

SUPPLEMENTAL MATERIALS

Figure S1 A shows the pulsed laser deposition (PLD) equipped with reflective high energy electron diffraction (RHEED) which can monitor the growth in-situ. Before growth, the SrTiO₃ (STO, perovskite structure) substrate shows the presence of the streaks along [100] direction, suggestive of essentially perfect crystalline ordering (figure S1 B(a)). During the deposition process, the perovskite diffraction pattern gradually comes out with some additional spots belonging to spinel structure (figure S1 B(b)) and transforms into the pure spinel diffraction (figure S1 B(c)). Because of the grating angle of RHEED, crystallography of the island part of sample will be diffracted in 3 dimension way. All the patterns are confirmed by the Ewald's spheres that are simulated by Single Crystal software (shown by those insets). The corresponding sample surface is exhibited in figure S1 B(d). By this approach, we can get the first glance of the fact that the island-like structure has spinel structure.

The detailed structure of this epitaxial nano-composite is studied via high resolution TEM (HR-TEM). From the low magnitude bright field image in figure S2(a), a typical perovskite-spinel nano-composite is revealed. The LMO nanopillars with lateral dimension of about 80nm distributing in the BFO matrix grew perpendicular to the substrate. From the cross-section fast Fourier transform (FFT) of film-on-substrate, matrix (BFO) and nanopillar (LMO) region, we can find the films are epitaxial not only in the normal but the horizontal direction, giving a cube-on-cube orientation relationship, which is a general result in perovskite-spinel system¹. We have also reconstructed the epitaxial relationship along interfaces by the crystal maker. As manifested by the crystal maker, the interface between the two phases lies in the (110) orientation. Besides, there are plenty of misfit dislocations across the interface breaking the perfect structural continuity between two phases and forming a

semi-coherent interface (figure S2(b)). On the other hand, we have also done the chemical identification through energy dispersive spectrometer (EDS) instrument (data not shown). It shows the $(\text{BFO})_{0.75}:(\text{LMO})_{0.25}$ target results in $\text{BiFe}_{0.67}\text{Mn}_{0.33}\text{O}_3$ matrix and $\text{LiMn}_1\text{Fe}_1\text{O}_4$ nanopillars constitutions, matching our expectation in design.

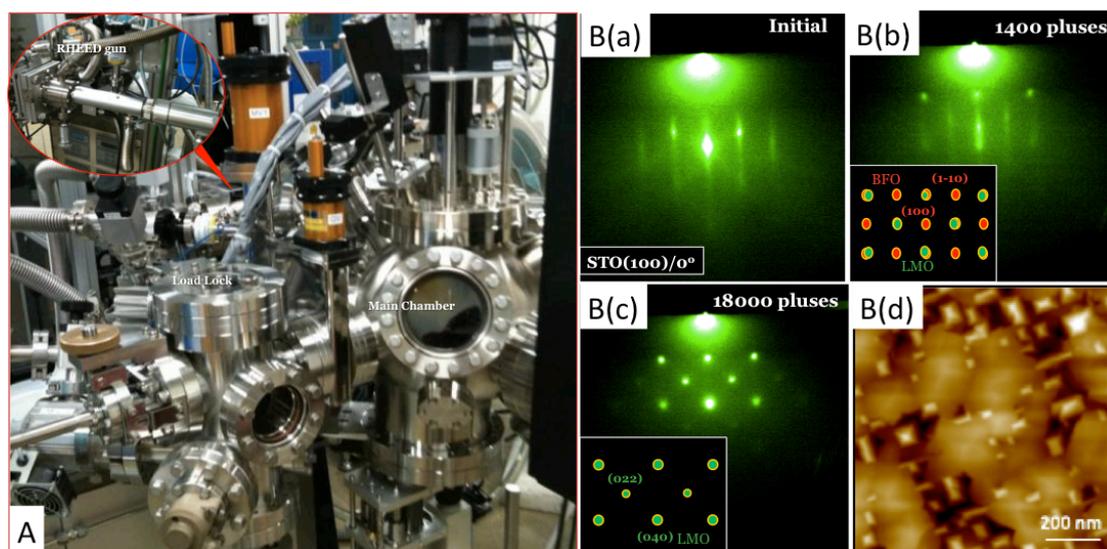


Figure S1. A: PLD system with RHEED gun. B (a)-(c): RHEED pattern recorded during deposition. B (d) The corresponding morphology of vertical heterostructure.

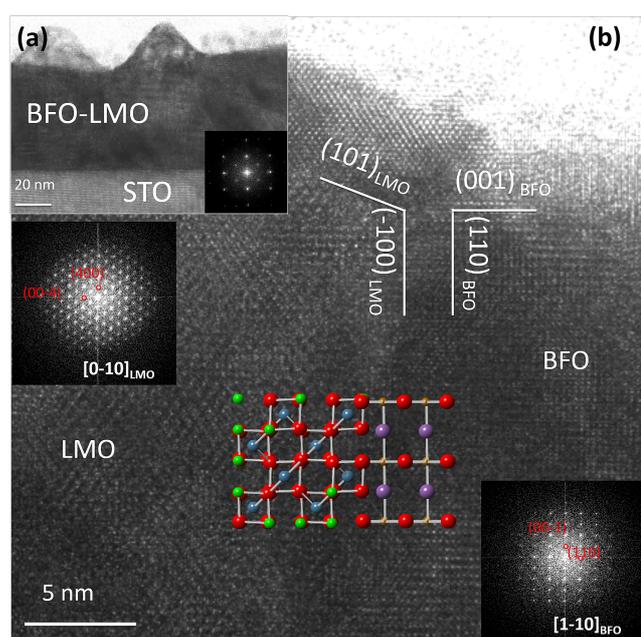


Figure S2. TEM investigation of nano-composite interface, (a) Low magnification bright field image; (b) HR-TEM image with FFT of each composite.

REFERENCE

1. Q. Zhan, R. Yu, S. P. Crane, H. Zheng, C. Kisielowski, R. Ramesh, *Applied Physics Letters*, **89** (2006).