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Supporting information for

Self-assembled multiferroic epitaxial $BiFeO_3$-$CoFe_2O_4$ nanocomposite thin films grown by rf magnetron sputtering

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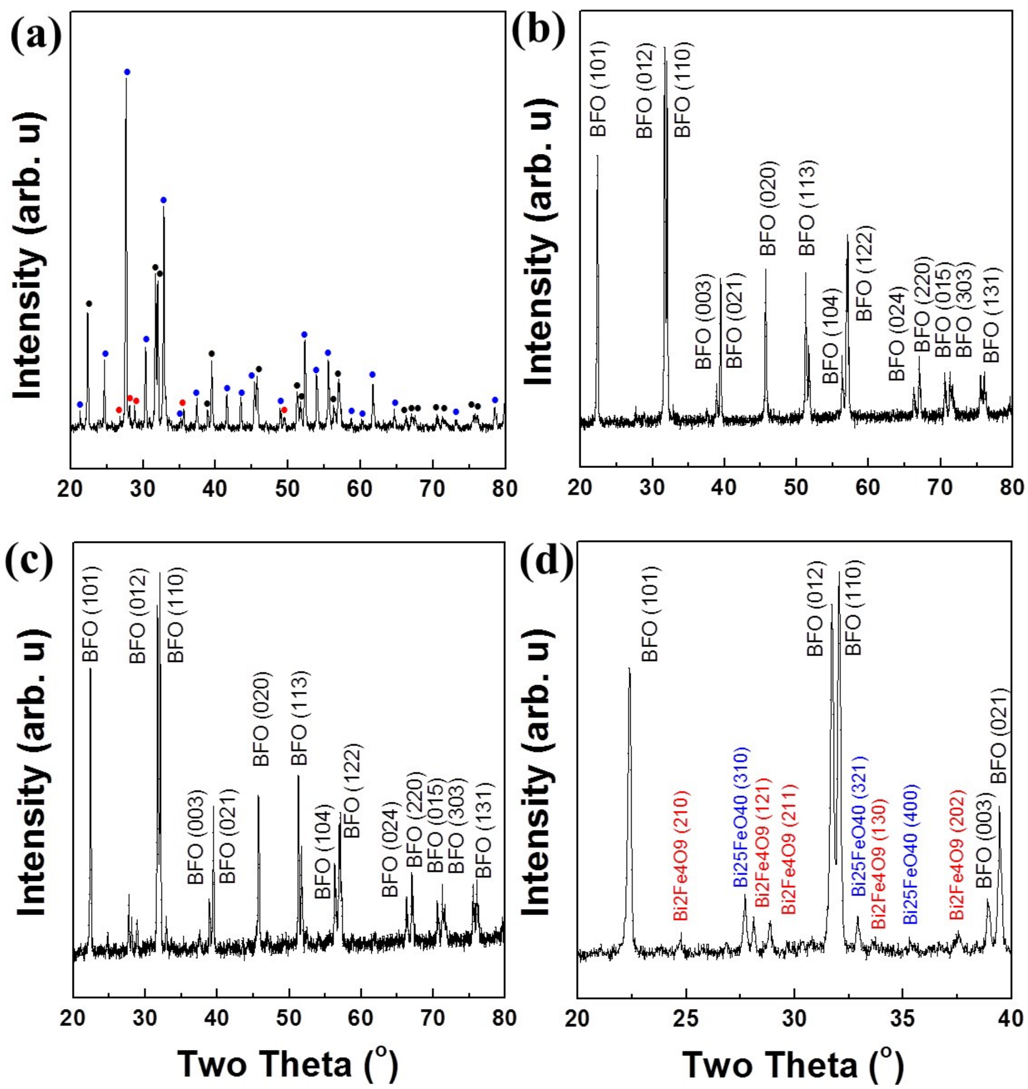

Figure S1. XRD patterns of Bi_2O_3-Fe_2O_3 mixture reacted at **(a)** 720, **(b)** 800 and **(c)** 850 °C for 3 h in air. The syntheses of $BiFeO_3$ were conducted using a solid-state reaction. A mixture of Bi_2O_3 (Samchun, Korea, 99.9 %) and Fe_2O_3 (Alfa Aesar, 99.9 %) powders was weighed and wet-ball milled with zirconia balls and ethanol for 24 h. After drying, the mixture was calcined at given temperatures with a heating and cooling rate of 5 °C/min. Two secondary phases of $Bi_{25}FeO_{40}$ (denoted with blue closed circles) and $Bi_2Fe_4O_9$ (red closed circles) were observed with $BiFeO_3$ (black closed circles) at 720 °C in the calcined powder. $BiFeO_3$ phases were formed at 750˚ (not shown here) and 800 °C without adding additional Bi to compensate loss during calcination by volatilization as in prior reports.[1-3] Secondary phases of Bi-rich $Bi_{25}FeO_{40}$ and Bi-deficient $Bi_2Fe_4O_9$ were detected in powders calcined at higher temperature of 850 °C. The relative peak intensity of $Bi_2Fe_4O_9$ is stronger than that of the lower temperature calcined samples suggesting Bi loss at higher temperatures.

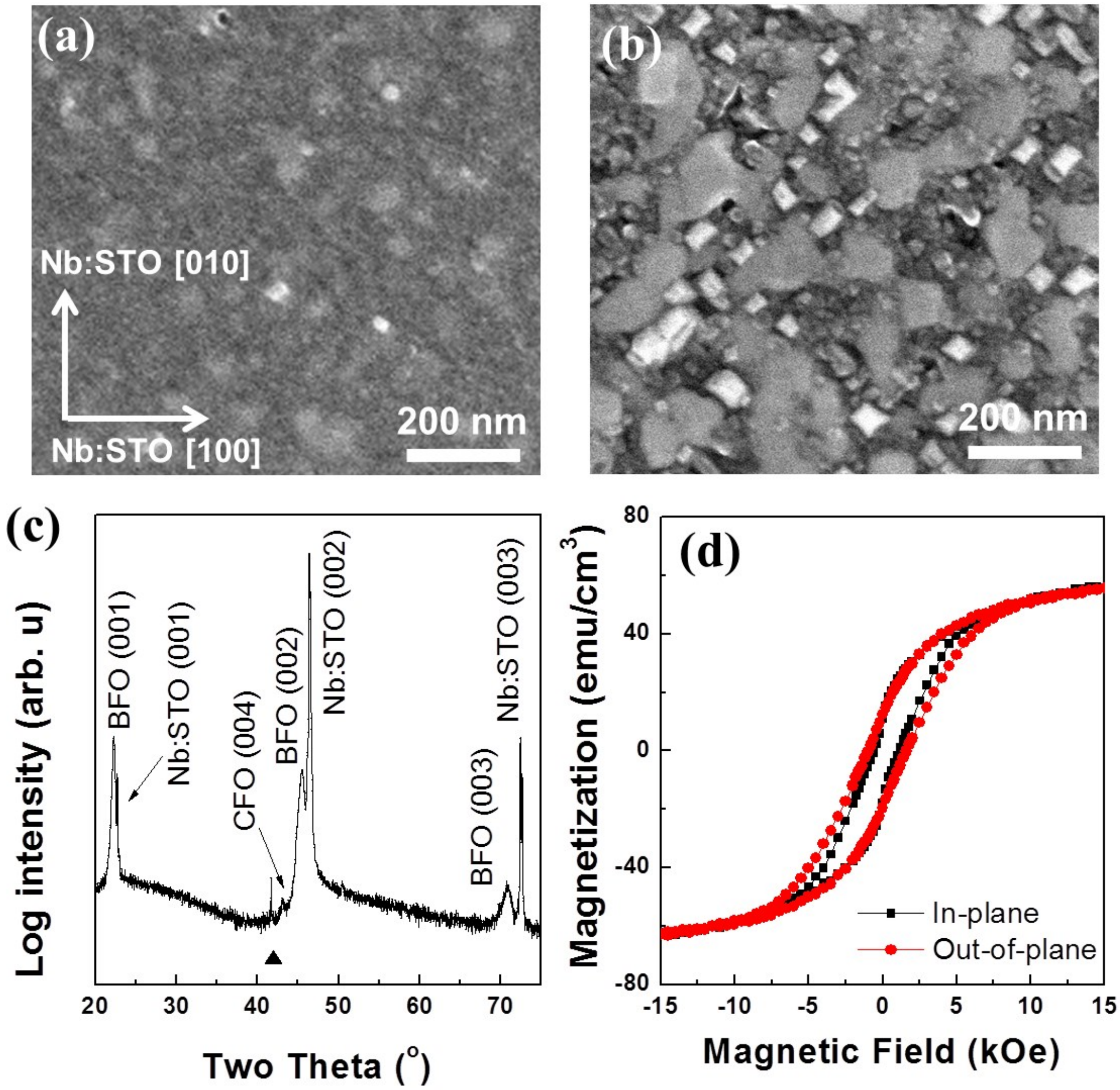

Figure S2. (a) Top view SEM image of a BFO-CFO nanocomposite grown at 480 ˚C then annealed at 600˚C. The arrows correspond to [100] and [010] R-BFO and CFO peaks and the Nb:STO substrate. **(b)** Top view SEM image of a BFO-CFO nanocomposite grown at 480 ˚C then annealed at 650˚C. **(c)** θ-2θ XRD pattern of the 650 ˚C annealed nanocomposite. The peak around 41.7 ˚marked with a triangle denotes K_β of Nb:STO (002). **(d)** In-plane and out-of-plane hysteresis loops of the 650 ˚C annealed nanocomposite thin film within an applied magnetic field range of -15 kOe to 15 kOe. The in-plane and out-of-plane directions correspond to the Nb:STO [100] and [001] directions.

Effect of Annealing (Figure S2)

Annealing a nanocomposite film grown at 480 ˚C for 1 hour at 600˚C (**Fig. S2 (a**)) produced facetted surface features. Annealing at 650˚C yielded a surface consisting of a larger number of rectangular features oriented along the substrate <110> with ~50 - 70 nm side length, assumed to be the spinel phase, within a discontinuous matrix, assumed to be perovskite. XRD measurements reveal only (00*l*) peaks of BFO near the substrate (00*l*) peak, and (004) of CFO near 43.0˚ (**Fig. S2 (c)**) which is consistent with the orientations in PLD-grown nanocomposites.

The out-of-plane lattice parameters of BFO and CFO in the annealed film were 3.966 ± 0.003 Å and 8.394 ± 0.004 Å respectively, close to the bulk values ($a_{bulk, BFO}$ = 3.965 Å[4], $a_{bulk, CFO}$ = 8.392 Å (JCPDS # 22–1086)). The strain relaxation in the annealed sputtered film differs from what is seen in PLD nanocomposites grown at high temperatures, where the simultaneous growth of the two phases leads to out-of-plane compressive strain in the CFO. The CFO in the annealed film is likely present as nanocrystals instead of through-thickness pillars. The magnetic hysteresis loops of the annealed nanocomposite thin film are displayed in **Fig. S2 (d)**. Both in-plane and out-of-plane curves do not reach saturation at 15 kOe applied field and therefore represent minor loops. The film is approximately isotropic with coercive fields of 800 ± 50 Oe and 1000 ± 50 Oe for in-plane and out-of-plane loops respectively. Isotropic behavior is consistent with a morphology consisting of nanocrystals distributed within the film.

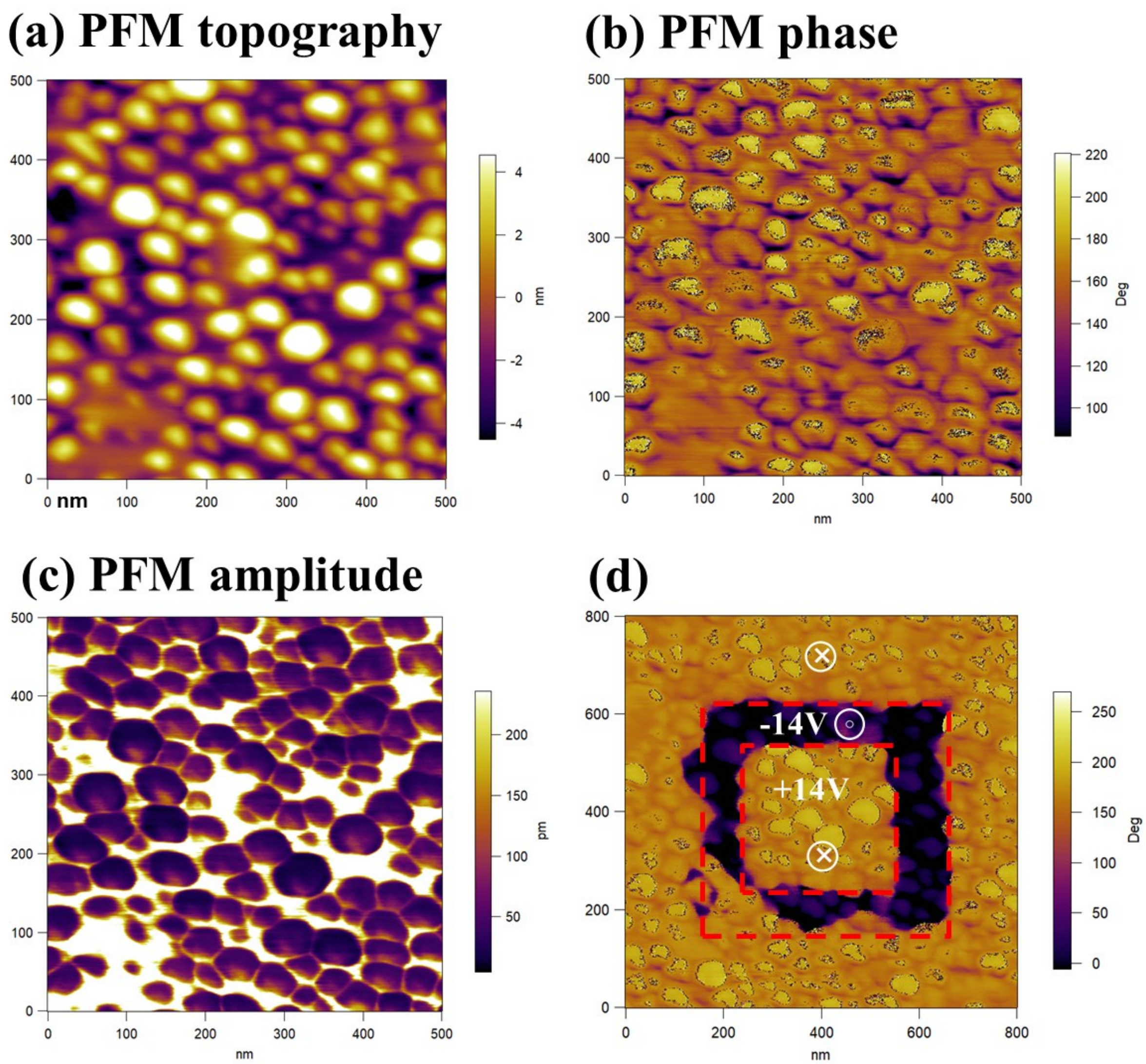

Figure S3. (a) PFM topography image of 200 nm thick BFO-CFO nanocomposite grown on Nb:STO substrate at 650 ˚C in 50 mTorr with Ar:O_2 ratio of 1:9 in 0.5 x 0.5 μm^2 area, **(b)** phase and **(c)** amplitude image of the piezo response of the same area shown in Fig. S3 (a) measured simultaneously. In the phase image the contrast indicates ferroelectric domains of BFO. (d) Writing and rewriting of BFO-CFO nanocomposite grown on Nb:STO substrate at 650 ˚C in 50 mTorr with Ar:O_2 ratio of 1:9 over an 0.8 x 0.8 μm^2 area in which in the middle square area was poled downwards with a bias voltage of 14 V while the outer part was upwards with a voltage of -14 V.

References

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