Electronic Supplementary Information

Synthesis of Co nanotubes by nanoporous template-assisted electrodeposition via incorporation of vanadyl ions

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Preparation of Co nanotubes

The Co nanotubes (NTs) were synthesized via electrodeposition in one bath by utilizing a commercial nanotemplate. Anodized aluminum oxide (AAO) membranes with nominal diameters of 200 nm (Whatman, Inc., Anodisc) were prepared by depositing a 300-nm layer of Ag on one side by of the membranes, completely covering the pores. The precursor solution was prepared by mixing 100 mM cobalt sulfate heptahydrate (Sigma–Aldrich, $Co(SO_4)_2 \cdot 7H_2O$) and 60 mM vanadium oxide sulfate hydrate (Sigma–Aldrich, $VOSO_4 \cdot xH_2O$). In addition, a small amount of nitric acid (Samchun Chemicals, HNO_3) was added to the solution to supply hydrogen ions and reduce the pH value to 1.9–2.1. In contrast, the Co precursor solution was composed of 100 mM cobalt sulfate heptahydrate and 200 mM boric acid. The electrodeposition system is composed of dual channel usable sourcemeter (Keithley, 2612B) in isothermal-isohumidity controlled incubator (Hanbaek Scientific technology, HB-101S-O). To infuse the precursor solution into the AAO pores, sonication was applied for 1 min. Subsequently, constant currents of 5, 10, 20, and 30 mA/cm^2 were applied to the electrodeposition system under ambient conditions. After electrodeposition, the samples were rinsed in deionized water several times to completely remove the residual acidic solution.

Characterization methods

To examine the nanomaterials buried in the AAO nanotemplate, the Ag layer that served as an electrode was removed using a solution composed of iodine. Sodium hydroxide was used to etch the AAO template and separate the nanomaterials. The morphologies of the synthesized Co NTs were examined using field-emission scanning electron microscopy (FE-SEM, Hitachi, Hitachi S-4300). The structural properties were substantiated using X-ray diffraction (XRD, Rigaku, D/MAX-2500V/PC) and transmission electron microscopy (TEM, JEOL, JEM-2100F). Furthermore, we applied a focused ion beam system (FIB, FEI, NOVA 600 NanoLab) to examine the microstructure using cross-sectional high-resolution (HR) TEM. Finally, the magnetic properties of the arrays were measured using vibrating sample magnetometry (VSM, MicroSense, EV 9-380V).

Effect of vanadyl ion concentration

The NTs were synthesized by changing the concentration of vanadyl precursor. All samples were fabricated under constant current density of 10 mA/cm^2. The amounts of vanadyl precursor used in Fig. S1 are 40, 60, and 80 mM respectively. When solution including less than 50 mM of vanadium precursor, nanowires (NWs) were synthesized instead of NTs. In case of higher vanadium precursor concentration, the NTs possessed a similar wall thicknesses of 25 nm. We think a certain amount of VO^{2+} ions is necessary to attract Co^{2+} ions and the optimum is 60 mM.

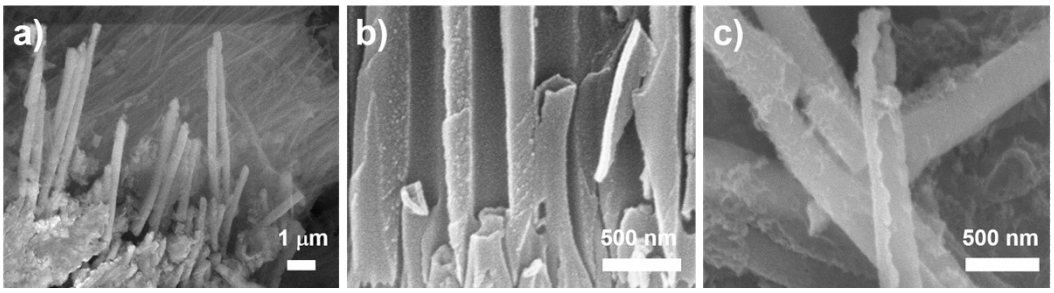

Fig. S1. SEM images of nanostructures where the ratios of VO precursor to Co ions are (a) 4:10, (b) 6:10, and (c) 8:10, respectively, fabricated under constant current density of 10 mA/cm^2.

TEM sampling through FIB system

The use of a FIB system for preparing TEM samples has been highlighted. First, an epoxy resin was used to cover a square-shaped Si wafer, on which the NTs were distributed, to protect the NTs from spoiling. Then, a 2-μm layer of Pt was deposited along the vertical direction of the NTs to shield them from the ion beam. Subsequently, Ga ions were used to mill the NTs vertically, and a slice of the NT was transferred to a TEM Cu grid.

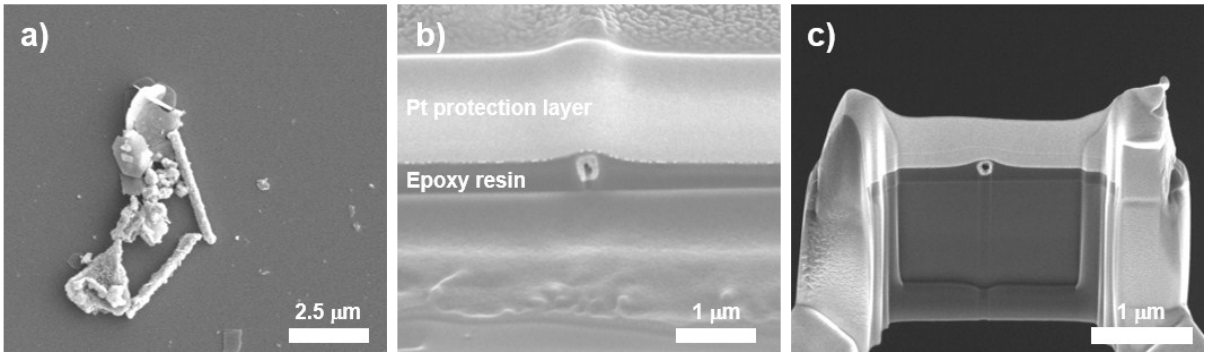

Fig. S2. TEM sample preparation process: (a) distributed epoxy resin covered NTs on a Si wafer, (b) cross-sectional image of a NT with Pt protection layer, and (c) harvested NT on a TEM Cu grid.

Calculation of saturation magnetization values

Unlike magnetic thin films, it is difficult to directly measure the volume-based saturation magnetization (M_s) values of NWs because precise determination of the magnetic volume is not trivial. Thus, most previous papers have reported normalized hysteresis loops based on measured magnetic moment (in emu) values. Nevertheless, monitoring the shape of hysteresis loops and their coercivity (H_c) values offers useful information about magnetic reversal behaviors. S. J. Yoon *et al.*[1] attempted to estimate the magnetic volume of CoFe NWs embedded in AAO nanotemplates. In this study, we have followed the same method. First, we expected that the diameter of the NTs (and NWs) would comply with the average pore diameter of the nanotemplate, 200 nm. Subsequently, the average height of the NTs (and NWs) was measured by SEM. Then, the pore density of the nanotemplate was determined based on top view images. For the NTs, the hollow space was considered for estimation. The estimated M_s and measured H_c values are listed in Table S1.

Table S1. Estimated M_s and measured H_c values for Co NW and NT arrays.

	M_s (emu/cm^3)	H_c (Oe), Field applied parallel to the NW (or NT) axis	H_c (Oe), Field applied perpendicular to the NW (or NT) axis
Co NW array	558	99	149
Co NT array	418	120	98

Reference

1. S. J. Yoon, B. G. Kim, I. T. Jeon, J. H. Wu and Y. K. Kim, *Appl. Phys. Express*, 2012, **5**, 103003.