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Exchange-Biased Hybrid Ferromagnetic-Multiferroic Core-Shell Nanostructures

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METHODS

Materials. All of the chemicals include the bismuth nitrate (Bi(NO$_3$)$_3$ 5H$_2$O), iron nitrate (Fe(NO$_3$)$_3$ 9H$_2$O), nickel chloride (NiCl$_2$) and 2-methoxyethanol were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. These precursors were used without any further purification. Anodic aluminum oxide (AAO) templates with a diameter of 300 nm were bought from PUYUAN NANO Corp and AAO templates with a diameter of 120 nm were obtained by a two-step electrochemical anodization process of aluminum sheet.

Synthesis. BiFeO$_3$ nanotubes were fabricated by sol-gel method. The sol-gel precursor was carefully optimized and prepared as follows: high purity Bi(NO$_3$)$_3$·5H$_2$O and Fe(NO$_3$)$_3$·9H$_2$O with a molar ratio of 1.15:1 were dissolved in 2-methoxyethanol. The concentration of the sol was adjusted to 0.3 M and pH of the sol solution was adjusted by adding appropriate amount of nitric acid. The sol was stirred for 1 hour at room temperature. AAO templates with two different pore sizes: 300 nm and 120 nm were then dipped into the sol for 15 min. The surface of the template was cleaned thoroughly before the heat treatment. Templates containing the precursors were annealed at 500 ℃, 600 ℃ and 700 ℃ respectively.

For the synthesis of Ni nanotubes, gold (Au) layer of thickness ~10 nm was first sputtered on one side of the AAO template with the BFO nanotubes inside. For the fabrication of Ni nanowires, copper (Cu) layer with a thickness ~ 200 nm was sputtered serving as the conductive contact. Then electrodeposition is carried out

potentiostatically at room temperature with a constant voltage of -1.0 V versus saturated calomel electrode (SCE) in an aqueous solution of nickel chloride ($NiCl_2$). Concentrations of the electrolytes were 2 M and 0.2 M for the deposition of Ni nanowires and nanotubes respectively. VersaSTAT 3 (Princeton Applied Research) was employed for electrodeposition by using VersaStudio Electrochemistry Software to control the applied potentials.

Characterization. The morphologies the nanostructures were characterized by high resolution scanning electron microscope (SEM; Hitachi S-4800 operated at an accelerating voltage of 10 kV) and Transmission electron microscope (TEM; JEOL 2011 with an accelerating voltage of 200 kV). Both the SEM and TEM analyses were performed after dissolving the AAO template in 1 M NaOH solution. Gold (copper)-coated side of a small piece of alumina template was attached to the carbon tape on the SEM holder. For TEM analysis, the AAO templates were completely dissolved in 1 M NaOH for 12 h at 60 ℃. After that the samples were washed thoroughly with distilled water. Then the samples were dispersed into ethanol and put into ultrasonic bath for about 30 s to make sure the nanostructures are well separated from each other. A few drops of solution were dripped onto TEM grid for analysis.

The structural analysis of the BFO nanotubes was obtained from X-ray diffraction (RIGAKU; D/MAX-2400) results. Atomic force microscopy (AFM; Nanonscope Ⅲa D3000) was used to give the surface profile of the AAO template filled with BFO nanotubes. The ferroelectric characteristic of the BFO nanotubes was studied by

ferroelectric tester (Radiant; Premier II). Magnetic hysteresis curves (M-H) of the Ni-BFO core-shell nanostructures were measured by vibrating sample magnetometry (VSM; Microsense EV-9).
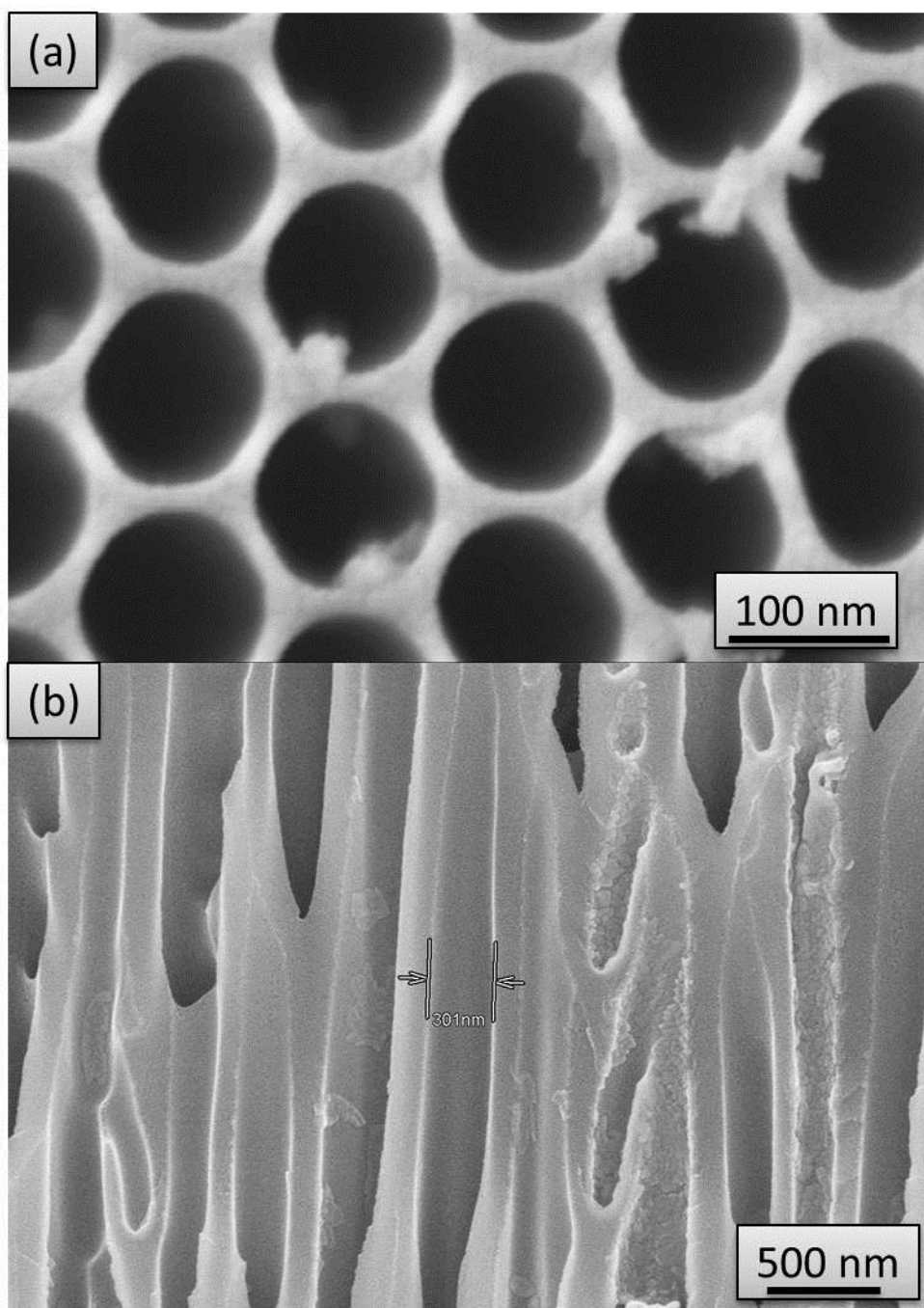

Figure S1. Characterizations of the AAO template: (a) A typical top view of the porous alumina template with a diameter of 120 nm; (b) A cross-sectional SEM image of the 300 nm diameter AAO template.
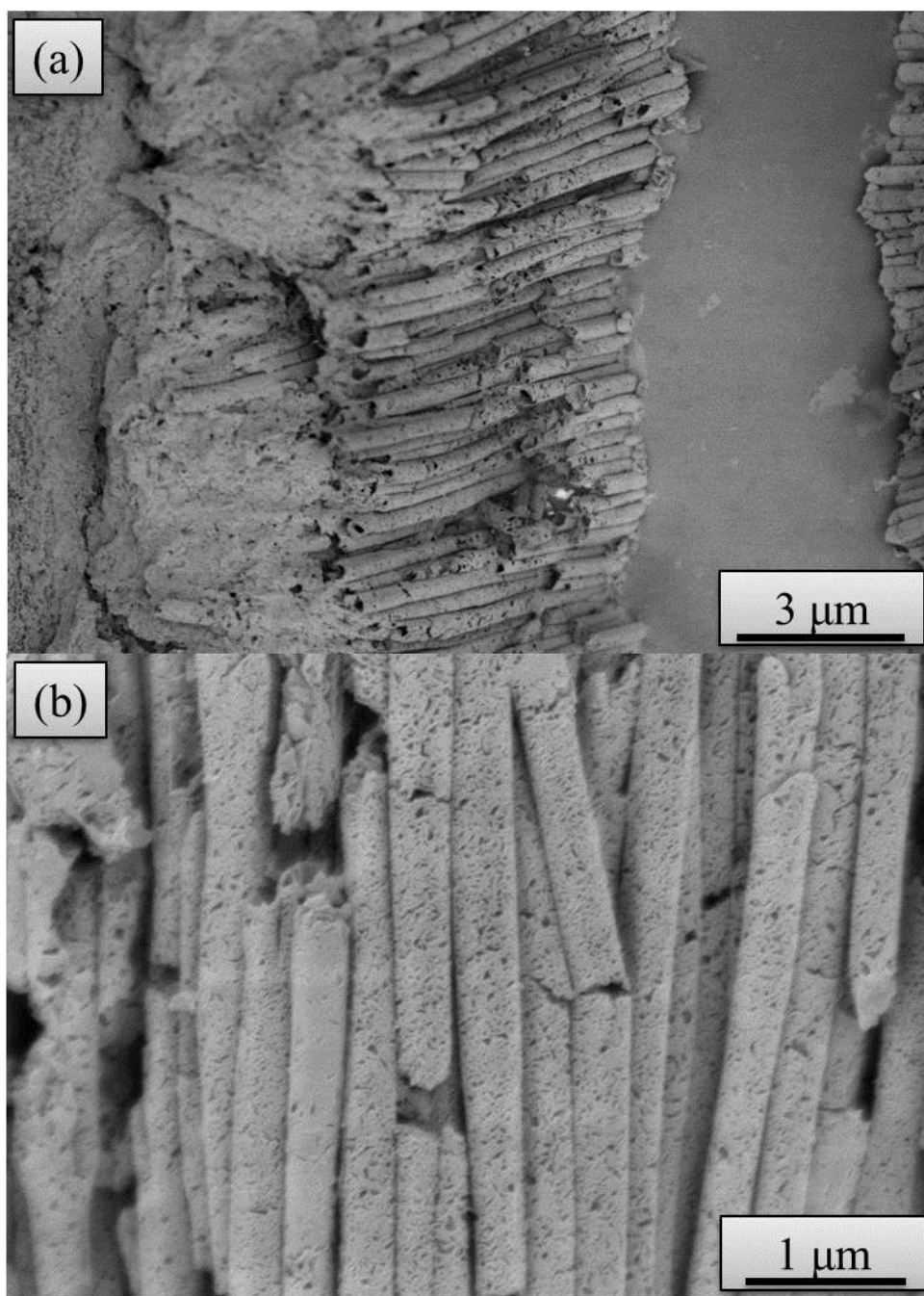
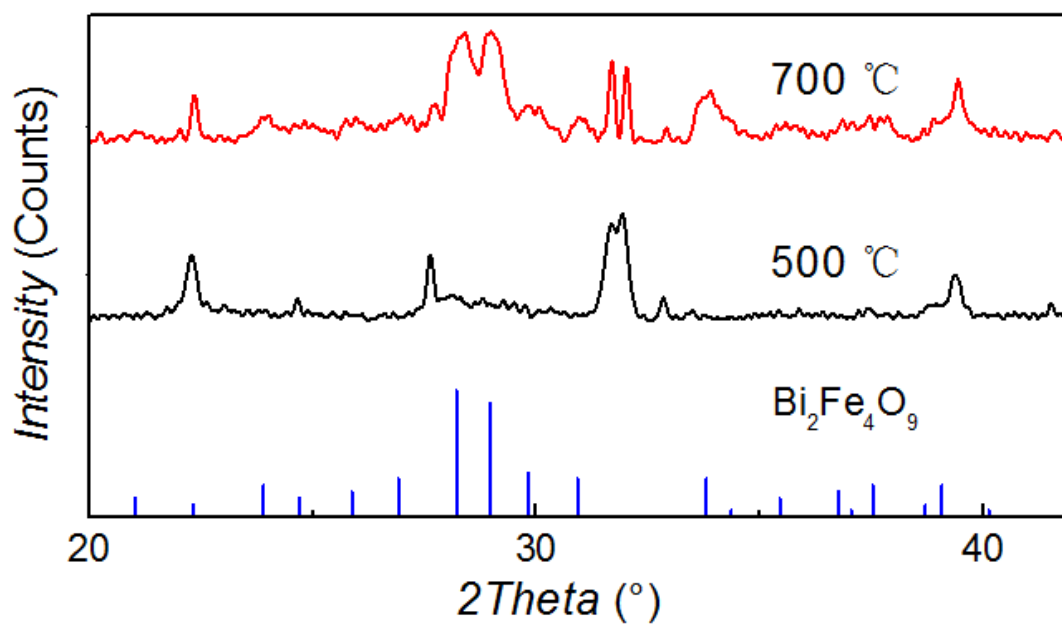Figure S2. SEM images of the porous 1D BFO nanostructures formed when the infiltration of the precursor is not sufficient.

Figure S3. XRD spectrum of the nanotubes annealed at 500 ℃ and 700 ℃, the standard XRD pattern of $Bi_2Fe_4O_9$ (JCPDS#20-0836) is also shown for comparison.
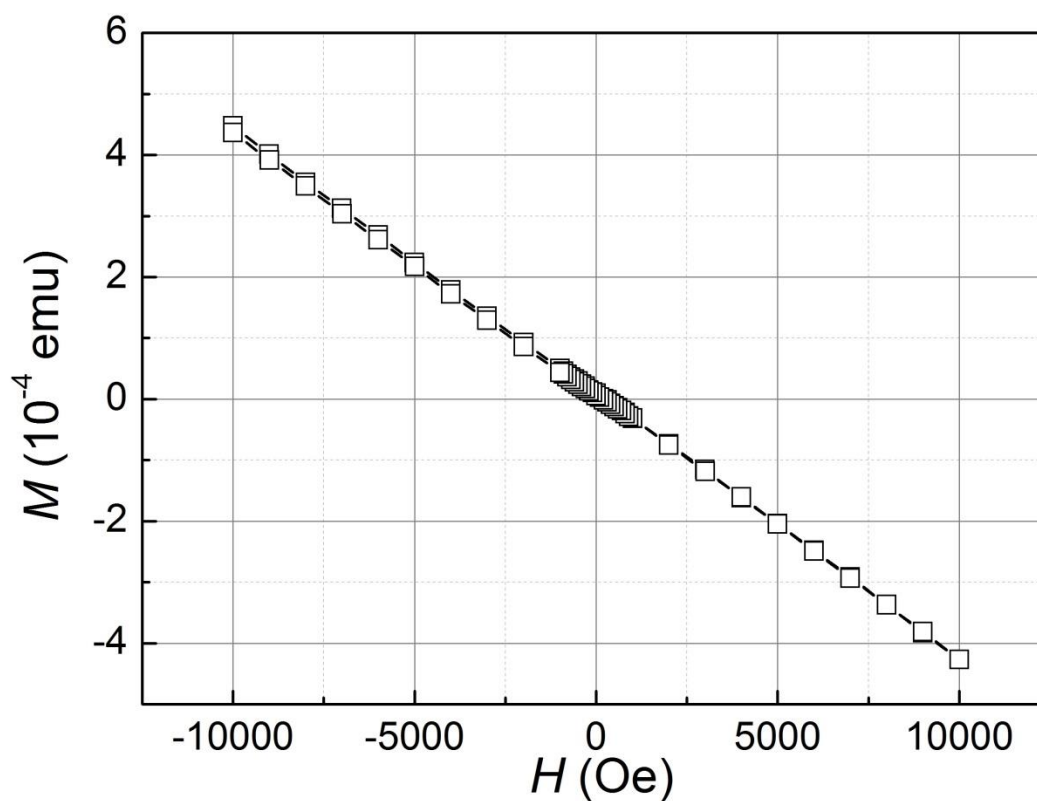

Figure S4. Magnetic hysteresis curve (M-H) of the BFO nanotubes measured by vibrating sample magnetometry (VSM) at room temperature.
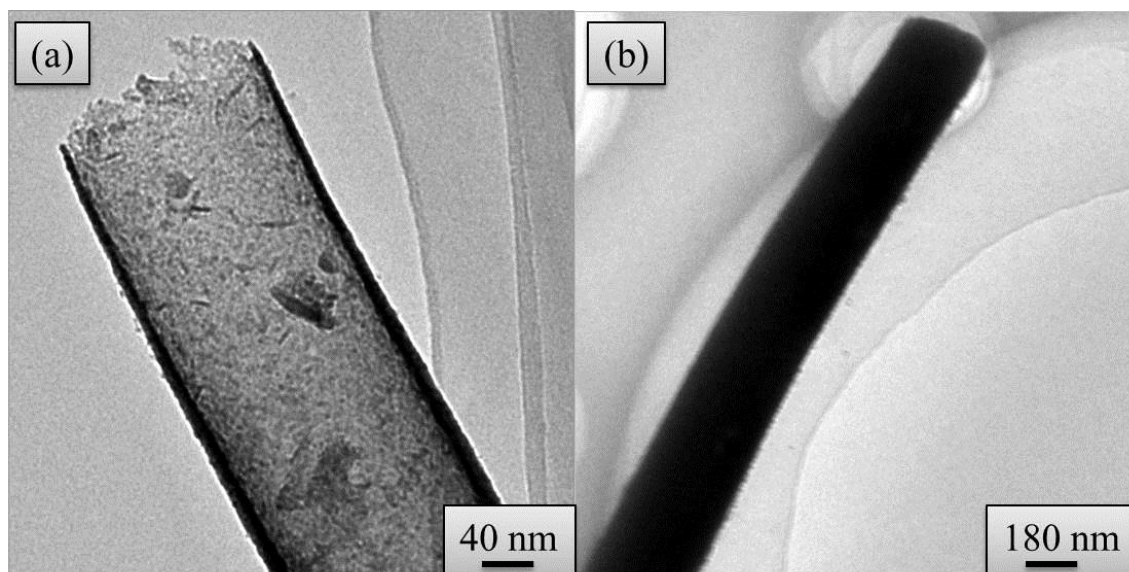
Figure S5. (a) TEM image of a single BFO nanotube; (b) TEM image of a single Ni-BFO nanowire fabricated by using the 300 nm AAO template, diameter of which is much larger than the penetration depth of electron.
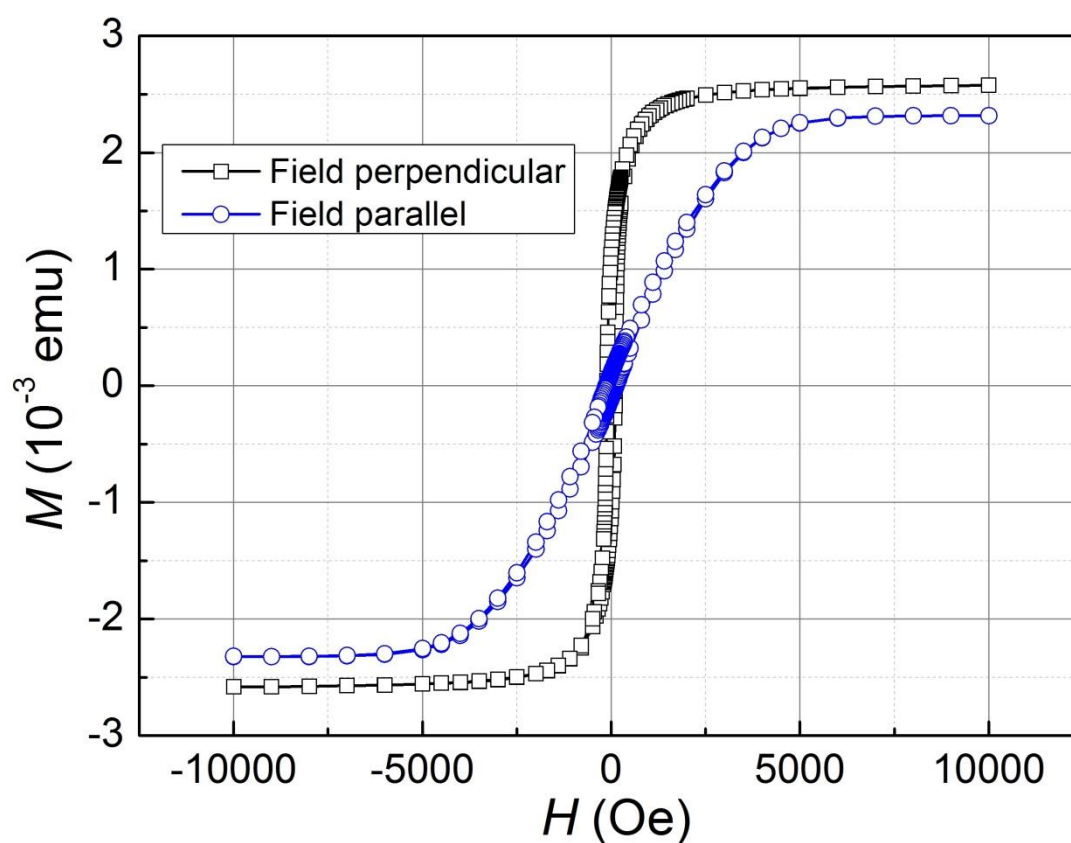

Figure S6. Hysteresis loops for magnetic fields applied parallel and perpendicular of the single phase Ni nanotubes deposited and left in the air for more than two months.
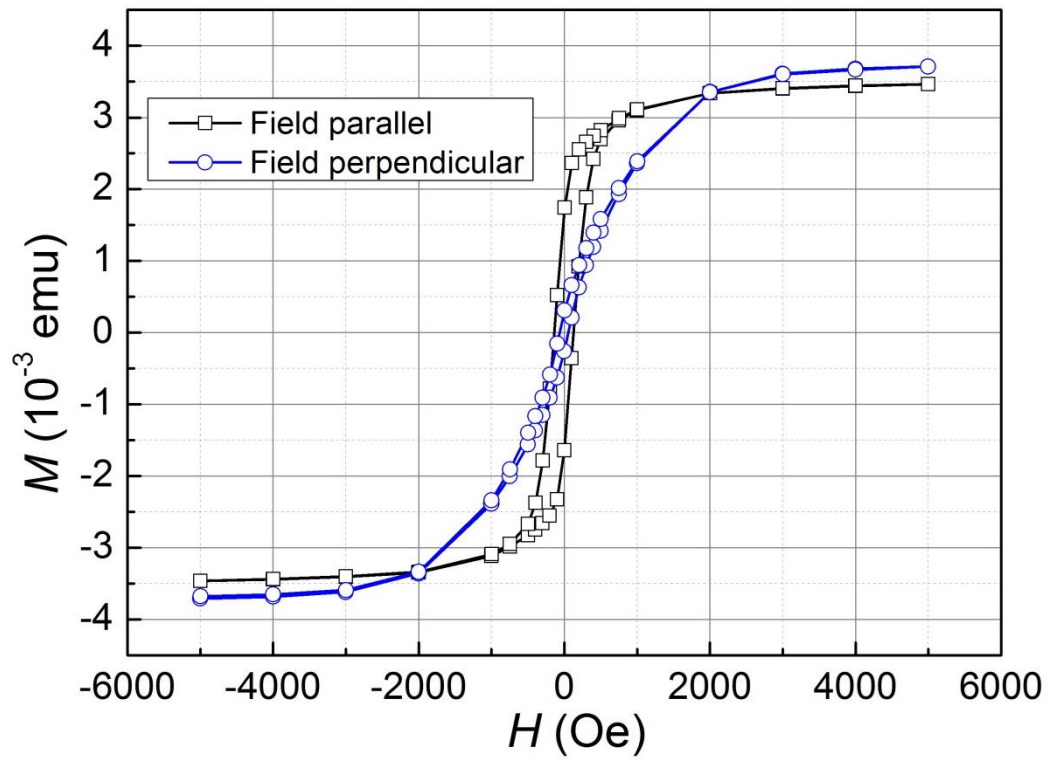
Figure S7. Hysteresis loops for magnetic fields applied parallel and perpendicular of the single phase Ni nanowires.