

Magnetic properties and Mössbauer spectroscopy of iron nanowire arrays prepared by electroless deposition in a magnetic field

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One-dimensional magnetic iron (Fe) nanowire arrays with tunable diameters have been deposited in the pore channels of the anodised aluminium oxide (AAO) template using the electroless chemical method. The AAO template is processed by a facile and simple approach to etch an insulating alumina barrier layer in the base of the template. The morphologies and crystal structures of Fe nanowires are characterised by field emission scanning electron microscopy, atomic force microscopy and X-ray diffraction. Mössbauer spectroscopy suggests that the nanowires are composed of ferromagnetic particles. The results of magnetic measurements by a superconducting quantum interference device indicate that the nanowire arrays have obvious magnetic anisotropy, and the easy magnetisation direction is oriented along the nanowire axial direction.

1. Introduction: Nanostructured magnetic materials have a variety of promising applications ranging from nanoscale electronic devices, sensors and high-density data storage media to controlled drug delivery and cancer diagnostics/treatment systems [1]. The one-dimensional (1D) structures such as nanowires, nanorods and nanotubes have attracted great interest in interconnects and functional blocks [2]. Template synthesis methods, such as electro-deposition [3–5], electroless deposition [6], sol–gel [7, 8], chemical polymerisation [9] and chemical vapour deposition [10], are very effective methods for fabricating 1D nanostructure materials. Among them, the electroless deposition method with anodised aluminium oxide (AAO) templates is believed to be a direct and cost-effective method to synthesise nanowire arrays. Meanwhile, the AAO template with different sizes and parallel porous channels can be controlled by changing the anodising conditions [11, 12].

It is well known that there is an insulating alumina barrier layer in the base of the AAO template after the second anodisation. Removing the barrier layer is the key to successfully synthesise 1D nanostructure materials. Many groups dissolve this barrier layer by dipping the template into a phosphoric acid solution after removing the backside aluminium (Al) sheet. Subsequently, they sputter an ultrathin layer of metal serving as an electrode on one surface side of the AAO template. Finally, the template is used to prepare different metal materials using electro-deposition. In this Letter, we report a facile approach to barrier layer thinning and perforation.

Previously, our research team has synthesised and characterised several monodisperse magnetic nanoparticle systems [13–17]. Here we demonstrate that iron (Fe) nanowires can be formed in AAO templates immersed in ferrous chloride (FeCl_2) solution by the electroless deposition method. This method provides a simple way to synthesise metal nanowires. Meanwhile, this Letter will help understand the growth mechanism and magnetic properties of ferromagnetic nanowires. The filling fraction of the Fe nanowires within the pores of AAO templates is very high (almost 100%). Mössbauer spectroscopy (MS) reveals that the Fe nanowires are ferromagnetic. Magnetic measurements of Fe nanowire arrays indicate that they exhibit obvious magnetic anisotropy behaviour and that the easy magnetisation axis is parallel to the axial direction of the wire.

2. Experiment: For many years, AAO templates with ordered pore arrays have been prepared under voltage in different

electrolytes [18]. AAO templates have also been fabricated via the two-step anodisation process [19–21]. After the second anodisation, the template was left in the same solution and the anodisation voltage was reduced stepwise with a rate of 1 V every 1 min. When the voltage was reduced to 5 V, the AAO template was connected as the cathode and the voltage of -5 V was applied for several minutes. Finally, the current rapidly increased in this process and the voltage was disconnected.

The formation of Fe nanowire arrays was achieved by immersing the template into a 50 ml Teflon autoclave with a permanent magnet (4000 Oe). The reaction solution is 1 M FeCl_2 aqueous solution. The AAO template was enveloped by the Teflon bracket, followed by hydrothermal treatment at 423 K and then cooled naturally to room temperature. The reaction time could influence the length and shape of the nanowires. The schematic picture of the synthesis is shown in Fig. 1. After rinsing with deionised water and ethanol several times, the resulting AAO template with Fe nanowires was dried overnight in vacuum. A similar approach could be used to prepare magnetic metal or metal alloy nanowires.

Microstructures of the Fe nanowire arrays were observed by a field emission scanning electron microscope (FESEM, SU-70) with energy dispersive X-ray spectroscopy (EDX) and atomic force microscopy (AFM). The phase of the resultant nanowires was checked by X-ray diffraction (XRD, Brucker-D8) with Cu-K α radiation. Mössbauer spectra (MS) with a source of ^{57}Co were used to investigate the micro-magnetic structure of the Fe nanowires and fitted using the Gauss-Newton method. Magnetic properties were measured using a superconducting quantum interference device (SQUID, Quantum Design). The direction of the field is parallel or perpendicular to the nanowire axis.

3. Results and discussion: As can be seen from Fig. 2, the AAO template by two-step anodisation has a hexagonal pores arrangement with a uniform pore diameter. The pore size is 60 ± 2 nm, as seen from the inset in the top right corner of Fig. 2. The length of the nanowire arrays could be finely controlled. Here the length is about $36 \mu\text{m}$ and the aspect ratio exceeds 600. An etching step was carried out for insulating alumina barrier layer thinning and perforation. With the purpose of removing the barrier layer at the bottom of the nanopores, the applied voltage was reduced stepwise right after the second anodisation. As the pore diameter is proportional to the voltage, the pores growing into the barrier layer with a smaller diameter are caused by the

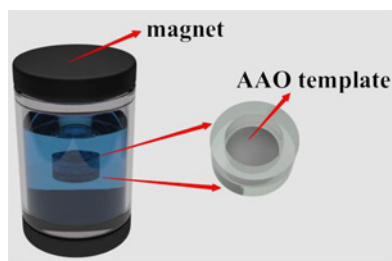


Figure 1 Schematic pictures of the formation of Fe nanowire arrays under a magnetic field

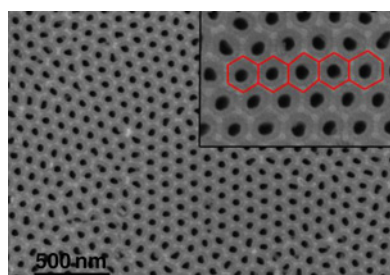


Figure 2 FESEM images of a typical porous alumina film by two-step anodisation

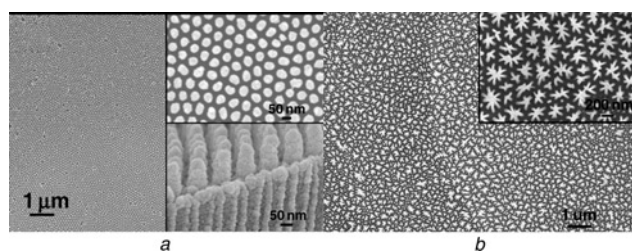


Figure 3 FESEM images of Fe nanowire arrays under different deposition times
a 3 h
b 6 h

stepwise reduction of the voltage. Small branched pores grow into the barrier layer and cause its perforation. When the current rapidly increased in a short time, the barrier layer was removed. After this process, rather uniform arrays of the AAO nanowells are formed.

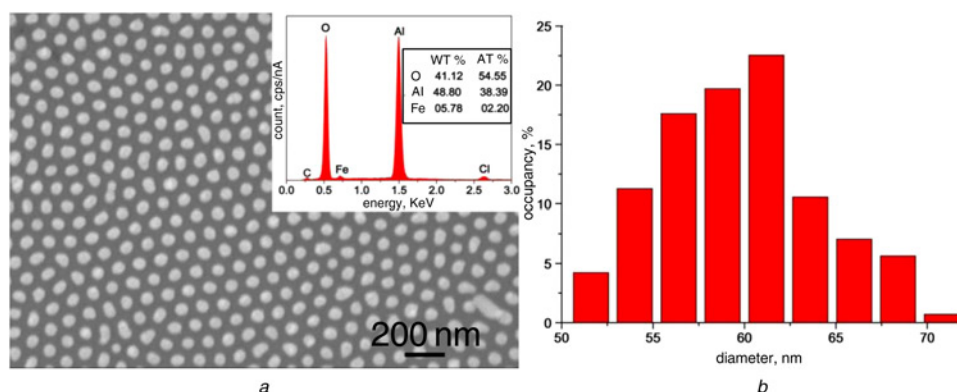


Figure 4 SEM top view image of the Fe nanowire arrays, and histogram of the wire diameter distribution
a SEM top view image of the Fe nanowire arrays
b Histogram of the wire diameter distribution
Inset in the top right corner (Fig. 4a) is the EDX analysis of Fe nanowire arrays

The morphologies of the Fe nanowire arrays are illustrated in Fig. 3. By adjusting the deposition time, uniform and highly ordered nanowires can be obtained in a short time (Fig. 3a), while the nanowires snuggled up together can be obtained within a longer time (Fig. 3b). In Fig. 3a, the right bottom inset is a cross-sectional scanning electron microscopy (SEM) image. The nanowires, which are tightly wrapped by the template, have the same size of the AAO nanopores (see the inset). The nanowire arrays depositing for 3 h are well aligned and parallel to each other. Fig. 3b shows that the nanowires depositing for 6 h are huddled together like a haystack. Therefore the morphology of Fe nanowires greatly depends on the growth time. Owing to the applied magnetic field in the process of deposition, the Fe nanowire arrays are very compact.

An SEM top view image of the Fe nanowire arrays is displayed in Fig. 4a and the histogram of the wire diameter distribution is shown in Fig. 4b. The diameter of the nanowires is 60 ± 2 nm, in good agreement with the pores size of the AAO template. Therefore the nanowires with different diameters can be obtained by changing the nanopore sizes of the AAO template. The EDX analysis of the Fe nanowire arrays is shown as the inset in Fig. 4a. The Figure indicates the presence of the Fe element apart from Al and O, suggesting that the composition of nanowires is Fe. The Al and O peaks belong to the AAO foil and the Cl element is from FeCl_2 . In the deposition process, the Fe ions get the electrons and are reduced to Fe on the Al surfaces (after etching the barrier layer). Then, with the duration of time, the nanowires are formed. This process can be considered as a galvanic cell reaction in which Al is oxidised to Al^{3+} and Fe^{2+} is reduced to Fe.

Fig. 5 shows the AFM images of the Fe nanowires fabricated on the surface of the AAO templates. The nanowires are uniform and highly ordered. Therefore large-scale uniform Fe nanowire arrays can be synthesised by electroless deposition. Furthermore, the XRD pattern shown in Fig. 6 indicates a single diffraction peak (1 1 0) of the cubic Fe phase (JCPDS File No. 03-1050), suggesting that the Fe nanowires are preferentially oriented in the [1 1 0] direction.

The MS shown in Fig. 7 is used to investigate the micro-magnetic structure of the Fe nanowire arrays. The spectrum was collected at room temperature, under a zero magnetic field, where the γ -ray was applied parallel to the nanowire axis ($\theta = 0$). The spectra were fitted by the Gauss-Newton method. The fitting parameters like isomer shift (I_s), quadrupole splitting (Q_s) and hyperfine field (H_f) are listed in Table 1. The spectra contain a single line spectrum and a six-line spectrum. The single line spectrum suggests a superparamagnetism nature, while the six-line spectrum indicates a ferromagnetic nature. The fraction of the ferromagnetic component is about 85%. Therefore the nanowires mainly show

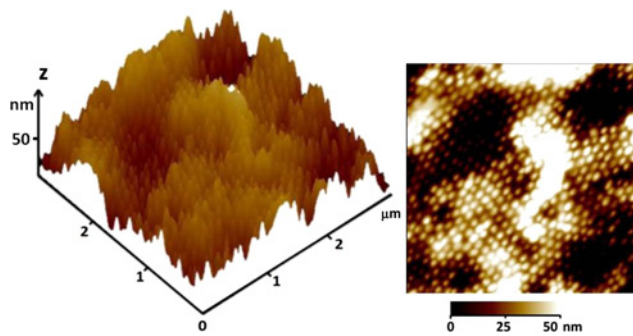


Figure 5 AFM images of Fe nanowire arrays fabricated on the surface of AAO templates

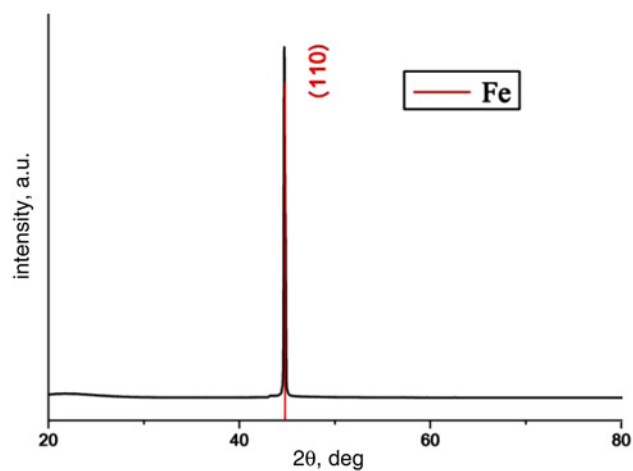


Figure 6 XRD of Fe nanowire arrays with a deposition time of 3 h

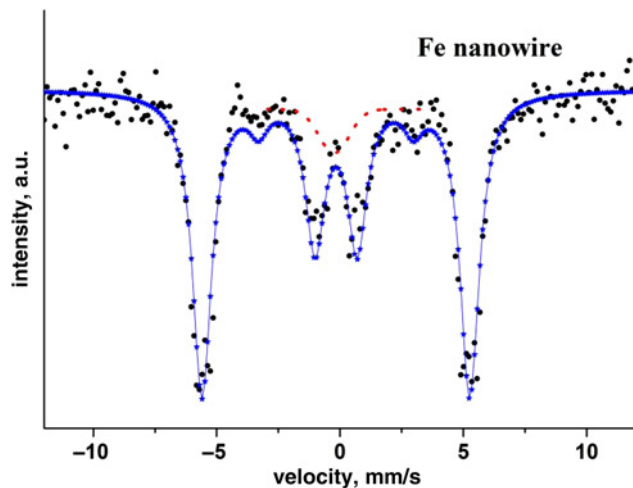


Figure 7 MS of Fe nanowires embedded in the AAO template

Table 1 Isomer shift (I_S), quadrupole splitting (Q_S) and hyperfine field (H_f) of Fe nanowire

I_S , mm/s	Q_S , mm/s	H_f , kOe
0.16 ± 0.01	0.001 ± 0.01	330.96 ± 0.37

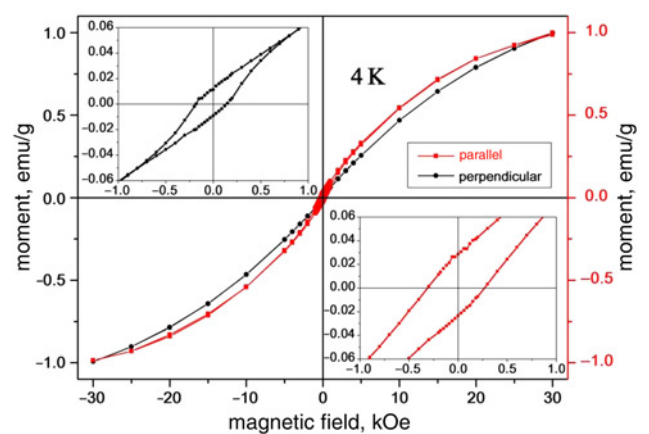


Figure 8 Magnetic hysteresis loops of Fe nanowires at 4 K with the applied field parallel (red line) and perpendicular (black line) to the film surface

the ferromagnetic phase. The relative intensity of the six-hyperfine transition is

$$I_1:I_2:I_3:I_4:I_5:I_6 = 3: \frac{4 \sin^2 \theta}{1 + \cos^2 \theta} : 1:1: \frac{4 \sin^2 \theta}{1 + \cos^2 \theta} : 3 \\ = 3:0:1:1:0:3$$

As seen from Fig. 7, the second and the fifth peaks in the six-line pattern do not show up, which indicates that the nanowire arrays have obvious perpendicular magnetic anisotropy [22]. Hence, we can conclude that the Fe nanowire arrays show ferromagnetism and the nanowires have perfect orientation.

The magnetic hysteresis loops ($M-H$, Fig. 8) of the Fe nanowire arrays are gauged at a maximum field of 30 000 Oe recorded at 4 K. The parallel represents the external magnetic field parallel to the nanowire axial direction and the perpendicular represents the applied magnetic field perpendicular to the nanowire axial direction. The coercivities (H_C) of the Fe nanowire arrays for parallel and perpendicular orientations are 310 and 180 Oe, respectively. This suggests that the easy magnetisation axis of the Fe nanowire arrays is parallel to the axial direction probably because of the shape anisotropy and magneto-crystalline anisotropy.

The easy magnetisation axis is a very important parameter in many applications. Therefore the magnetism of the arrays in parallel to the axial direction of the nanowires is often studied. The temperature dependences of the zero-field-cooled (ZFC) and field-cooled (FC) magnetisations in a magnetic field of 500 Oe are shown in Fig. 9. The field is applied parallel to the axial direction of the

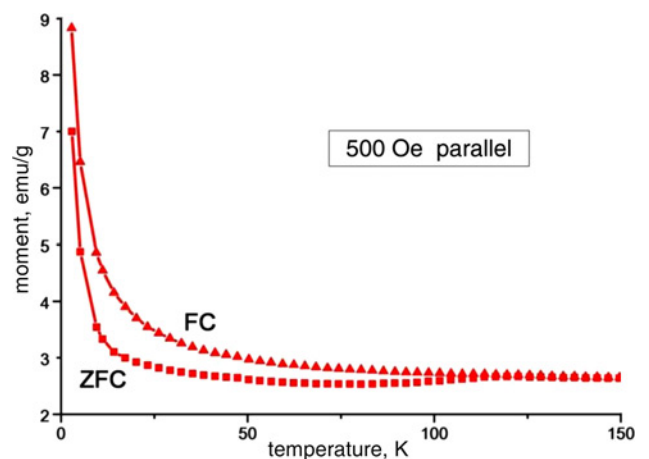


Figure 9 ZFC and FC magnetisation curves for the Fe nanowire arrays measured under a 500 Oe field parallel to the wire axial direction

nanowires. The blocking temperature (T_B), which refers to the bifurcation of the ZFC and FC curves, is 120 K, far below room temperature. No peak in Fig. 9 is seen, suggesting that the nanowires are not in a superparamagnetic state. The nanowire arrays mainly show ferromagnetism because the sample contains a small fraction of the superparamagnetic component, as demonstrated in the MS.

4. Conclusion: In summary, Fe nanowire arrays with tunable diameters have been successfully prepared using a simple and facile method. The barrier layer can be removed by decreasing the applied voltage in a stepwise manner after the second anodisation is complete. The Fe nanowire arrays exhibit obvious magnetic anisotropy behaviour, showing ferromagnetism. The easy magnetisation direction is oriented along the nanowire axial direction, which makes for possible use as high-density magnetic storage media. Our Letter provides a simple way to synthesise magnetic metals or metal alloy nanowires.

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6 References

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