

Diameter dependent multiferroic functionality in hybrid Core/Shell nanowires

U. Khan,^a M. Irfan,^a W. J. Li,^a N. Adeela,^b L. Pan,^a Q. T. Zhang^a and X. F. Han^a

Hybrid core/Shell (CS) nanowires (NWs) and nanoshells (NSs) have been given potential considerations because of their response towards spintronics applications like magnetic high storage devices, magnetic sensors, and their particular interest for magnetocaloric systems, electrochemical capacitors and specific demand for biomedical treatments.¹⁻⁴ Although a lot of considerations have been given to simple magnetic NWs and NSs but still there are very few reports on such hybrid structures.

The proper functionality of hybrid CS nanostructures comprising with antiferromagnetic (AFM) and ferromagnetic (FM) interface, to control the thickness of AFM material is crucial parameter. In present case, BCO NSs as an AFM, have been fabrication through economical, and easy approached Sol-Gel method. It is tricky to control the thickness of BCO NSs embedded in Alumina template (AAO), for that, different ways were adopted and the conclusive method to increase the thickness carries (i) make sol as thick as it can, (ii) heat the template at 250C prior to dipping procedure for 20 min, (iii) sputter one side with 2-5nm to increase the adhesive process, (iv) heat operated AAO template after minor mechanical cleaning and anneal it at particular required temperature to get exact phase.

It can be seen in Fig. S1 that the hollow space between BCO NSs is 70nm and 50nm in non-sputtered and sputtered one side of AAO template. Herein, it is difficult to observe BCO thickness while embedded in AAO template due to its oxidizing nature. But the conclusive part is the smaller hollow space between boundary walls whereas thickness of BCO NSs can be seen

in Fig. 3a. Herein, we only mention the results related with 100nm, the other diameters have the similar results that are omitted.

Afterwards, FM NWs that is metallic Co, were fabricated by using chemical electrodeposition technique. Electrodeposition, potentiostatically, was performed by using 3 electrode cell, one is the Pt foil of thickness (20x10x0.3)mm used as counter electrode, second is the saturated calomel electrode (KCl) as reference electrode and AAO template operated as working electrode with Cu seed layer of 200nm. The solution used for metallic Co is 0.145 M $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (2g/50ml) and 0.565 M H_3BO_3 (1.75g/50ml). This recipe was achieved after repetitive experiments performed at -0.95V for 1.7 h under magnetic field stirring.

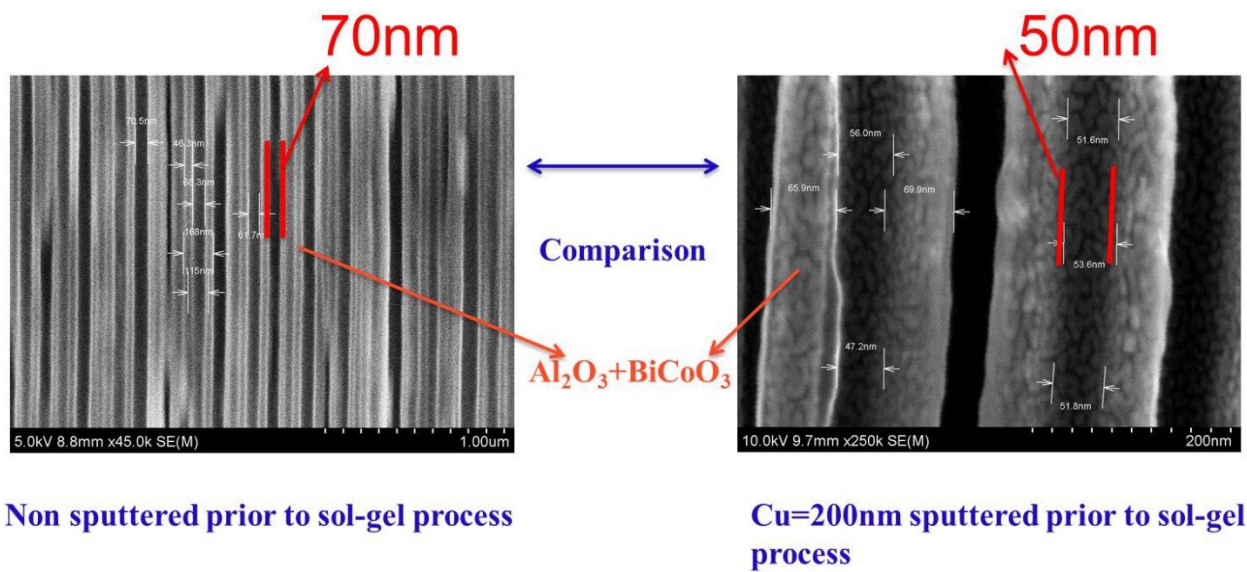


Fig. S1 Comparison between sputtered and non-sputtered AAO template after dipping in BCO Sol.

Synthesis Process:

The preparation of CS NWs embedded in AAO nanomembranes for SEM characterizations is very tricky. Since, Co NSs and Co/BCO NWs are fabricated inside AAO template therefore it is important to detach them from AAO. Therefore, Chemical etching plays vital role in this regard.

Precautions must have to give for the selection of etching solution because NSs of BCO are thin and in most of the cases etching solution may react them as well along with AAO templates. It is worth to mention that the etching solution varies with different materials. In some cases, we have to control the molarity of etching solution and in other cases we have to select some different solution which must be inert to corresponding material. In present case, we use 0.2 M NaOH solution as chemical etchant and samples were reacted at room temperate for 15 min and 1h in case of NSs and NWs, respectively.

The pore density and in results volume of total no of NWs/NSs is very essential for magnetic parameters, that is, exchange length, stiffness constant, etc. Therefore, the size distribution of 100nm of AAO (SEM image is shown in Fig. S2a) is shown in Fig. S2b.

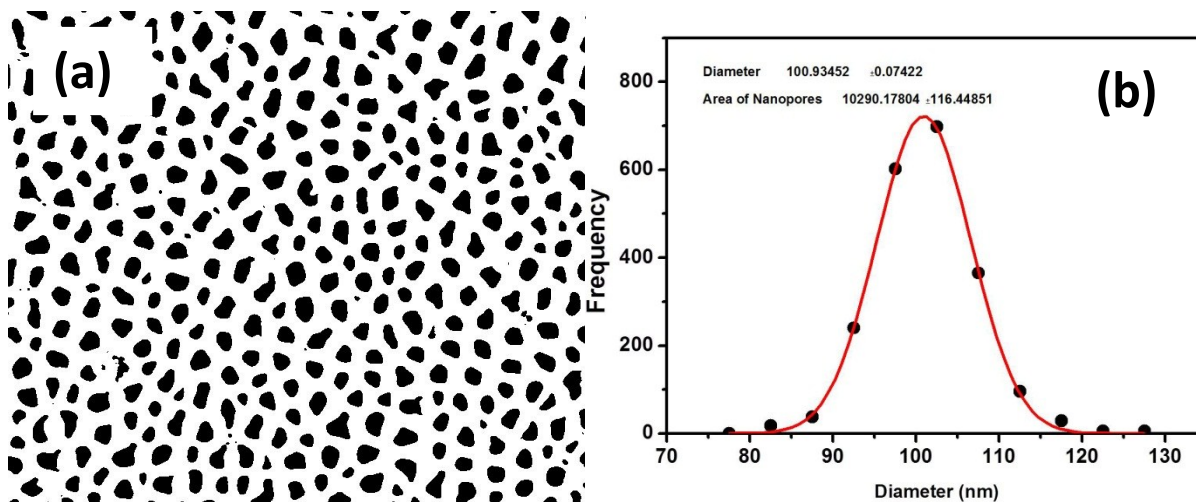


Fig. S2 SEM micrograph of 100nm of AAO template is shown in (a) whereas as distribution curve of 100nm diameter of AAO template is mentioned in (b).

The pore density of AAO templates was calculated by imageJ software in order to calculate the volume of nanowires. The diameter and area of nanopores is pretty much consistent with 100nm and 10290 nm², respectively as shown in Fig. S2b. Therefore, the no of NWs, and area of NWs

can be calculated by ImageJ software to estimate total no of NWs/NSs by using the following

expression, $V = N * \pi R^2 L;$

where, R is the radius of pore, L is the length of the wire, and N is the total no of nanowires.

Table S1: The parameters determined with Fullprof software for Co/BCO Core/Shell nanostructures.

Core/Shell	Atom	x	y	z	Occ.
Shell (Tetragonal)	Bi	0	0	0	0.94
Space Group (<i>P4mm</i>)	Co	0.5	0.5	0.13	0.06
$a_{core} = 2.966 \text{ \AA}$	O1	0.5	0.5	0.13	1
$c_{core} = 4.288 \text{ \AA}$	O2	0.5	0	0.78	1
Core (Hexagonal)					
Space Group (<i>P63/mmc</i>)					
$a_{shell} = 2.50 \text{ \AA}$	Co	0.23	0.76	0.25	1
$c_{shell} = 4.05 \text{ \AA}$					

References

- 1 S. S. P. Parkin, M. Hayashi and L. Thomas, *Science*, 2008, **320**, 190.
- 2 I. M. Miron, T. Moore, H. Szabolcs, L. D. Buda-Prejbeanu, S. Auffret, B. Rodmacq, S. Pizzini, J. Vogel, M. Bonfim, A. Schuhl and G. Gaudin, *Nat. Mater.*, 2011, **10**, 419.
- 3 A. K. Wanekaya, W. Chen, N. V. Myung, A. Mulchandani, *Electroanalysis*, 2006, **18**, 533.
- 4 M. Contreras, R. Sougrat, A. Zaher, T. Ravasi, and J. Kosel, *Int. J. Nanomed.*, 2015, **10**, 2141.