle irradiation of single-crystal mica are shown to contain diamond-shaped nanopores with uniform size and orientation. Ni prisms deposited in these templates show anisotropic magnetic properties along all three axes of the prisms. The manipulation of isolated Ni nanowires in a variety of suspensions, and a quantitative analysis of the dynamics of the self-assembly of these nanowires under the control of external magnetic fields is described. Surface functionalization with porphyrin molecules yields fluorescent Ni nanowires that have potential for use in biotechnology and other applications.

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1. Introduction

Nanowires are quasi-one-dimensional entities with large aspect ratios and lateral dimensions in the 1–100 nm range. One approach to fabricating such structures that is attracting increasing attention is electrodeposition into nanoporous templates [1]. This approach offers several advantages,
surface roughness, directly reflect the properties of the pores, templates with well-controlled pore morphology are crucial for nanowire fabrication by this technique.

Of particular interest are magnetic nanowires made of ferromagnetic elements such as Co or Ni, and alloys such as Permalloy. Due to the large aspect ratio of the nanowires, their magnetic properties are dominated by shape anisotropy. After a nanowire has been magnetized, its magnetization remains along the wire’s long axis, with only two possible orientations. Such a nanowire may be very well approximated as a magnetic dipole, and depending on the geometrical arrangement and the proximity of the nanowires, inter-wire dipolar interactions can play an important role. In an array of magnetic nanowires in a template, the dipolar interactions are negligible for wires with low densities but substantial for wires with high densities. For free magnetic nanowires removed from the template and suspended in a solution, dipolar forces between nearby wires help determine the type of ordered, multi-wire structures that can be assembled. Since 1993, when arrays of electrodeposited magnetic nanowires were reported [1], many groups have actively pursued a variety of magnetic nanowires, see, e.g. Ref. [5]. Most of these efforts have been directly at magnetic nanowire arrays in templates, but recently, manipulation of magnetic nanowires in suspension has been reported [6]. Together with the multifunctionality made possible by multi-section nanowires, freestanding magnetic nanowires provide many new avenues for fruitful exploration.

In this work, we describe several recent developments in nanoporous templates and Ni nanowires. Using single-crystal mica, we have created arrays of diamond-shaped nanopores with uniform size and orientation. In Ni prisms deposited in these templates, we have observed anisotropic magnetic properties along all three axes of the prisms. We also describe the manipulation of isolated Ni nanowires in a variety of suspensions, and studies of interactions between these nanowires. Finally, we describe briefly surface-functionalized, fluorescent Ni nanowires and various prospects for future applications of nanowires.

2. Nanowire fabrication

In fabricating nanowires by electrodeposition, one side of the porous template is usually coated with a metal layer, which serves as a working electrode in a three-electrode deposition cell. The electrodeposition takes place inside the nanopores, starting from the metal layer. While the principle of the electrodeposition process is simple, the quality of the nanowires depends critically on the detailed composition of the electrodeposition solution and the deposition characteristics. The Nickel nanowires used in the experiments described here were grown from a solution of 20 g l$^{-1}$ NiCl$_2$·6H$_2$O, 515 g l$^{-1}$ Ni(H$_2$NSO$_3$)$_2$)·4H$_2$O, and 20 g l$^{-1}$ H$_3$BO$_3$ at −1.0 V (Ag/AgCl).

2.1. Nanoporous templates

The quality of the electrodeposited nanowires also depends critically on the nanoporous template, which defines the geometrical shape and areal density of the nanowires. A variety of templates with a range of pore sizes and pore densities are available. These include polycarbonate membranes [7] and mica crystals [8] containing etched nuclear particle tracks, alumina templates formed from anodic oxidation of aluminum [9], and diblock co-polymers [10]. The pores in alumina and in diblock co-polymers are partially or highly ordered, and have very high pore densities ($10^8$–$10^{11}$ cm$^{-2}$). On the other hand, while pores made by nuclear track etching are randomly located, the pore density can be varied over a wide range by controlling the fluence of the energetic nuclei. The template material also limits the maximum operating temperature of the nanowire array. In the case of organic templates, this can be quite low.

Commercially available ultrafine filters (e.g., Nuclepore, Anodisc) can be and have been used as templates, but they are often less than satisfactory since their intended purpose is not nanowire fabrication. The pore densities are generally quite high, and the resulting proximity of neighboring nanowires can lead to strong inter-wire interactions that can influence the magnetic response of arrays. This is particularly true for
commercial alumina templates. As for commercial polycarbonate membranes, in addition to their low operating temperature, their most severe problem is that the pores are often not parallel. The pores can be splayed more than $20^\circ$ from the normal to the template plane, severely compromising the interpretation of the arrays’ measured properties. Many aspects of the study of magnetic nanowires require templates with characteristics that are not available commercially.

2.2. Diamond-shaped nanopores in mica

The nuclear-track-etched nanopores in polycarbonate membranes are approximately circular in cross section, whereas those in mica have a diamond shape. To fabricate pores in mica, $\alpha$-particles with energy 6 MeV from a 100-$\mu$Ci Cf$^{252}$ source are used to form damage tracks in 5-$\mu$m thick mica single crystals along the [0 0 1] direction. The collimation of the $\alpha$-particles, $5^\circ$ in our case, can be controlled by the separation between the source and the mica. The density of the particle tracks, and hence that of the nanowires in the array, is proportional to the irradiation time, and for our apparatus, the density of pores per cm$^2$ is $10^3$ times the irradiation time in seconds [11]. The damage tracks are then etched by 20 wt% HF (11.4 M). Because the etching rate along the tracks is much faster than both the lateral etch rate and

![Fig. 1. (a, b) Scanning electron microscope images of etched particle tracks in single-crystal mica. (c) Projection of the atomic arrangement in the (001) plane of mica illustrating that the pore walls correspond to the oxygen-terminated planes in the mica structure.](image)
that for undamaged mica, when the tracks are etched through, nanopores with small cross section and small taper angle (0.02°) are created.

The most unusual aspect of the nanopores in single-crystal mica is that all the pores are diamond-shaped with inner angles very close to 60° and 120° as shown in Figs. 1(a) and (b). Furthermore, all of the pores in a given sample have the same size and orientation [12]. By correlating the results of scanning electron microscopy and X-ray diffraction on the etched mica crystals, we find that the orientation of the diamonds is exactly the same as that of the mica unit cell. Furthermore, the four sides of the diamonds are parallel to the four oxygen-terminated planes within the unit cell as shown in Fig. 1(c). This establishes that the diamond-shaped pores have their origin in the mica crystal structure. The uniform diamond shape, regardless of pore size, arises because the oxygen-terminated planes are those with the slowest etch rate, and the pore axes are aligned because the template are single crystals.

3. Magnetic properties of Ni nanowire arrays in mica

The strong magnetic anisotropy found in ferromagnetic nanowires is due principally to shape anisotropy. This anisotropy can be determined by measurements with the magnetic field applied parallel (H||) and perpendicular (H⊥) to the wires’ long axis. For Ni wires with circular cross section, such as those grown in polycarbonate membranes, there is no magnetic anisotropy within the plane perpendicular to the wire axis [1].

An array of Ni nanowires grown in a single-crystal mica template is a collection of aligned Ni prisms, each of which can be defined by the three axes: c (along the wire), and a and b (along the two diagonals of the diamond). The magnetic properties for fields applied in the plane perpendicular to c are no longer isotropic, and the results for H_a and H_b are significantly different. We stress that because the Ni prisms are all co-aligned and because inter-wire interactions are negligible since n is small, the magnetic properties measured from an array of Ni prisms are those of a single Ni prism.

Representative hysteresis loop of Ni prisms with the magnetic field along the a-, b-, and c-axis are shown in Fig. 2, demonstrating the anisotropy between the three symmetry axes. The easy axis is the c-axis, as the hysteresis loop along the c-axis has the highest remnant magnetization M_r. As the size of the Ni nanowires is decreased, both the coercivity and remnant magnetization (expressed as the squareness, defined as M_r/M_s, where M_s is the saturation magnetization) increase as shown in

![Fig. 2. Hysteresis loops of an array of Ni nanowires d = 100nm and 5μm long with the field applied along the a- and b-axis of the diamond pores and along the wire (or c)-axis.](image-url)
Fig. 3. Note that the squareness of Ni wires deposited in commercial Nuclepore templates is noticeably smaller for the same wire diameter [1]. This is due to the splaying of the nanopores in the commercial templates noted above.

A series of hysteresis loops of the Ni prisms have been measured with the magnetic field applied at an angle $\theta$ with respect to the $c$-axis. The remnant magnetization $M_r(\theta)$, shown in Fig. 4, clearly illustrates uniaxial anisotropy with a period of $\pi$. The solid curve that describes excellently the experimental data is not a fit but simply $|\cos \theta|$. This is because the wire axis is the magnetic easy axis, and regardless of the direction of $H$, at $H = 0$, the magnetization will be along the wire direction. The remnant magnetization $M_r(\theta)$ is therefore just $M_r(0)\cos \theta$, the projection of the remnant magnetization along the wire direction onto the measured direction.

Within the plane of the diamond, the magnetic properties are not isotropic. This is illustrated by the saturation field as a function of the angle $\phi$ with respect to the $a$-axis. As shown in Fig. 4 the saturation field shows a uniaxial symmetry. Because the magnetocrystalline anisotropy for Ni is small, the measured anisotropy is predominantly due to the diamond shape. The measured results can be well described by assuming two uniaxial anisotropy constants $K_a$ and $K_b$ along the $a$- and $b$-axis

$$H_{\text{sat}} = \left(2K_a/M_s\right)\cos^2 \phi + \left(2K_b/M_s\right)\sin^2 \phi,$$

with $K_a = 1.13 \times 10^6$ and $K_b = 8.2 \times 10^6$ erg cm$^{-3}$.

Fig. 4. (Top) Remanence as a function of the angle $\theta$ at which the field is applied with respect to the wire direction. (Bottom) Saturation field in the plane of the diamond cross section as a function of $\theta$ with respect to the $a$-axis.

4. Assembly and functionalization of suspended magnetic nanowires

In addition to their unique properties in templated arrays, magnetic nanowires have interesting behavior when removed from the templates, and placed in fluid suspensions. First, their large magnetic shape anisotropy and high remnant magnetization makes suspended nanowires highly
orientable and easily manipulated in small external magnetic fields. This can be used to control the inter-wire dipolar forces, and hence to obtain assembly of ordered structures. In addition, the nanowires can be surface-functionalized with a variety of organic molecules that can influence how the nanowires interact with their environment. These properties give magnetic nanowires potential for applications in biotechnology and separations chemistry. Some preliminary results have been reported previously [6]. Here we describe experiments that explore effects of different fluids on the production of nanowire suspensions, the assembly of magnetic nanowires into ordered chains, and the functionalization of magnetic nanowires with fluorescent porphyrin molecules.

4.1. Preparation of nanowire suspensions

Cylindrical Ni nanowires were grown as described in Section 2, using 50-μm-thick alumina filter templates (Anodisc, Whatman, Inc.) with a nominal minimum pore diameter of 100 nm. These templates yield wires with average radius \( a = 180 \pm 20 \text{ nm} \). The nanowires were removed from the alumina templates by reaction in 0.5 M KOH at 50°C, and collected either by placing a small magnet on the side of the flask or by centrifugation. The magnetic collection procedure exposes the wires to fields in excess of 1 kG, and permanently magnetizes them with their magnetic moments parallel to the long axis. With either procedure, after several rinsings the wires could be resuspended in a variety of solvents with sonication. Nanowires suspended in low viscosity liquids such as water, ethanol, and isopropanol precipitate in the course of several minutes. In addition, aggregation occurs due to inter-wire magnetic forces. To minimize aggregation and precipitation, the nanowires were suspended in more viscous media such as 1:1 hexadecane (C\(_{16}\)H\(_{34}\)):octadecane (C\(_{18}\)H\(_{38}\)) mixtures or ethylene glycol. These suspensions are much more stable. For example, in hexadecane:octadecane the nanowires remained suspended for periods of days at room temperature.

4.2. Chain formation from suspended nanowires

The response of suspensions of nanowires to magnetic fields was investigated under optical and fluorescence microscopes. Even in the most viscous solvents, the nanowires align parallel to the field, and move in response to magnetic field gradients. Controlled assembly of the nanowires may be achieved by applying a small external magnetic field \( H < 20 \text{ G} \) to a nanowire suspension. Since the initially isolated wires all align parallel to \( H \), their tendency toward random aggregation is suppressed, and instead the inter-wire interactions lead to the formation of head-to-tail chains. This occurs both in the suspension, and on the bottoms of our glass experimental cells, where the chains can extend over hundreds of microns [6]. We have studied the dynamics of chain formation on the cell bottoms via video microscopy. Fig. 5 shows four video frames from the joining of two short chains composed of two and three nanowires, respectively, carried out in ethylene glycol at \( T = 20°C \) and \( H = 4 \text{ G} \). From these data, the chains’ locations can be determined for each frame, and the end-to-end separation vs. time for the event in Fig. 5 is shown in as Trace 3 in Fig. 6. The large circles indicate the data points corresponding to the frames in Fig. 5. Fig. 6 also shows data for a second event in ethylene glycol (Trace 4), along with two events observed in water at \( T = 35°C \) (Traces 1 and 2). The separation vs. time

![Fig. 5. Video microscopy images showing attractive interaction between two Ni nanowire chains in ethylene glycol, coaligned in a 4 Oe external field.](image-url)
curves are qualitatively similar for all joining events, but the significantly higher viscosity of ethylene glycol ($\mu_{\text{EG}} = 0.02 \text{P}$ at $T = 20^\circ\text{C}$; $\mu_{\text{H}_2\text{O}} = 7 \times 10^{-3} \text{P}$ at $T = 35^\circ\text{C}$) results in much slower motion. The chain lengths and physical parameters for these events are given in Table 1.

All of the nanowire motion studied here occurs at very small Reynolds number ($R < 10^{-5}$), and therefore viscous drag is the dominant hydrodynamic effect [13]. Thus, a nanowire or nanowire chain’s velocity is $\mathbf{v} = \mathbf{F}/D$, where $D$ is the appropriate drag coefficient and $\mathbf{F}$ is the total applied force [14]. For nanowires moving along a flat substrate, the inter-wire magnetic forces are the dominant contribution to $\mathbf{F}$. At distances large compared to the wire radius $a$, the magnetic field of a wire or chain of wires of total length $L$ is that of an extended dipole with magnetic charges $\pm Q_m = \pm M \pi a^2$ separated by $L$, where $M$ is the wire’s magnetization. This approximation is accurate to within 0.05% for distances greater than $5 \mu$m from the wires’ ends. The magnetic force between wires or chains is given by the equivalent Coulomb forces between these magnetic charges.

For all the events shown in Fig. 6 the wires or chains are nearly co-linear. In this case, the force between two wires or chains of lengths $L_1$ and $L_2$ is

$$f(r) = -Q_m^2 \left( \frac{1}{r^2} - \frac{1}{(r + L_1)^2} - \frac{1}{(r + L_2)^2} \right) + \frac{1}{(r + L_1 + L_2)^2},$$

(2)

where $r$ is the end-to-end separation. The time-dependence of $r(t)$ is determined from the one-dimensional equation of motion $dr/dt = Df(r)$, where $D = D_1 D_2/(D_1 + D_2)$ is the reduced drag coefficient. We note that $r(t)$ has simple limiting cases of the form

$$r(t) = r_0 (1 - t/t_0)^{\alpha}$$

(3)

when $r \gg L_1, L_2$, where $\alpha = \frac{1}{2}$ (the limit of two point dipoles), and when $r \ll L_1, L_2$, where $\alpha = \frac{1}{3}$. This latter case provides a good description of the data for Event (2) in Fig. 6, but Eq. (3) does not describe most data sets unless the exponent is allowed to vary in the range $0.24 < \alpha < 0.29$.

The full equation of motion with Eq. (2) may be integrated analytically to give the inverse of $r(t)$ in the form

$$t(r) = k(F_1(L + r_0, L_1, L_2) - F_1(L + r, L_1, L_2)),$$

(4)

where $L = (L_1 + L_2)/2$. The somewhat lengthy expression for the function $F_1$ is given in Ref. [6].

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![Fig. 6](image.png)

*Fig. 6. Separation vs. time for four chain-formation events in a 4Oe external field. Events (1) and (2) were in water, and events (3) and (4) were in ethylene glycol. Large circles (a)–(d) on curve (3) correspond to the four panels in Fig. 4. The solid lines are fits described in the text and in Table 1.*

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### Table 1
Parameters describing the four joining events shown in Fig. 6

<table>
<thead>
<tr>
<th>Event</th>
<th>Solvent</th>
<th>$L_1$ ($\mu$m)</th>
<th>$L_2$ ($\mu$m)</th>
<th>$r_0$ ($\mu$m)</th>
<th>$k$ ($\text{s} \mu\text{m}^{-2}$)</th>
<th>$D/\mu$ ($\mu$m)</th>
<th>$D_{\text{calc}}/\mu$ ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{H}_2\text{O}$</td>
<td>6.4</td>
<td>16.4</td>
<td>37.2</td>
<td>$1.48 \times 10^{-6}$</td>
<td>25.2</td>
<td>17.2</td>
</tr>
<tr>
<td>2</td>
<td>$\text{H}_2\text{O}$</td>
<td>57.2</td>
<td>124.0</td>
<td>28.9</td>
<td>$2.13 \times 10^{-7}$</td>
<td>243.8</td>
<td>89.2</td>
</tr>
<tr>
<td>3</td>
<td>$\text{EG}$</td>
<td>29.3</td>
<td>17.0</td>
<td>19.8</td>
<td>$1.59 \times 10^{-5}$</td>
<td>45.9</td>
<td>31.7</td>
</tr>
<tr>
<td>4</td>
<td>$\text{EG}$</td>
<td>9.1</td>
<td>10.2</td>
<td>16.6</td>
<td>$5.09 \times 10^{-5}$</td>
<td>27.5</td>
<td>17.3</td>
</tr>
</tbody>
</table>

$L_{1,2}$ are the wire or chain lengths. $r_0$ and $k$ are fitting parameters, as described in the text. $D/\mu$ and $D_{\text{calc}}/\mu$ are the ratio of the reduced drag coefficient and the fluid viscosity, as derived from $k$, and calculated from standard hydrodynamics, respectively. The uncertainties in $L_1$, $L_2$, and $r_0$ are all $\pm 0.1 \mu$m. The uncertainty in $k$ is $\pm 1\%$. See text for discussion of the drag coefficients.
This yields a description of the motion in terms of two parameters, the initial separation $r_0$, and $k = D/Q_m^2 L_1 L_2$, which measures the relative strength of the drag and magnetic forces. As shown by the solid curves through all the data sets in Fig. 6, this model provides a good description for a wide range of chain lengths, initial separations, and fluid viscosities. The values of $r_0$ and $k$ determined in these fits are given in Table 1.

As noted in Section 2, accurate determination of the remnant magnetization of nanowires grown in alumina is difficult due to inter-wire interactions in the templates. However, extrapolating the data in Fig. 3, we estimate that these nanowires have $M \sim 0.7 M_{sat}$, where $M_{sat} = 485 \text{Oe}$ is the room temperature, bulk saturation magnetization of Ni. This allows us to obtain an estimate for the reduced drag coefficient $D$ from $k$, but we caution that there is a nearly 50\% overall uncertainty in these numbers, arising principally from variations in the nanowires’ radius that results from non-uniformities in the pore sizes of the alumina templates. Values of $D/\mu$ are also given in Table 1.

The very similar numbers obtained for $D/\mu$ for joining events such as (1) and (4), that involve individual nanowires, suggest that the drag coefficient is proportional to the fluid viscosity. This result is not unexpected, since in the limit where a nanowire or chain is far from the cell bottom, its drag coefficient is $D = 6 \pi \mu r$, where the effective radius $\rho$ may be determined by approximating the wire or chain as a prolate ellipsoid [15]. Calculated values $D_{calc}/\mu$ based on this approximation are given in Table 1, and show good general agreement with the measured values. Scaling with fluid viscosity is again clearly seen. Such experiments could be refined in the future by using nanowires, such as those grown in mica templates, that have a more uniform cross section, and with an improved analysis of the drag forces that treats wire–substrate interactions.

Fig. 7. Ni nanowires functionalized with Hematoporphyrin IX, and immobilized on a glass slide. Prior to immobilization, the nanowires were suspended in ethanol (a, d), water (b, e), or ethylene glycol (c, f) for 5 days. The upper panels (a)-(c) show optical images of the nanowires, while the lower panels (d)-(f) show fluorescence images of the same nanowires.
4.3. Surface functionalization of Ni nanowires with fluorescent porphyrins

By functionalizing the surfaces of suspended nanowires with organic molecules, additional control and enhancement of their properties and behavior can be achieved. One example of this is the modification of their optical properties by coating with fluorescent chromophores. We note that the production of luminescent non-magnetic nanowires was recently reported [16a,b]. Here we describe the surface functionalization of Ni nanowires with a fluorescent porphyrin.

Magnetic nanowires were functionalized with fluorescent Hematoporphyrin IX, \([8,13\text{-bis}(1\text{-hydroxyethyl})\text{-3,7,12,17-tetra-methyl-21H,23H-porphine-2,18-dipropionic acid}],\) which has two intense, red fluorescence bands \((\lambda_{\text{max}} = 626 \text{ and } 696\text{ nm in ethanol})\), and two carboxylic acid groups that bind strongly to metal oxides and to the native oxide films on metals, such as nickel [17a,b]. Reaction of the nanowires with millimolar concentrations of Hematoporphyrin IX for 24 h in ethanol at room temperature resulted in surface binding. The carboxylic acid functional groups on Hematoporphyrin IX most likely bind to the nanowires as carboxylate linkages, or possibly as ester links [17a,b]. In either case it is important to characterize the stability of the surface linkages under a variety of conditions. The stability was tested in three common solvents, ethanol, ethylene glycol, and water. The functionalized nanowires were placed in the pure solvent for 5 days. They were then collected magnetically, resuspended in ethanol solution, and spun out onto glass slides. Fig. 7 shows optical and fluorescence microscopy images of single, porphyrin-functionalized Ni nanowires. The observation of fluorescence along all of the nanowires suggests a uniform surface coverage and shows high stability in all three solvents, indicating a wide range of applicability of optical coatings of this type.

5. Summary

These studies demonstrate some of the novel and potentially useful properties of electrodepos-...