

# Electrochemical fabrication and magnetic properties of highly ordered silver–nickel core-shell nanowires

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## Abstract

Ordered silver–nickel core-shell nanowire arrays were successfully fabricated by electrodeposition. The ordered silver nanowire arrays embedded in a porous alumina template were first fabricated from an aqueous solution of  $\text{Ag}(\text{NO}_3)_2$  and  $\text{Ac}(\text{NH}_3)$ . After removing out the template, the obtained silver nanowire arrays were subsequently electrodeposited with nickel at 1.6–2.6 V and 60 °C using the electrolyte composed of  $\text{NiSO}_4$ ,  $\text{NiCl}_2$  and  $\text{H}_3\text{BO}_3$ . Transmission electron microscopy observation revealed that a  $\sim 15$  nm thick nickel film was coated on the surface of the silver nanowires with about 200 nm in diameter. It was found that the silver nanowires with nickel coating showed enhanced magnetic properties in comparison to that of pure silver nanowires. The magnetic force microscope image of silver–nickel core-shell nanowires showed magnetic domain state. In addition, the hysteresis loops of the silver–nickel nanowire arrays showed a coercive field of 180 Oe, almost independent of the applied magnetic field. However, it was observed that a larger magnetic domain was found in parallel direction than that in perpendicular direction.

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## 1. Introduction

The fabrication of magnetic metal arrays has been intensely investigated recently because they shows potential utilization in magnetic recording [1–5]. It was reported that magnetic period nanostructure arrays as an ultra-high-density magnetic storage can achieve recording densities of more than 100 Gbit/in.<sup>2</sup>, which is more than the continuous magnetic film of 40 Gbit/in.<sup>2</sup> [6–8]. Arrays of ferromagnetic nanodots, nanowires or nanotubes may be fabricated by several methods such as e-beam lithography, imprint technology or template. However, the porous template can be considered as one quicker and cheaper method to prepare highly perpendicular magnetic anisotropy structure [9–11] because anode alumina oxide (AAO) has high oriented porous structure with uniform and nearly parallel pores that can be organized for the pseudo ordered nanowires or nanotubes array.

On the other hand, it is well known that the ferromagnetic element such as Fe, Co, Ni and their alloy have higher saturation magnetization as well as Curie temperature, and lower crystalline anisotropy. Furthermore, magnetic properties are strongly influenced by the dimension and crystal properties, which also depend on the physical structure of templates and growth mechanism of wires or tubes. However, these ferromagnetic element or alloy exhibits a lower magnetic anisotropy because these materials were usually polycrystalline and possessed random magnetic domain. Thus, one new structure and process was proposed in order to obtain higher magnetic anisotropy in this study. The silver–nickel core-shell nanowires arrays by electrodepositing in AAO templates were synthesized and their magnetic properties were characterized. Furthermore, the effect of experimental conditions on the morphology of the core-shell nanostructure will be also discussed.

## 2. Experimental

Highly ordered AAO templates with pore diameter of about 200 nm were used from commercial porous alumina templates (Whatman 6809 7013). In the first stage, the silver electrolyte solution was prepared from  $\text{Ag}(\text{NO}_3)_2$  (0.005–0.02 M) and  $\text{Ac}(\text{NH}_3)$  (0.4 M). One side of AAO templates was sputtered

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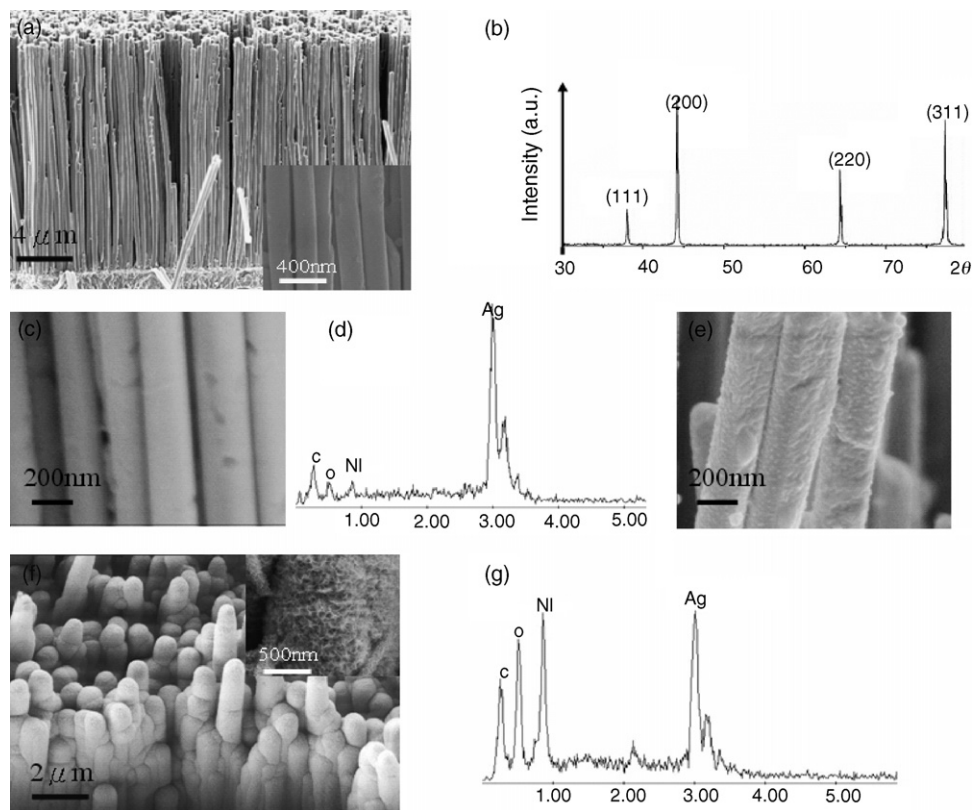


Fig. 1. (a) and (b) SEM image and its XRD spectrum of silver nanowires array, (c), (e) and (f) appearance and surface condition of nanowires under nickel electrodepositing at 1.6 V for 3, 6 and 30 min, respectively, and (d) and (g) corresponding composition of the nanowires electrodepositing for 3 and 30 min, respectively.

with 200 nm Au film as electrode layer. The coated template was first immersed in an aqueous solution and kept at low vacuum environment to enhance the solution into the pores. Subsequently, silver nanowire arrays were deposited in the pores from the electrolyte solution under constant current of 4 mA and voltage of 0.6–1.5 V at room temperature. For obtaining the isolated silver nanowire arrays, the sample was dissolved in 5 wt% NaOH solution at 25 °C for 20 min and then slightly washed several time to remove the original AAO template.

In the second stage, nanoscale nickel layer was coated on the silver nanowire surface by nickel ions electrodepositing. The electrolyte solution was prepared from  $\text{NiSO}_4 \cdot \text{H}_2\text{O}$  (0.8 M),  $\text{NiCl}_2 \cdot \text{H}_2\text{O}$  (0.48 M),  $\text{H}_3\text{BO}_3$  (0.6 M) and  $\text{H}_2\text{O}_2$  (30%, 0.01 M) and named as Watts bath which is one kind of typical nickel plating bath. The  $\text{NiSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot \text{H}_2\text{O}$  were used as the source for the major nickel hydrated ions and  $\text{H}_3\text{BO}_3$  worked as buffer agent in this bath with the pH value controlled between 2.0 and 5.2. The applied potential varied from 1.6 to 2.6 V and the temperature was controlled at 60 °C as electrodepositing. Then, silver–nickel core-shell nanowires were obtained.

The microstructure and morphology were characterized by transmission electron microscopy (TEM, JEOL JEM-2010F) and scanning electron microscopy (SEM, LEO 1530). X-ray diffraction (XRD, PW1700) and energy dispersive spectra are employed to study the crystal structure and chemical composition of silver–nickel core-shell nanowires. Atomic force microscope (AFM, SEIK SPA 300HV) and magnetic force microscope (MFM, SEIK SPA 300HV) imaging of nanowires exhibited surface morphology and magnetic domain state. The magnetic properties of silver–nickel core-shell nanowires were characterized using a vibrating sample magnetometer (VSM, DMS MODEL-1660).

### 3. Result and discussion

Silver nanowires grew up directly by electrodepositing into self-ordered nanopores AAO templates in acid silver ionic electrolyte with silver concentration from  $5 \times 10^{-3}$  to  $2 \times 10^{-2}$  M.

The electrodeposition was carried out with constant current of about 4 mA under the voltage in the range of 0.6–1.5 V. The scanning electron microscope (SEM) image of the nanowires is shown in Fig. 1(a). Most wires are about 200 nm in diameter and 23 mm in length on 2 μm thick bottom gold electrode within the pores, indicating all silver nanowires remain similar growth rate during the electrodeposition process so that more uniform and equal length silver nanowires can be obtained. The obtained nanowires were independently parallel with each other and the aspect ratio was estimated about 115. The gap among the synthesized nanowires was estimated from few nm to several 10 nm. The crystal structure of silver nanowires array was investigated by X-ray diffraction pattern. Fig. 1(b) shows the Ag face-centered cubic structure according to JCPDS card.

The formation of nickel coated layer or core-shell structure can be elucidated based on the reduction effect of nickel ions by electrodeposition. When the electrical field was applied along the wires during deposition, the  $\text{Ni}^{2+}$  ions were first moved into the gap between nanowires and reduced on the surface of the silver nanowires. Furthermore, it was found that the surface condition and composition of the nanowires varied with electrodeposition time from 3 to 30 min at 60 °C under an applied potential of 1.6 V, as shown in the SEM images of Fig. 1(c)–(g). In a short period of electrodeposition (3 min versus 6 min), the surface condition of the nanowires seems not to change obviously and remains smooth, implying that the coated Ni layer is very uniform. However, for a longer electrodeposition, i.e.,

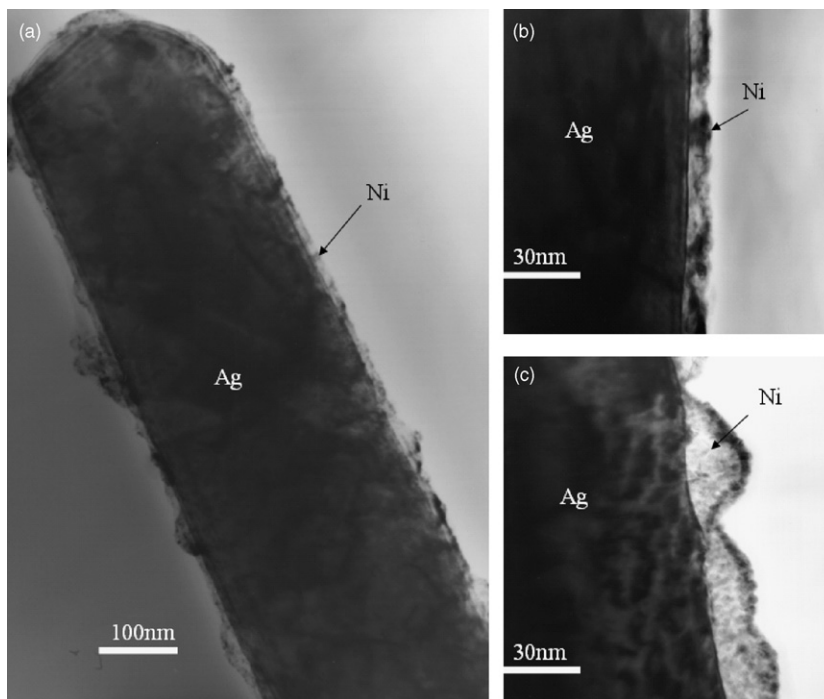


Fig. 2. (a) and (b) TEM images of nickel electrodeposited at 1.6 V for 3 min, and (c) formation of nickel particles after longer electrodeposition.

30 min, it was observed that many different type wires were formed and the surface became rougher as shown in Fig. 1(f). It could be deduced that several silver nanowires were covered by nickel layer to form capsular structure. A more detailed micrograph of the Ag–Ni core-shell structure was presented in the

TEM images of Fig. 2. As it was electrodeposited for 3 min, the thickness of the nickel layer coated on silver nanowire surface was approximately to 15 nm as measured from Fig. 2(b). As the electrodeposition was kept for 30 min, Fig. 2(c) shows that many 5–7 nm nickel grains of different crystalline orienta-

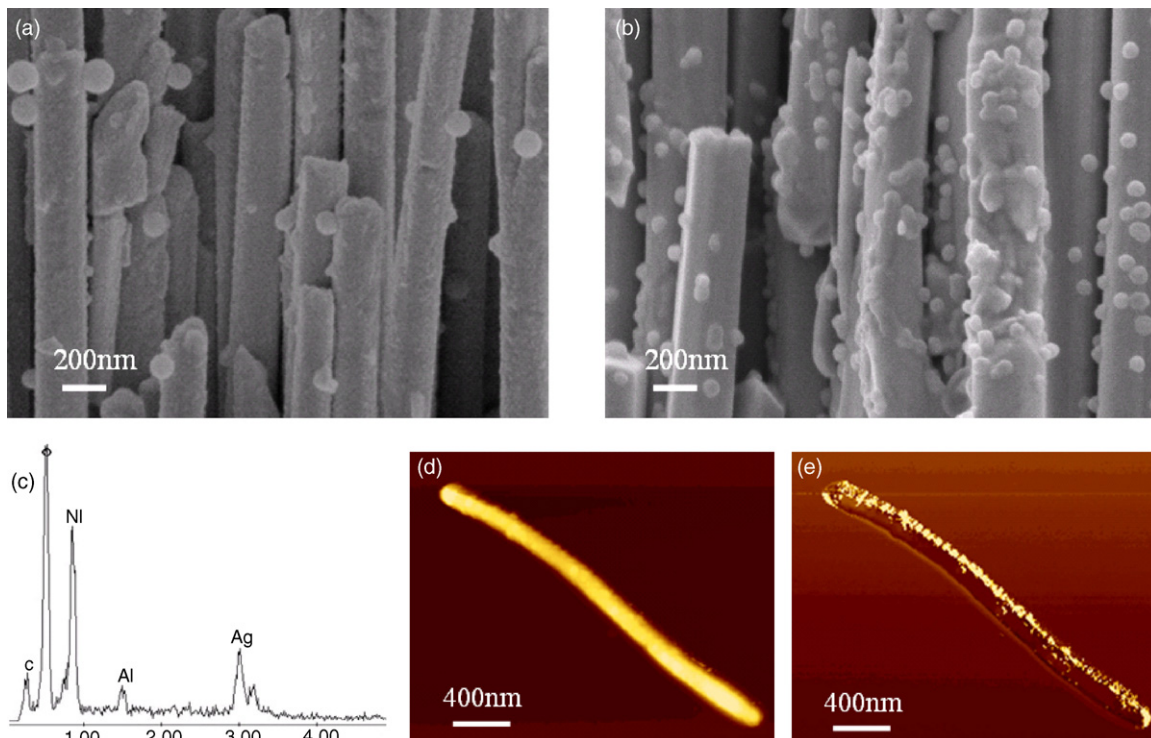


Fig. 3. (a) SEM image of nickel electrodeposition at 2.1 V for 3 min, and (b)–(e) SEM, EDS, AFM and MFM images of nickel electrodeposition at 2.6 V for 3 min, respectively.



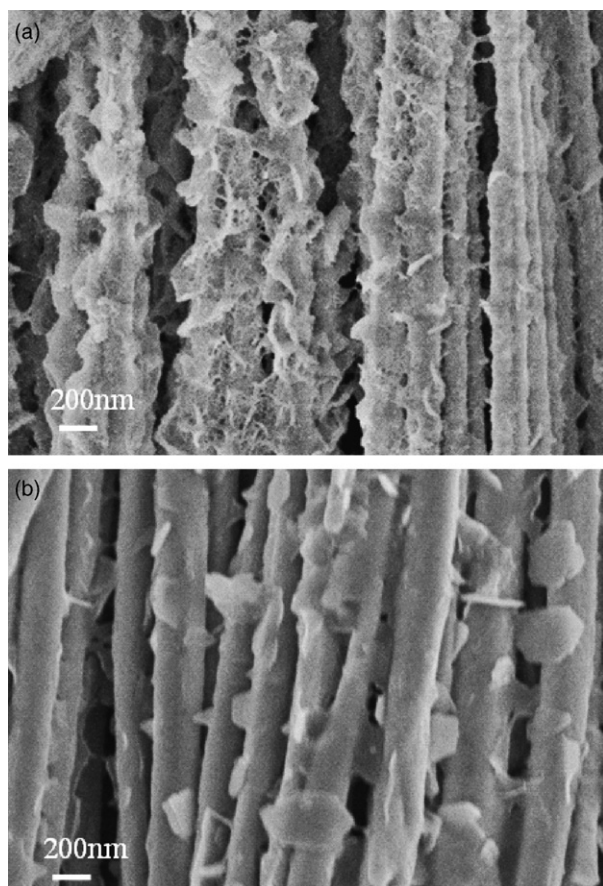


Fig. 4. (a) and (b) SEM images of nickel–cobalt electrodeposition with  $\text{Ni}^{2+}:\text{Co}^{2+} = 2:1$  and  $1:2$  at 2.1 V for 3 min, respectively.

tions were developed in the deposited Ni layer, leading a rougher surface.

Moreover, as various electrodepositing potentials were applied, different structure and morphology could be observed. Fig. 3(a) shows the SEM image of the Ag–Ni nanowires under an applied potential of 2.1 V for 6 min. The surface becomes rougher in comparison to that electrodeposited at 1.6 V. Besides, some small spherical nickel grains with the size of 50–100 nm were generated on the nanowire surface. A further increasing potential up to 2.6 V caused more spherical particles to be formed on the nanowire surface as shown in Fig. 3(b). Energy dispersion X-ray spectra of Fig. 3(c) confirm the presence of pure spherical nickel. The AFM image of the core-shell nanowires in Fig. 3(d) indicates that the spherical nickel particles were coated on the nanowires. Furthermore, the magnetic force microscope (MFM) image in Fig. 3(e) exhibits many discrete magnetic nanoscale domains, as shown in bright contrast part, on the surface of silver nanowire.

On the other hand, it was reported that the cobalt–nickel alloy can show enhanced coercivity in comparison with pure nickel nanowire arrays [12]. Therefore, in this study, the role of cobalt in the magnetic properties was further investigated. The cobalt ions were added into the Watts bath by using  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  and relative ion ratio of  $\text{Ni}^{2+}:\text{Co}^{2+}$  was adjusted to be 2:1 and 1:2. The electrodeposition was carried out at an applied potential of 1.6 V. It was observed that it exhibits a special structure, dis-

tinguished from that of pure nickel type. Fig. 4(a) shows the irregular cobalt–nickel alloy with scrap-like shape obtained on silver nanowire surface in the condition of  $\text{Ni}^{2+}:\text{Co}^{2+} = 2:1$ . In contrast, for  $\text{Ni}^{2+}:\text{Co}^{2+} = 1:2$ , cobalt–nickel alloy sheets were formed on the surface of the Ag nanowires as shown in Fig. 4(b). The morphology transition from scrap to sheet that may be related to the change of crystal structure because nickel and cobalt belong to FCC and HCP, respectively. More detailed analysis and comparison are under investigation.

The magnetic properties of the core-shell nanowire arrays were investigated using vibrating sample magnetometer. Fig. 5

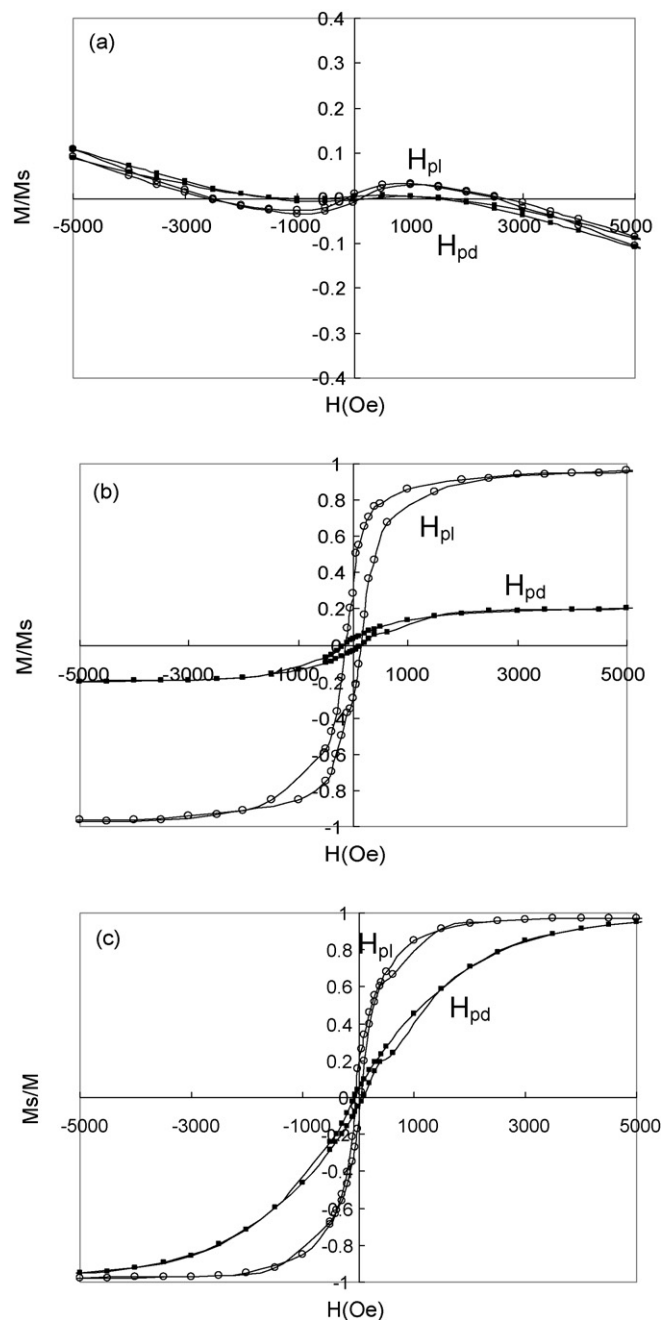


Fig. 5. (a) Hysteresis loop of pure silver nanowire arrays measured at room temperature, and (b) and (c) hysteresis loop of silver–nickel core-shell nanowire arrays under nickel electrodeposition at 1.6 and 2.6 V for 3 min, respectively.

shows the hysteresis loop of the silver–nickel core-shell nanowires array measured at room temperature. The  $H(\text{pl})$  and  $H(\text{pd})$  represented external magnetic field parallel to nanowires and perpendicular to nanowires, respectively. While the silver nanowires was not yet coated with nickel, no clear hysteresis loop was detected as shown in Fig. 5(a), indicating that silver does not show magnetic characteristics.

In contrast, as the silver–nickel core-shell was fabricated under an applied potential of 1.6 V, distinct hysteresis loop appears in Fig. 5(b), indicating the formation of nickel crystalline structure. It was also found that both saturation magnetization ( $B_s$ ) and remanence ( $B_r$ ) of  $H(\text{pl})$  were larger several times than those of  $H(\text{pd})$ . However, the coercive field ( $H_c$ ) measured in both  $H(\text{pl})$  and  $H(\text{pd})$  orientations are close (about 180 Oe). As compared with the  $H_c$  of pure Ni or Co nanowires (about 300–1300 Oe), it implies that the core-shell array are more suitable for magnetic recording. As the silver–nickel core-shell was synthesized at a higher applied potential of 2.6 V, it was observed that both  $B_s$  and  $B_r$  values in both  $H(\text{pl})$  and  $H(\text{pd})$  are nearly equal as evidenced from Fig. 5(c). However, the hysteresis loop of the silver–nickel core-shell fabricated at 1.6 and 2.6 V shows different magnetic anisotropy and this indicates that the easily magnetized direction was parallel to the nanowires axis. In other words, nickel layer could generate larger magnetic domain in parallel direction than that in perpendicular direction. Therefore, it can be concluded that the strong magnetic anisotropy exists in silver–nickel core-shell structure.

#### 4. Conclusions

A two-stage process including AAO process and electrodeposition was applied to fabricate the ordered silver–nickel

core-shell nanowire arrays. Transmission electron microscopy (TEM) observation reveals that a 15 nm thick nickel film was coated on the surface of the silver nanowires with about 200 nm in diameter. The silver nanowires with nickel coating show enhanced magnetic properties compared to that of pure silver one. The magnetic force microscope (MFM) image of silver–nickel core-shell nanowires exhibits magnetic domain state. The hysteresis loop of the array demonstrates strong magnetic anisotropy with the easily magnetized direction perpendicular to the core-shell nanowires axis.

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