Supplementary Information

Highly ordered core-shell $CoFe_2O_4$-$BiFeO_3$ nanocomposite arrays from dimension confined phase separation and their interfacial magnetoelectric coupling properties

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Fabrication of CFO-BFO nanocomposite arrays

The CFO-BFO nanocomposite arrays were deposited on $SrTiO_3$ (STO) (001) single crystal substrate via pulsed laser deposition (PLD) with anodic aluminum oxide (AAO) membrane as shadow mask. The AAO mask was prepared by a two-step anodization process. A high-purity aluminum foil (purity ~ 99.999 %, thickness ~ 0.5 mm thick) was first electropolished in a mixture of $HClO_4$ and C_2H_5OH (1:3 v/v) at 20 V for 4 min. Then the as-polished Al foil was anodized in three different solutions: (1) 1 wt% phosphoric acid under a constant voltage of 195 V at 1 °C for 20 h, (2) 0.3 M oxalic acid under a constant voltage of 40 V at 1 °C for 20 h, and (3) 0.2 M sulfuric acid under a constant voltage of 25 V at 1 °C for 20 h. Afterwards, the first anodized Al foils were soaked into a mixed solution of 5 % H_3PO_4 and 1.8 wt % CrO_3 at 45 °C for 20 h to remove the oxidized layer, and then subjected to the second anodization under the same condition as the first one for 200 s to get proper thickness. A thin Polystyrene (PS) layer

was spin-coated onto the AAO membrane, and then the remaining Al was etched away with a mixture of $CuCl_2$ and HCl. The barrier layer was removed by floating the membrane in 5 wt % H_3PO_4 at 30 °C for 45 min. The free standing AAO stencils were transferred to the STO substrate, and the PS layer was removed by $CHCl_3$. A mixture target $(CoFe_2O_4)_{0.35}/(Bi_{1.1}FeO_3)_{0.65}$ (Kurt J. Lesker Ltd.) was used for deposition at $T \sim 700$ °C, $P_{O2} \sim 10^{-2}$ torr, $f \sim 5$ Hz and $E \sim 1$ J cm^{-2} via PLD (KrF excimer laser, $\lambda = 248$ nm). After PLD, the sample was cooled down in a 1 bar O_2 atmosphere. Post-annealed sample was heated to 800 °C for one hour in a tube furnace with Bi2O3 powder to prevent possible Bi element evaporation. The AAO mask was then removed by a sticky tape and ordered CFO-BFO nanocomposite arrays were obtained.

Instruments and measurements

SEM investigations were performed with a JEOL JSM-6701F microscope. The samples for TEM were thinned by standard mechanical and focused-ion-beam techniques. TEM investigations were conducted with a JEOL HRTEM. The FFT images and HRTEM signal profiles were analyzed with Digital Micrograph (Gatan Inc. Version 3.7.1). PFM was performed using Asylum MFP system with Pt coated tips (Nanosensors Inc). Magnetic properties were characterized with a MPMS SQUID VSM (Quantum Design, sensitivity $\leq 10^{-8}$ emu).

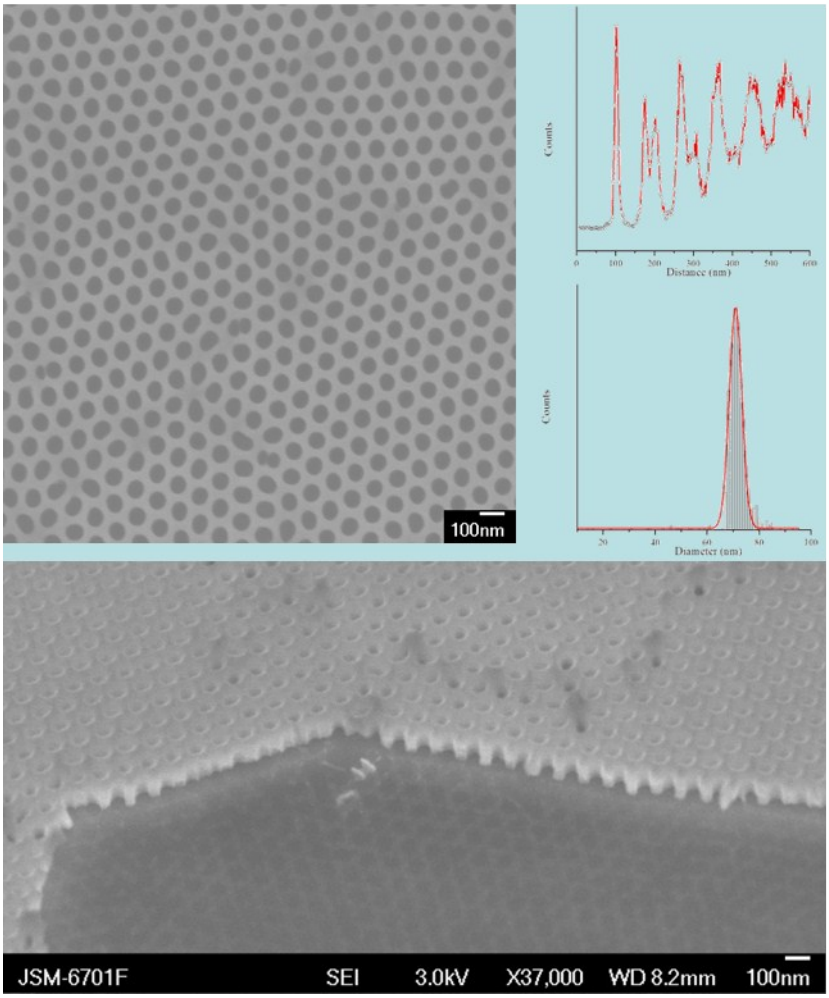

Fig. S1 Top and 45° side FE-SEM views, pair correlation and size distribution curves of ultrathin AAO stencil derived from 0.3 M oxalic acid. (d ~ 60 nm, h ~ 120 nm)

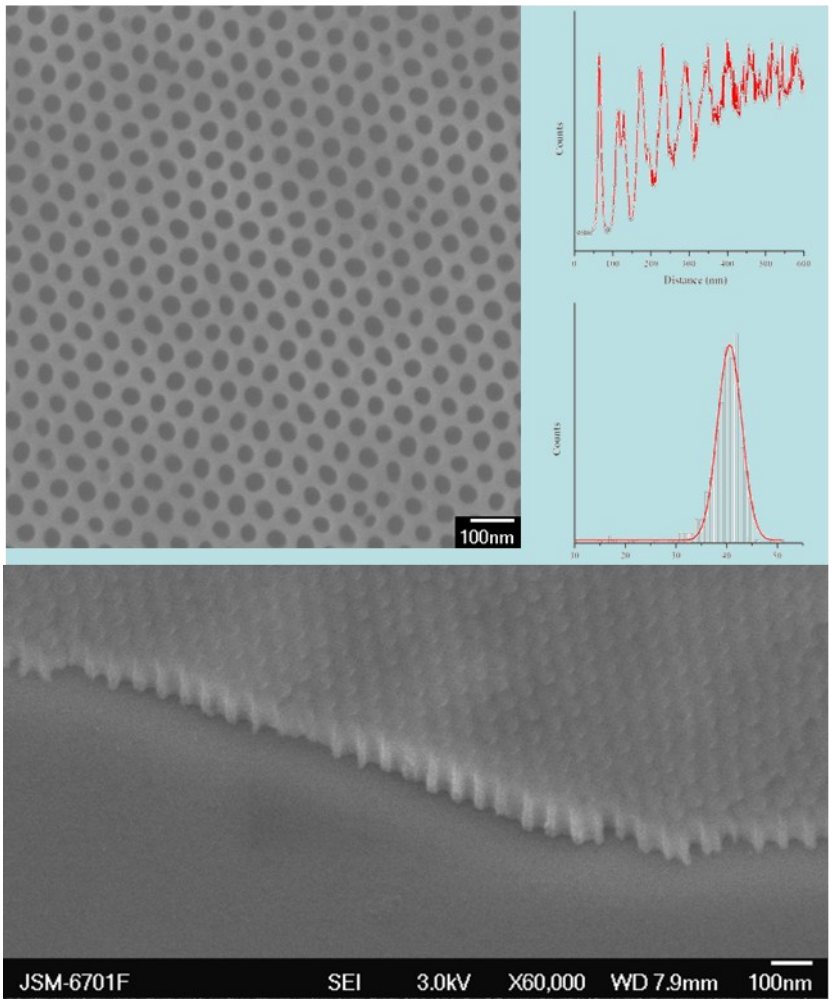

Fig. S2 Top and 45° side FE-SEM views, pair correlation and size distribution curves of ultrathin AAO stencil derived from 0.2 M sulfuric acid. (d ~ 40 nm, h ~ 70 nm)