Individually grown cobalt nanowires as magnetic force microscopy probes

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AC electric fields were utilized in the growth of individual high-aspect ratio cobalt nanowires from simple salt solutions using the Directed Electrochemical Nanowire Assembly method. Nanowire diameters were tuned from the submicron scale to 40 nm by adjusting the AC voltage frequency and the growth solution concentration. The structural properties of the nanowires, including shape and crystallinity, were identified using electron microscopy. Hysteresis loops obtained along different directions of an individual nanowire using vibrating sample magnetometry showed that the magnetocrystalline anisotropy energy has the same order of magnitude as the shape anisotropy energy. Additionally, the saturation magnetization of an individual cobalt nanowire was estimated to be close to the bulk single crystal value. A small cobalt nanowire segment was grown from a conductive atomic force microscope cantilever tip that was utilized in magnetic force microscopy (MFM) imaging. The fabricated MFM tip provided moderate quality magnetic images of an iron-cobalt thin-film sample. *Published by AIP Publishing.* <https://doi.org/10.1063/1.4997310>

Magnetic nanoparticles are well studied structures due to their potential use in various applications such as data recording and targeted drug delivery.¹ Magnetic nanowires have received relatively less attention than their semiconductor counterparts, despite having properties suitable for a wide range of applications including magnetic force microscopy (MFM) probes,^{2–4} sensors,⁵ and live cell manipulators.⁶ Alumina templates are commonly used for the large-scale growth of magnetic nanowires by electrochemical deposition.^{7,8} In this method, a large number of nanowires reside in a solution after the removal of the template. The characterization of an individual nanowire and device fabrication require further steps for the isolation of the targeted nanowire.

The directed Electrochemical Nanowire Assembly (DENA) method enables the single-step growth and interconnection of crystalline nanowires with external electrodes.^{9–13} In this method, a saturated water-soluble salt solution of the target material is deposited between a pair of electrodes and an individual nanowire grows from one electrode to the other with the application of the AC voltage as depicted in Fig. 1. A set of DENA growth parameters including voltage amplitude and frequency, electrode design, and salt solution concentration were previously established for indium and gold nanowires.^{9,10} The DENA method was also used in the growth of other metallic nanowires from their salt solutions such as copper, platinum, silver, and palladium.^{14–17} Polymeric nanowire growth was also demonstrated using the DENA method.^{13,18} Previously, the DENA method was identified as a dendritic solidification process.⁹

The DENA method allows simple tuning of nanowire diameters by changing the frequency of the applied AC potential.⁹ Gold nanowires with submicron to 45 nm diameters were previously grown using the DENA method.^{9,10} A high degree of control on the position of the as-grown individual nanowire is feasible in the DENA method as the nanowire growth can be paused before reaching the counter electrode (Fig. 1), and the nanowire can be transferred on to any target substrate with micromanipulators. DENA also enables the direct interfacing of the nanowires with planar electrodes (e.g., prepared by photolithography) during growth, facilitating characterization of their electronic transport properties.¹¹ These properties demonstrate that DENA is an ideal individual nanowire growth method for studying the properties of materials at nanodimensions and for device fabrication.

Here, we use DENA to grow individual cobalt nanowires from saturated salt solutions. Structural properties were identified using both scanning (SEM) and transmission (TEM) electron microscopy. Magnetic properties of individual cobalt nanowires were characterized using a vibrating sample magnetometer (VSM). Small segments of cobalt nanowires were grown from non-magnetic conducting atomic force microscopy (AFM) cantilever tips, and these modified cantilevers were utilized in magnetic force microscopy (MFM) imaging.

Aqueous salt solutions were previously shown to be effective for nanowire growth using the DENA method,^{9–11} making hydrated salts of the target metals ideal for obtaining clear stock solutions. In this context, cobalt (II) sulfate hepta-hydrate (98%, Alfa Aesar) salt was employed to obtain low concentration to saturated cobalt salt solutions (0.1 M to 3 M) in deionized (DI) water. The tapered tip tungsten electrodes were prepared by etching 0.5 mm diameter annealed tungsten wires (Alfa Aesar) in two molar sodium hydroxide

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FIG. 1. (a) Computer rendered image of the DENA growth setup, showing a pair of electrochemically etched tungsten electrodes immersed in the growth solution. An individual nanowire grows from one electrode to the other with the application of AC potential. The inset shows an optical image of a 400 nm diameter cobalt wire that was extracted from the growth solution and structurally analyzed as shown in Fig. 2. (b) An illustration of the permanent magnet assisted wire extraction method.

solution with the application of 14 V DC potential between the tungsten wire and a counter electrode that was submerged in the sodium hydroxide solution. The tungsten wires were manually immersed in and removed from the solution at a frequency of about 1 Hz during the etching process until visually sharp and tapered electrodes were obtained. The radii of curvature of these electrodes were about $1\ \mu\text{m}$, and the variation of the sharpness of the electrode tips did not have any effect on the nanowire diameters. However, relatively dull electrodes caused growth of multiple wires from the electrode tip by providing a larger number of high electron density reduction sites for the cobalt ions. A pair of etched tapered tungsten electrodes were installed on three dimensional translational stages and were placed above a glass slide on an inverted optical microscope (Fig. 1). The glass slides were silanated (with RainX) in order to make their surfaces hydrophobic, enabling the stock solution to form a droplet instead of spreading on the substrate surface.

After adjusting the electrode separation to $\sim 100\ \mu\text{m}$, a small droplet ($\sim 30\ \mu\text{l}$) of the stock cobalt solution was deposited between the electrodes such that both electrodes resided in the droplet as shown in Fig. 1. A function generator (Stanford Research Systems-DS345 or BK Precision 4065) was used to apply a square wave potential with frequencies $\geq 20\ \text{MHz}$ to the electrodes. The wire growth started from the sharp tip of the grounded electrode at $V_{pp} > 3\ \text{V}$, and the growth was terminated by reducing the voltage amplitude before the growing wire reached the counter electrode. The cobalt nanowires remained intact after the removal of the AC potential.

Three-dimensional translational stages were used to position the tungsten electrodes before and during growth and to extract the nanowires after growth and place them on target substrates for magnetic and structural characterization. Alternatively, as the nanowires were pure cobalt and ferromagnetic in nature, we also employed strong permanent magnets to remove the fibers from the growth solution, as depicted in Fig. 1(b). In this magnet-assisted approach, the target substrate was fixed to the permanent magnet surface and thereby pulled the nanowire from the solution, adhering the fiber to the target substrate.

Cobalt nanowires were transferred onto silicon substrates and TEM grids for structural characterization. The SEM image in Fig. 2(a) shows a $100\ \mu\text{m}$ long cobalt nanowire that was transferred onto a holey-carbon coated TEM grid after directly pulling out of the solution where the

nanowire remained in contact with the growth electrode and was placed on the TEM grid with the three-axis microtranslational stage. The high magnification SEM image in the inset of Fig. 2(a) shows this cobalt nanowire to have, roughly, a square cross-sectional profile with a side length of $\sim 400\ \text{nm}$. The high resolution TEM image of the same cobalt nanowire in Fig. 2(b) depicts highly ordered atomic planes [Fig. 2(b)], where the lattice spacing between adjacent planes was measured to be $2.5\ \text{\AA}$. Figure 2(c) shows a selected area electron diffraction pattern of this nanowire that was collected using an area selection aperture of $10\ \mu\text{m}$ and a $200.0\ \text{kV}$ electron beam. The pattern is composed of bright, discrete spots (with a second, much fainter set of spots also visible). The set of red spots overlaying this image constitutes a simulated diffraction pattern (obtained using SAED3b, U Nebraska Software for Electron Diffraction Analysis) that required the standard hexagonal lattice parameters for cobalt $a = b = 0.25071\ \text{nm}$ and $c = 0.40695\ \text{nm}$ and assumed a zone axis of $[1\bar{1}0]$.¹⁹ Agreement with the observed diffraction pattern is strong, indicating that the nanowire is

FIG. 2. (a) SEM image of a DENA grown $100\ \mu\text{m}$ long cobalt nanowire transferred onto a holey carbon TEM grid. The scale bar is $20\ \mu\text{m}$. The tilted and higher magnification SEM image in the inset shows that the wire has a square cross-sectional profile with a width of $400\ \text{nm}$. The scale bar is $500\ \text{nm}$ for the inset. (b) High resolution TEM image of the edge of the same cobalt wire shows the highly ordered atomic planes. (c) Simulated electron diffraction pattern over the observed electron diffraction pattern of the crystalline cobalt nanowire viewed along the incident electron beam direction $[1\bar{1}0]$. (d) Real space schematic corresponding to the electron diffraction pattern in panel (c).

hexagonal cobalt, belonging to the P63/mmc space group. Epitaxial growth of cobalt in the cubic phase is also possible at temperatures greater than 710 K, but since the cobalt nanowires in this study were grown at room temperature using the DENA method, the hexagonal crystal structure is expected.²⁰ The real space image that corresponds to this diffraction pattern is depicted in Fig. 2(d). Previously, DENA grown indium and gold nanowires were also shown to exhibit a crystalline structure.^{8,9}

The DENA method enables facile nanowire diameter control by adjusting the AC voltage frequency as formerly demonstrated with gold and indium nanowires. Nanowire diameters were reduced below 100 nm by increasing the AC voltage frequency for both materials.⁷ The correlations between various parameters including growth velocity, AC voltage frequency, solution concentration, and the nanowire diameter were identified through a rigorous theoretical analysis with the solution of the diffusion equation: $\partial c(r, t) / \partial t = -\nabla \cdot \vec{j}$, where $c(r, t)$ is the concentration profile and $\vec{j}$ is the flux of the cations.⁷ In the present study, cobalt nanowire diameters were controlled by varying the AC voltage frequency and the solution concentration. As shown in Fig. 3, the average diameters of the individually grown cobalt nanowires decreased from 672 ± 58 nm to 37 ± 2.5 nm as the AC voltage frequency was increased from 20 MHz to 30 MHz and the growth solution concentration was reduced from 2 M to 0.1 M. The solution concentration was fixed at 2 M while changing the AC voltage frequency, and a fixed frequency of 30 MHz was used in the growth of cobalt nanowires from different concentration solutions.

Magnetic characterization of cobalt nanowires was performed using a Vibrating Sample Magnetometer (VSM). Figure 4 shows the VSM hysteresis loops of an individual cobalt nanowire on a silicon substrate, measured along the directions parallel and perpendicular to the elongated axis. The displayed loops were corrected from the diamagnetic signals of the substrate and the sample holder. This nanowire was grown longer than 1 mm to increase the magnetic moment of the sample to levels above the minimum signal detection limit of the VSM equipment by increasing the volume of the sample. The nanowire growth electrode was

FIG. 3. Cobalt nanowire diameter control from the submicron to nanoscale by varying the AC voltage frequency (red curve, squares) and solution concentration (blue curve, triangles). The insets show the same magnification SEM images of cobalt nanowires grown with one molar (left) and two molar (right) cobalt salt solutions, visually showing the decrease in the wire diameter with the decreasing concentration. Scale bars in the insets represent 1 μ m.

FIG. 4. Room temperature cobalt wire in-plane hysteresis curves with the applied field parallel (0°) and perpendicular (90°) to the wire axis. The inset shows the SEM image of the 1 mm long cobalt wire used in this measurement. The scale bar represents 200 μ m.

slowly moved away from the counter electrode during the growth to obtain these longer cobalt wires. The hysteresis along both directions is essentially the same with a small coercivity field (H_c) magnitude of ~ 100 Oe. Hexagonal cobalt's magnetocrystalline anisotropy energy density $K_1 = 5 \times 10^6$ erg/cm³ is known to be on the same order of magnitude as its shape anisotropy energy density $\sim K_S = \pi M_S^2 = 6.0 \times 10^6$ erg/cm³, causing a competition between the two anisotropies in the alignment of the magnetization.²¹ This leads to a slightly weaker effective anisotropy along the nanowire axis, resulting in the reduction of the coercive field and the remanent magnetization along the direction of the nanowire axis. The small coercivity in the hysteresis curves also indicates that the nanowire might have a polycrystalline structure. As depicted in the low magnification TEM image in Fig. S1 in the [supplementary material](#), the cobalt nanowire in Fig. 2(a) exhibits a polycrystalline structure with nanoscale grains with an average size of ~ 25 nm. The longer cobalt nanowire that was used in the magnetic characterization experiment (inset in Fig. 4) is expected to have a similar polycrystalline structure as both wires were grown with the same parameters. The polycrystalline nature of the nanowire causes the magnetocrystalline anisotropy axes to display a broad distribution, assisting in overcoming the wire's shape anisotropy.²² Furthermore, given the nanowire volume of $\sim 10^{-10}$ cm³ (obtained via SEM image analysis), the measured magnetic moment at saturating field values (~ 10 kOe) of 0.36 μ emu implies a saturation magnetization of 1440 emu cm⁻³, which is comparable to the bulk single crystal cobalt value.²³ We also note that the large difference in the saturation field between two directions is likely due to the demagnetizing field, which is much stronger along the normal direction to the elongated axis, and that the low remanence (M_r) in both directions is probably due to the demagnetizing field and the low intrinsic magnetocrystalline anisotropy.

As a possible application, DENA grown cobalt nanowires were used in manufacturing magnetic force microscopy probes. Previously, Yang and coworkers have employed nickel and cobalt nanowires as MFM tips.² Their multi-step approach included the growth of nanowires with an anodized alumina template and the attachment of an individual nanowire to a gold coated silicon AFM probe with

dielectrophoresis. In other multi-step nanostructure based MFM probe studies, cobalt-iron coated carbon nanotubes were initially attached to silicon cantilevers³ and iron-filled carbon nanotubes were attached to conventional scanning force microscopy probes.⁴ In our single-step approach, short cobalt nanowire segments were directly grown from the tips of platinum coated conducting atomic force microscope (CAFM) cantilevers. The metal coating was essential to make the cantilever function as an electrode and to grow the short cobalt nanowire directly from the cantilever tip. Regular AFM cantilevers are manufactured from crystal silicon, and they cannot be used as electrodes as they have very high resistance. As shown in the $40\times$ magnification optical image in Fig. 5(a), the CAFM cantilever was placed on its side on a silanated glass slide and an etched tungsten electrode was used as the counter electrode. The growth was terminated after about a $2\mu\text{m}$ long cobalt nanowire segment grew from the cantilever tip, and the sample was removed from the salt solution. Figure 5(b) shows the SEM image of another CAFM cantilever tip with a cobalt nanowire segment. This particular nanowire segment had a larger diameter ($1.5\mu\text{m}$) as it started to grow and tapered down to a tip with a 100nm radius of curvature, making it a suitable geometry for MFM imaging. Other MFM probes with different geometry cobalt wire segments were also fabricated such as the one depicted in the optical microscopy image of panel (a) in Fig. 5. Energy dispersive spectroscopy (EDS) mapping of the fabricated MFM probe samples revealed the composition of the nanowire segment as cobalt as shown in Fig. 5(d).

The fabricated probe in Fig. 5(b) was tested in the MFM imaging of an iron platinum (FePt) thin film sample grown on a strontium titanate (SrTiO_3) substrate. MFM imaging

was carried out using a Digital Instruments Dimension 3100 atomic force microscope. Figure 5(c) shows the $10\mu\text{m} \times 10\mu\text{m}$ MFM scan, which revealed the following magnetic characteristics of the FePt sample. (1) The magnetic domains consisted of island-like structures with different shapes rather than stripes. (2) The island size varied between 300 and 500nm . (3) The total areas of dark and bright regions were almost identical due to the demagnetized state of the sample and its large out-of-plane anisotropy, which confined the magnetization along the vertical up and down directions. It is also important to note that the MFM data in Fig. 5(c) are shown as provided by our instrument. Obviously, the frequency shift scale contains an arbitrary offset as it starts from 0Hz unlike usual MFM imaging, where the repulsive and attractive interactions are generally associated with positive and negative frequency shifts, respectively. Dark and bright contrasts are present in the MFM image of Fig. 5(c); however, the nature of the forces is ambiguous due to the limited representation of the frequency shift scale. Furthermore, since the cantilever was originally coated with non-magnetic metals (chromium and platinum), MFM imaging would not be possible without the small DENA grown cobalt nanowire segment, which produces enough magnetic force between the cantilever and the sample surface in the MFM scan. A CAFM cantilever without the cobalt nanowire segment was also tested in the MFM imaging of the same sample, and no MFM image was produced. The same FePt thin film sample was imaged with a commercial MFM probe, and the resolution of the nanowire probe MFM image was observed to be lower than the one obtained with the commercial probe as depicted in Fig. S2 in the [supplementary material](#). The resolution of the nanowire probe MFM images will be improved in a future detailed study.

These results demonstrate that the DENA method can be utilized in the facile growth of individual, magnetic, diameter controlled, and high-aspect ratio cobalt nanowires. Due to these properties, DENA grown cobalt nanowires are ideal platforms in the study of fundamental physical phenomena such as quantized magnetotransport²⁴ and domain wall motion control.^{3,25} To this end, DENA grown individual cobalt nanowires will be utilized in variable temperature magnetotransport and Magneto-optic Kerr Effect (MOKE) measurements. Other device applications of cobalt nanowires, including sensors and live cell manipulation, will be explored.

See [supplementary material](#) for a low-magnification TEM image of a cobalt nanowire and a side by side comparison of magnetic images recorded with a cobalt nanowire and a commercial MFM probe.

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FIG. 5. (a) Optical microscopy image of the cobalt wire grown from the tip of the CAFM cantilever on the left (enclosed in the white dashed circle). The tungsten counter electrode is visible on the right side. (b) SEM image of another cobalt wire segment grown from the tip of the platinum coated AFM cantilever. The scale bar represents $1\mu\text{m}$. (c) Magnetic force microscopy (MFM) image of a FePt thin film sample obtained with the manufactured probe in panel (b). The scale bar is $2\mu\text{m}$. (d) SEM elemental analysis mapping shows the composition of the structure in panel (b), where silicon (blue), platinum (yellow), and cobalt (red) were identified, showing that the wire segment is mainly composed of cobalt.

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