Electronic Supplementary Information (ESI)

Novel gradient-diameter magnetic nanowire arrays with unconventional magnetic anisotropy behaviors

Jing Wang[a], Zhili Zuo[a], Liang Huang[a], Muhammad Asif Warsi[b], John Q. Xiao*[b], Jun Hu*[a]

[a]College of Chemical Engineering, Zhejiang University of Technology, Zhejiang 310014, P.R. China. E-mail: hjzjut@zjut.edu.cn.

[b]Department of Physics and Astronomy, University of Delaware, Newark, DE 19716, USAE-mail: jqx@udel.edu.

Experimental details

Materials

High-purity aluminum sheet (0.25 mm thickness, 99.999% purity) was purchased from Shanghai China aluminum industry co. LTD. Sulfuric acid (98 wt %), phosphoric acid (6 wt %), chromic acid (1.8 wt %), percloric acid (3 wt %), ethanol (99 wt %), $CuCl_2$ solution (0.2 M), H_3BO_3 (≥ 99.5 %), $CoSO_4·7H_2O$ (≥ 99%), $NiSO_4·6H_2O$ (98 %), $FeSO_4·7H_2O$ (≥ 99 %), $C_6H_8O_6$ (99 %) and $Na_3C_6H_5O_7$ (99 %) were obtained from Shanghai Aladdin biochemical technology co. LTD. All chemicals were analytical reagent and used as received without any further purification.

Materials Characterization

Morphology, crystalline structure and composition of the GDMNWs were analyzed using a Hitachi S-4800 field-emission scanning electron microscopy (SEM), operated at 5 kV, a JEOL 1200 transmission electron microscopy (TEM), operated at 200 kV. The TEM specimens were prepared by dispersing the GDMNWs in ethanol onto ultrathin carbon-coated copper grids. The average composition of the nanowires was measured from energy dispersive spectra (EDS, JEOL JSM-5600LV). Magnetic properties of the as-prepared samples were tested by a vibrating sample magnetometer (VSM, TOEI-5S-15).

Preparation of AAO with gradient-diameter nanochannels

The anodic aluminum oxide (AAO) templates with gradient-diameter pores were prepared by using a well-established two step anodization process on aluminum foils. Details of the template preparation have been reported in previous paper[1, 2]. Firstly, a high-purity aluminum sheet were annealed at 500 ℃ for 5 h, and then electropolished in a 1:3 volume mixture of percloric acid and ethanol for 3 min under a voltage of 18 V. Secondly, a two-step anodization process was then carried out with 0.3 M sulfuric acid for 30 min to form porous alumina membrane on aluminum sheet. Thirdly, the membrane was removed in a mixture of phosphoric acid and chromic acid at about 40 ℃, and the Al sheet was anodized again in 0.3 M sulfuric acid under a starting voltage of 25 V for 10 min, and followed by gradually increasing the voltage until 110 V in 60 min, the rate of rising voltage was about 1.4 V/min. In order to increase the thickness the AAO templates, the aluminum sheet kept being anodizing under a voltage of 110 V for 10 min. Following the thickness increasing step, prepared samples were immersed in 0.3 M phosphoric acid at 30 ℃ for 30 min to widen the pore diameter. During the second-step anodization, the AAO template with gradient-diameter holes was formed because its pore diameter is proportional to the voltage. After the second anodization, the remaining aluminum was removed by chemical etching using $CuCl_2$ solution at 40 ℃. Finally, a thin Cu layer was sputter-deposited on one side of the AAO template to serve as a cathode during electrodeposition.

Other AAO template with uniform-diameter pores were anodized using a constant anodizing voltage.

Electrodeposition of GDMNWs

This AAO template with Cu layer served as a cathode in the electrodeposition in a common two electrode plating cell, and a graphite plate was used as the anode. The corresponding electrolyte is a mixture of H_3BO_3 (0.65 M) and $CoSO_4{\cdot}7H_2O$ (0.29 M), $NiSO_4{\cdot}6H_2O$ (0.29 M), $FeSO_4{\cdot}7H_2O$ (0.29 M), a little $C_6H_8O_6$ and $Na_3C_6H_5O_7$ in aqueous solutions. Boric acid was used as buffer solution. Ascorbic acid was applied to prevent the oxidation of ferrous to ferric. Sodium citrate makes the deposition rates of the three metal ions consistent. The pH is about 3.0. The electrodeposition voltage is 3 V (DC) at room temperature. The deposition time was 30 min.

Method of calculating saturation magnetization M_s (emu/cm^3)

M_s represents the magnetic moment per unit volume (emu/cm^3) of the sample. We need to calculate the actual volume of the nanowire arrays in the sample (V_{FeCoNi}) using the following equations:

$$D_{\mathrm{FeCoNi}}V_{\mathrm{FeCoNi}}+D_{\mathrm{Al}}V_{\mathrm{Al}}+D_{Air}V_{Air} = m_{\mathrm{sample}} \quad (1)$$

$$V_{\mathrm{FeCoNi}}+V_{\mathrm{Al}}+V_{Air} = V_{\mathrm{sample}} \quad (2)$$

$$V_{\mathrm{FeCoNi}}+V_{Air} = V_{\mathrm{pore}} \quad (3)$$

where D_{FeCoNi} (~8.34 g/cm^3), D_{Al} (~3.97 g/cm^3), and D_{Air} are the average density of FeCoNi, Al_2O_3, and air respectively. V_{CoFeNi}, V_{Air}, and V_{Al} are the actual volume of FeCoNi nanowire arrays, empty pores, and Al, respectively. V_{pore} is the total volume of all nanopores. m_{sample} is the total weight of the sample. We neglect the mass ($D_{Air}V_{Air}$) of air in empty pores.

We measured the total volume (V_{sample}) and weight (m_{sample}) of the sample for hysteresis loop measurement. We calculate the volume of all nanopores (V_{pores}). For cylindrical nanochannel, the bottom shape of nanochannel is regarded as circle, and the length of the nanochannel is regarded as height of the cylinder. For gradient-diameter nanopores, we calculated the volume of the single nanopore ($V_{\mathrm{single\ pore}}$) by the equation:

$$V_{\mathrm{single\ pore}}=\pi/3\times(r^2+R^2+rR)\times h \quad (4)$$

where h is the length, r and R are the thin-end radius and thick-end radius of gradient-diameter nanowire, respectively.

We then count the number of nanopores (N) in the sample based on the porosity of the AAO template to compute the V_{pores}, which is subtracted from V_{sample} to determine V_{Al}. The value of V_{FeCoNi} can thus be determined from Eq.(1):

$$V_{\mathrm{FeCoNi}} = \frac{m_{sample} - D_{Al}\times V_{Al}}{D_{FeCoNi}} \quad (5)$$

Finally, the value of saturation magnetization M_s is equal to the ratio of the relative saturation magnetization (M) obtained from the initial hysteresis loops and V_{FeCoNi}.

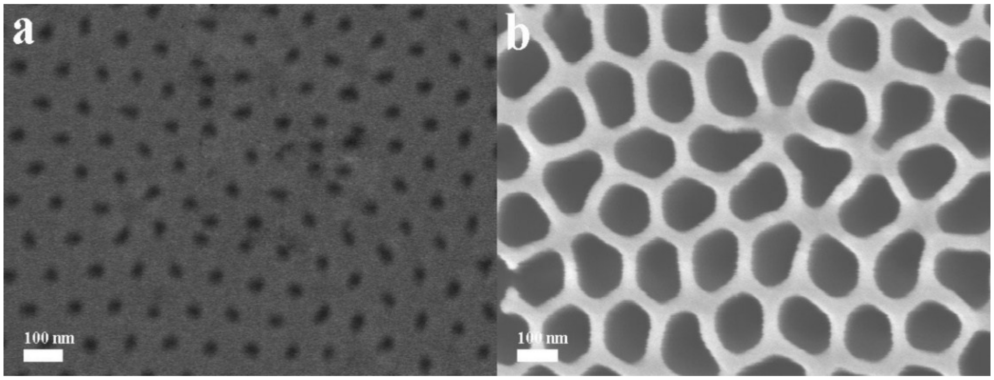

Fig. S1. SEM image of AAO of (a) thin end, (b) thick end

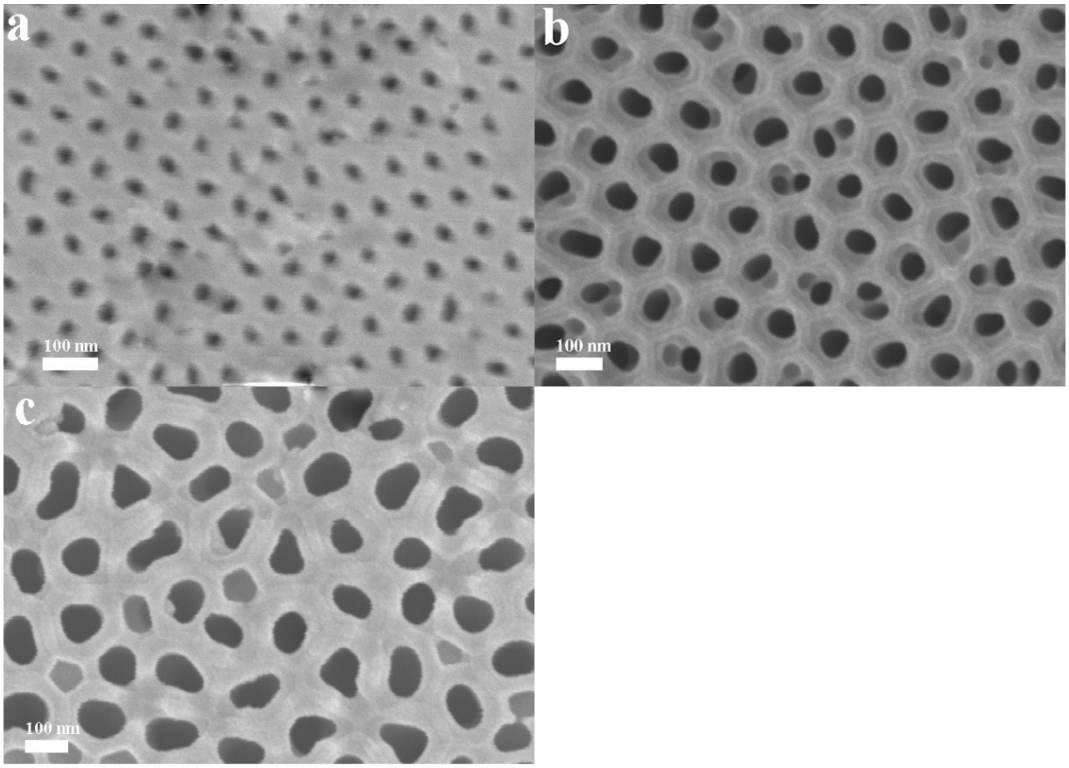

Fig. S2 SEM image of AAO with uniform diameter (a) D=26.3±3.2 nm, (b) D=74.8±1.9 nm, (c) D=117±4.6 nm

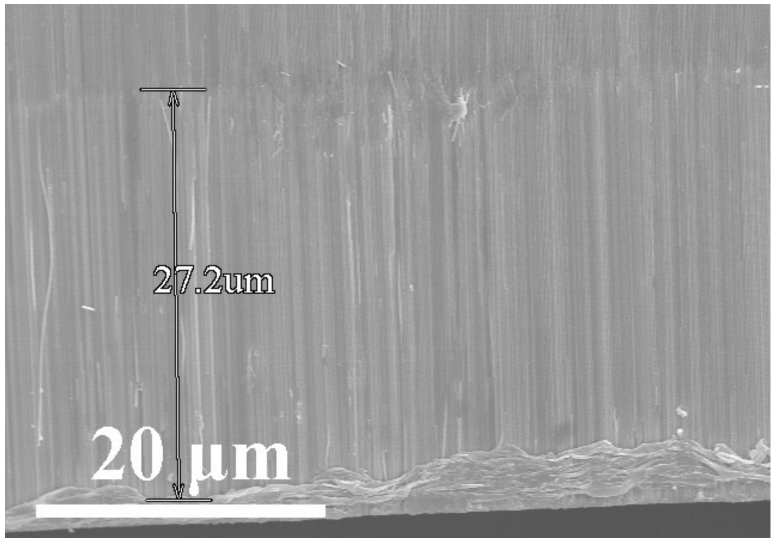

Fig. S3 SEM cross section image of AAO template with GDMNWs

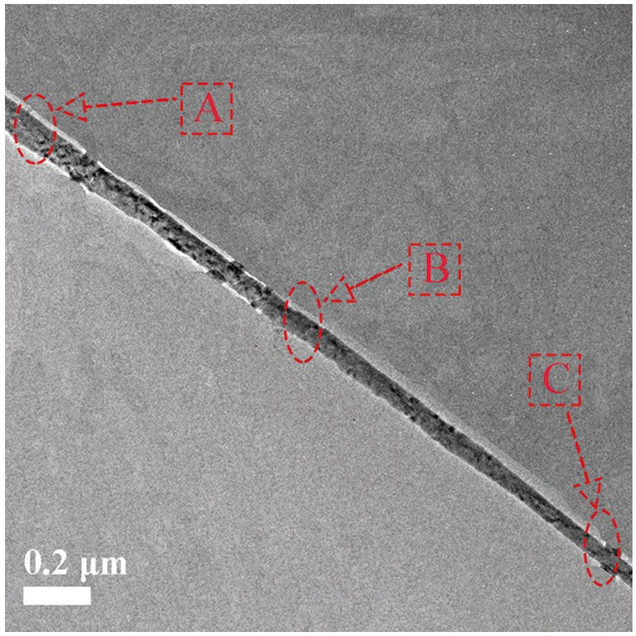

Fig. S4 TEM image of single gradient-diameter Fe-Co-Ni magnetic nanowire. Thick end A, middle part B and thin end C are three locations where EDX has been performed to check the compositions.

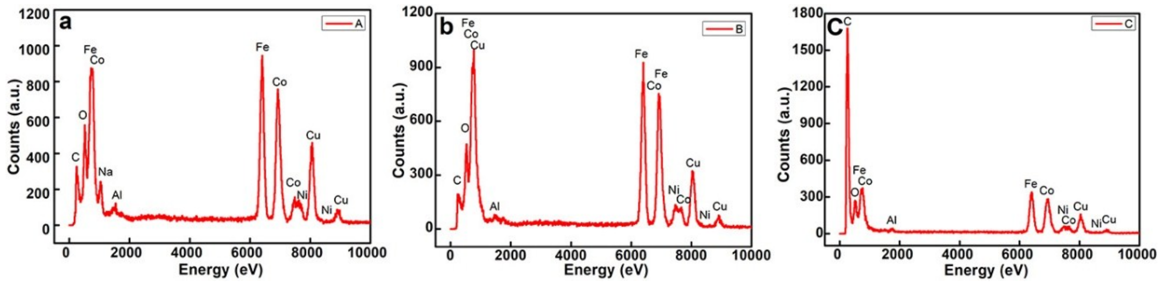

Fig. S5 EDS diagrams of thick end A (a), middle part B (b) and thin end C (c) of single gradient-diameter nanowire as shown in Fig. S4.

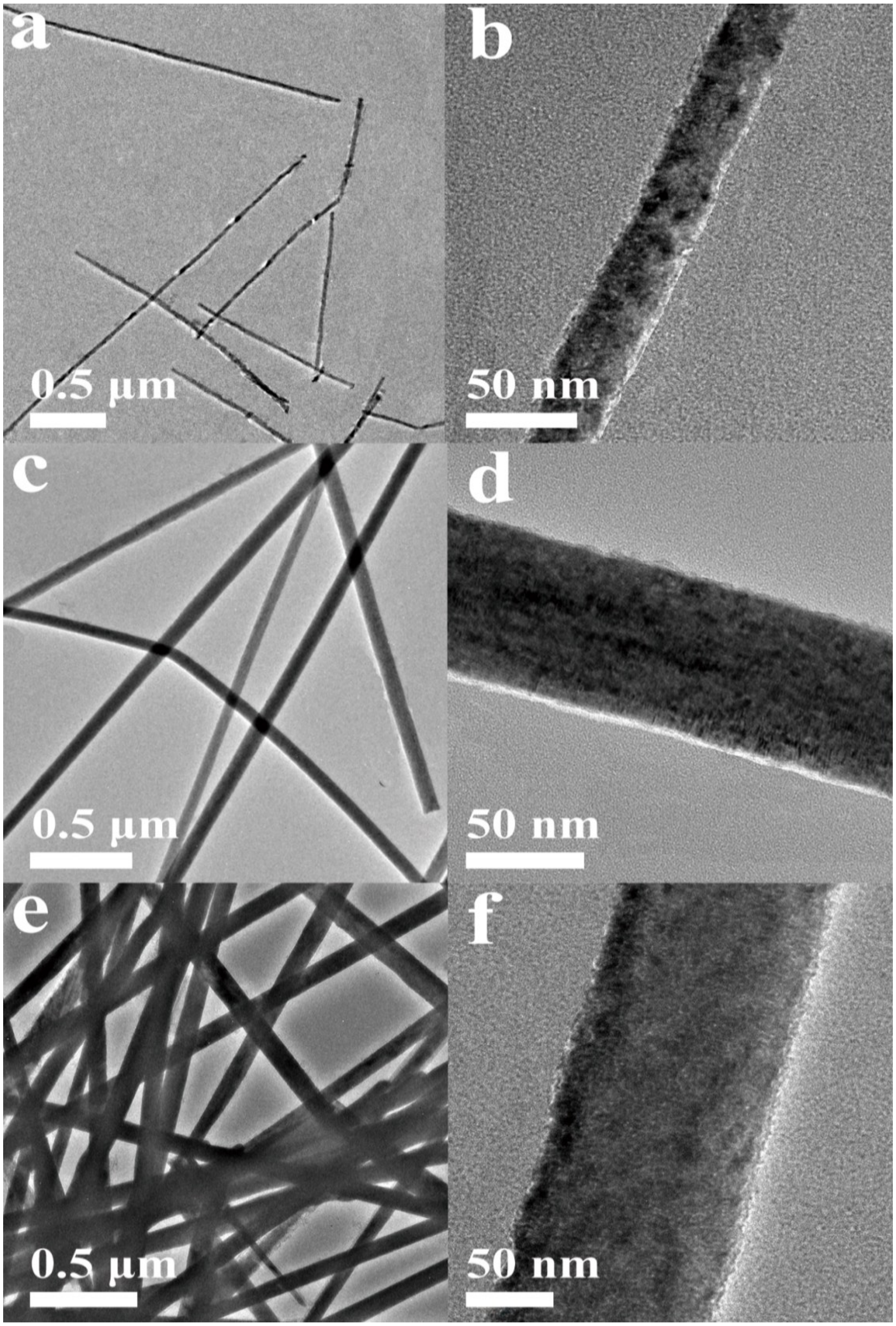

Fig. S6. TEM image of UDMNWs-1 (a) and single nanowire (b) of UDMNWs-1, TEM image of UDMNWs-2 (c) and single nanowire (d) of UDMNWs-2, TEM image of UDMNWs-3 (e) and single nanowire (f) of UDMNWs-3.

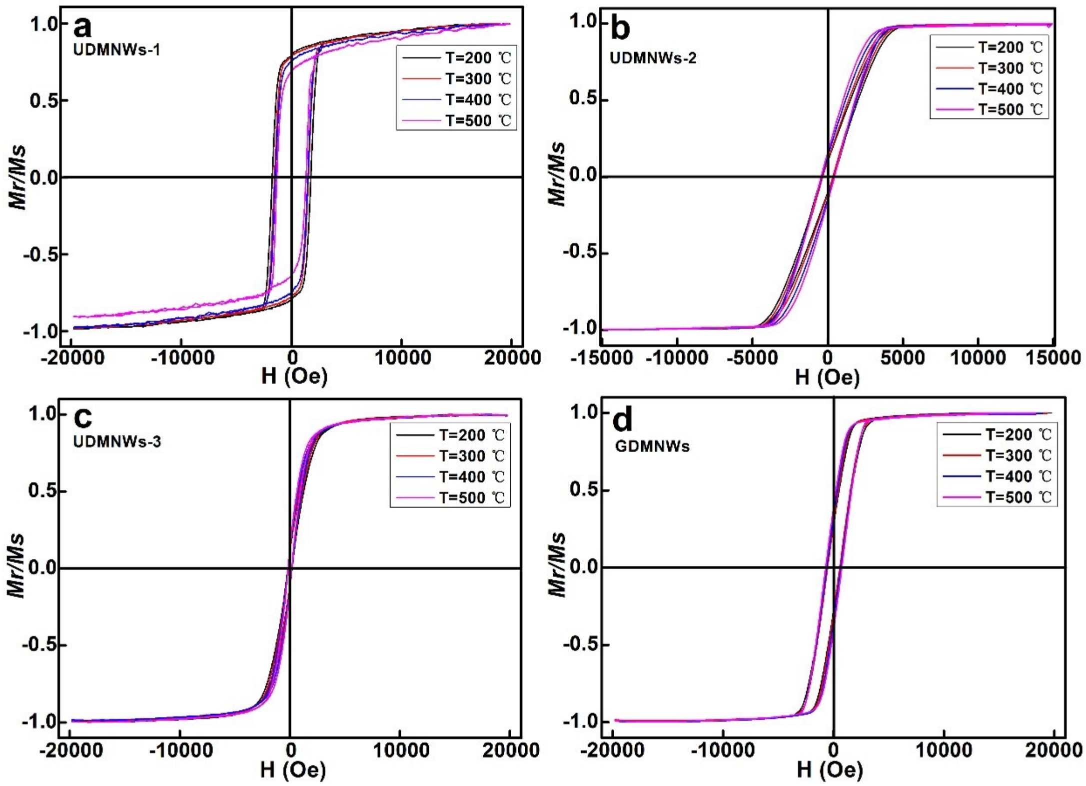

Fig. S7 Temperature-dependent hysteresis loops of (a) UDMNWs-1, (b) UDMNWs-2, (c) UDMNWs-3 and (d) GDMNWs.

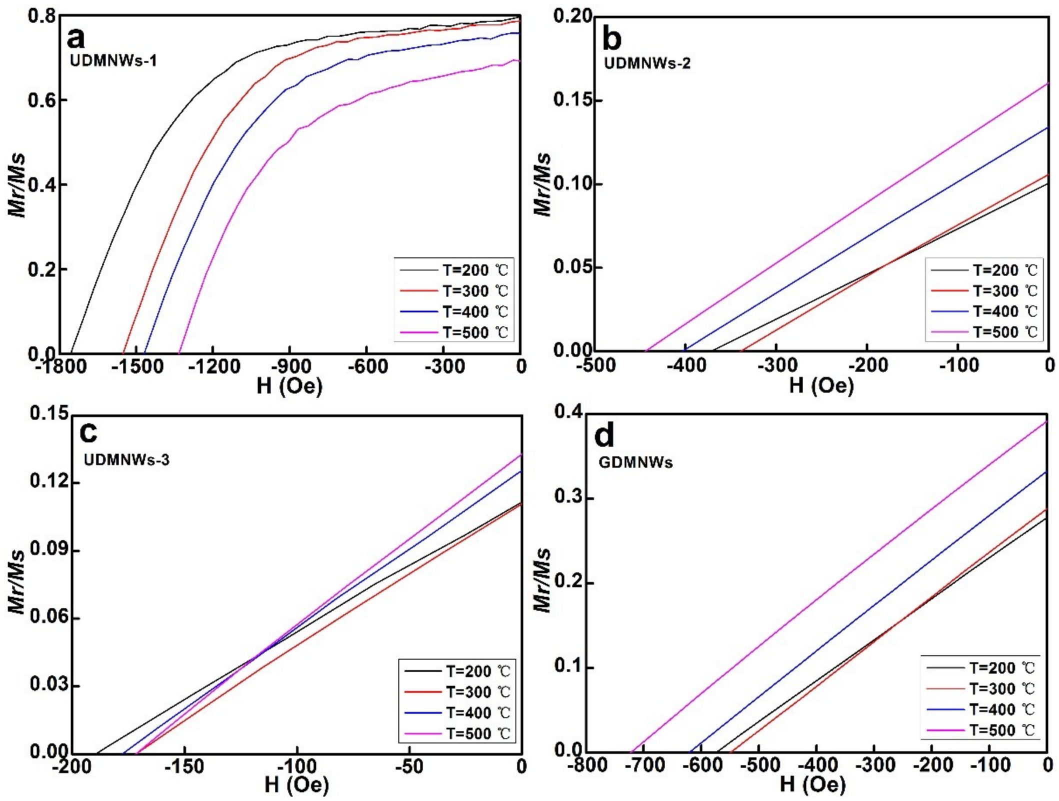

Fig. S8. Demagnetization curves of UDMNWs-1 (a), UDMNWs-2 (b), UDMNWs-3 (c), and GDMNWs (d) at elevated temperatures (from 200 to 500 ℃).

Table S1. Values of the diameter, edge-to-edge wire separation and the ratio of distance/diameter in AAO template with variously uniform diameter.

AAO template	Diameter *d* (nm)	Wire separation *s* (nm)	Separation/diameter (*s/d*)
AAO-1	26.3±3.2	84±3.4	3.19
AAO-2	74.8±1.9	76.1±5.6	1.02
AAO-3	117±4.6	103±8.4	0.88

Table S2. EDS analysis of single gradient-diameter nanowire.

Element	C (K)	O (K)	Na (K)	Fe (K)	Co (K)	Ni (K)	Cu (K)
Atomic (%)	60.98	9.51	0.29	10.13	10.11	4.13	4.82

Table S3a. The distribution of Fe, Co, and Ni at A as shown at Fig. S4.

Element	Fe	Co	Ni
Atomic (%)	50.9	41.9	7.2

Table S3b. The distribution of Fe, Co, and Ni at B as shown at Fig. S4.

Element	Fe	Co	Ni
Atomic (%)	49.5	43.0	7.5

Table S3c. The distribution of Fe, Co, and Ni at C as shown at Fig. S4.

Element	Fe	Co	Ni
Atomic (%)	49.8	42.4	7.8

Table S4. Values of the diameter, edge-to-edge wire separation and the ratio of separation/diameter in nanowire arrays with variously uniform diameter.

UDMNWs	Diameter *d* (nm)	Wire separation *s* (nm)	Separation/diameter (*s/d*)
UDMNWs-1	28.4 ± 1.4	84±3.4	2.95
UDMNWs-2	77.3±3.7	76.1±5.6	0.98
UDMNWs-3	122.3±6.4	103±8.4	0.84

Table S5. Values of the H_c, M_r/M_s and K_{eff} measured in four samples for each applied field direction.

Diameter	$H_{c\|\|}$ (Oe)	$H_{c\perp}$ (Oe)	$M_{r\|\|}/M_{s\|\|}$	$M_{r\perp}/M_{s\perp}$	K_{eff} (erg/cm^3)
UDMNWs-1	1999	278	0.963	0.044	6.72×10^7
UDMNWs-2	372	55	0.106	0.01	2.21×10^7
UDMNWs-3	266	87	0.091	0.017	1.76×10^7
GDMNWs	435	111	0.243	0.018	5.61×10^7

Where '$\|\|$' and '$\perp$' represent that the applied field H is parallel and perpendicular to nanowire axis, respectively.

Table S6. The $H_{c||}$ of the UDMNWs and GDMNWs at different measured temperatures.

Nanowire diameter	UDMNWs-1	UDMNWs-2	UDMNWs-3	GDMNWs
$H_{c||}$ (room temperature)	1999 Oe	372 Oe	266 Oe	435 Oe
$H_{c||}$ (T= 200 ℃)	1753 Oe	372 Oe	190 Oe	575 Oe
$H_{c||}$ (T= 300 ℃)	1552 Oe	339 Oe	171 Oe	549 Oe
$H_{c||}$ (T= 400 ℃)	1473 Oe	404 Oe	178 Oe	621 Oe
$H_{c||}$ (T= 500 ℃)	1336 Oe	443 Oe	171 Oe	722 Oe

References

[1] X. W. Wang and Z. H. Yuan, *Phys. Lett. A*, 2010, **374**, 2267-2269.

[2] H. Masuda and K. Fukuda, *science*, 1995, **268**, 1466-1468.