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Flexible Multiferroic Bulk Heterojunction with Giant Magnetoelectric Coupling *via* the van der Waals Epitaxy

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ABSTRACT Magnetoelectric nanocomposites have been a topic of intense research due to their profound potential in the applications of electronic devices based on the spintronic technology. Nevertheless, in spite of significant progress made in the growth of high-quality nanocomposite thin films, the substrate clamping effect still remains as a major hurdle in realizing the ultimate magnetoelectric coupling. To overcome this obstacle, an alternative strategy of fabricating self-assembled ferroelectric-ferrimagnetic bulk heterojunction on flexible muscovite *via* the van der Waals epitaxy is adopted. In this study, we investigated the magnetoelectric coupling in self-assembled BiFeO₃ (BFO)-CoFe₂O₄ (CFO) bulk heterojunction epitaxially grown on flexible muscovite substrate. The obtained heterojunction is composed of vertically aligned multiferroic BFO nanopillars embedding in the ferrimagnetic CFO matrix. Moreover, due to the weak interaction between the flexible substrate and bulk heterojunction, the interface is incoherent and, hence, the substrate clamping effect is greatly reduced. The phase-field simulation model also complements our results. The magnetic and electrical characterizations highlight the improvement in magnetoelectric coupling of BFO-CFO bulk heterojunction. A magnetoelectric coupling coefficient of 74 mV/cm·Oe of this bulk heterojunction is larger than the magnetoelectric coefficient reported earlier on flexible substrates. Therefore, this study delivers a viable route of fabricating remarkable ME heterojunction and yet flexible electronic devices that are robust against extreme conditions with optimized performance.

KEYWORDS: Magnetoelectric · bulk heterojunction · clamping effect · van der Waals epitaxy · flexible

In magnetoelectric (ME) materials, the inherent ME coupling allows the tuning of electric polarization (magnetization) by an external magnetic (electric) field.^{1,2} Since the dawn of millennium, biphasic ME composites combining superior electrical and/or magnetic properties of the constituents into multifunctional thin-film configuration through the engineered bulk heterojunction have received much attention due to their strong magnetoelectric coupling¹⁻⁵ over single-phase multiferroics at room temperature. The sizeable ME effects observed in various forms of ferroelectric-ferromagnetic bulk heterojunctions have triggered extensive researches for their profound potential applications in the field of memory and sensor devices based on the spintronic technology.¹⁻⁶ The ME property, manifested in terms of the magnetostrictive and piezoelectric coefficients of the constituent components, relies on the intimate elastic coupling across the interfaces, which can be further tailored by choice, design the volume fractions of components and the composite architecture. For example, a laminar multilayer film (2-2 structure) shows better ME coupling than that of particulate-matrix nanocomposite (0-3 structure) due to larger interfacial area at the bulk heterojunctions.¹ However, in the multilayer configuration, the substrate clamping effect has been identified as the primary reason in reducing the structural coupling of constituent layers and, hence, limits the maximum attainable ME coupling.⁷ To resolve this issue, a self-assembled pillars-matrix bulk heteroepitaxy (1-3 structures) with high volume-to-interface ratio has been explored due to relatively smaller substrate clamping effect.^{1,8,9} More advanced architectures like the quasi-particles-matrix (0-3) nanocomposites² and the well-ordered (0-0) BFO-CFO nanodots³ show the improved ME coupling due to substantial release of substrate clamping.^{2,3,10} However, the major obstacle encountered by all these approaches in the growth of ME composites is still the clamping effect induced by the rigid substrates, which always weakens the ME coupling.^{1-3,11,12} Thus, to further

advance the development of more effective magnetoelectric composites, such an inherent deficiency should be surmounted by resorting to proper substitution for rigid substrates commonly used at present.

In the present research, we demonstrate an alternative strategy capable of overcoming this key issue by fabricating an unconstrained self-assembled BFO-CFO bulk heteroepitaxy on a two-dimensional (2D) layered substrate *via* the van der Waals (vdW) epitaxy, which does not impose stringent lattice matching of the constituent phases and substrate and can significantly reduce defect density and the substrate clamping.¹³⁻¹⁹ This salient feature is beneficial in realizing large magnetostrictive and piezoelectric coefficients, and eventually, enhances ME coupling in the self-assembled BFO-CFO heteroepitaxy grown on muscovite mica substrate. In addition, the viability of growing various functional oxides *via* vdW epitaxy on mica²⁰⁻²⁴ has been demonstrated recently for next-generation flexible devices owing to its unique set of features such as being light-weight, transparent, flexible with atomically smooth surface, chemically inert and high-temperature stability. The investigation on magnetic and electrical properties BFO-CFO/mica heterojunction highlights the enhancement of ME coupling. Moreover, these heterojunctions are compact, lightweight and can be easily attached to conformal geometries. Thus, we believe that the present work will provide a proficient route to realize flexible yet remarkable ME heterojunction.

RESULTS AND DISCUSSION

Free-Clamping Model. The inherent strong structural coupling between BFO and CFO phases allows the change of ferroelectric polarization by an applied magnetic field.^{1,25-27} However, the in-plane (IP) structural coupling²⁸ of BFO and CFO is limited by the substrate

clamping effect compared to the ideal strain-free bulk geometry as illustrated in the schematic of Figure 1a. In our designed heterojunction shown schematically in Figure 1b, the self-assembled BFO-CFO heteroepitaxy on 2D layered muscovite relying on the weak vdW bonding between the bulk heterojunction and substrate minimizes the clamping effect and thus, it can enable effective ME effect *via* structural coupling. To support our hypothesis, phase-field simulation was carried out to evaluate the strain-mediated ME coupling of BFO-CFO heteroepitaxy with and without substrate clamping effect. The modeling of the strain-mediated ME coupling in thin film nanocomposites based on simple energetic arguments exhibits a significant dependence on the elastic boundary conditions on the bottom substrate and the top surface.^{29,30} Phase-field simulations on BFO-CFO nanocomposites grown on SrTiO₃ (STO) substrate³¹ and membrane without substrate clamping (mica) were performed.

The phase field model considers a thin film with thickness $h = 90$ nm, which consists of BFO pillars with lateral width $d = 150$ nm embedded in the CFO matrix. A periodic IP boundary condition is employed. Temporal evolution of the ferroelectric polarization P in BFO and the magnetization M in CFO is simulated by solving the time-dependent Ginzburg-Landau equation³¹ and the Landau–Lifshitz–Gilbert equation using a semi-implicit Fourier-spectral method.³² The strain distribution in the nanocomposite system is obtained by solving the elastic equilibrium with eq 1

$$\frac{\partial [c_{ijkl}(\varepsilon_{kl} - \varepsilon_{kl}^0)]}{\partial x_j} = 0 \quad (1)$$

using a Fourier spectral iterative perturbation method³³ based on Khachaturyan's theory of mesoscopic elasticity.³⁴ ε^0 is the stress-free strain generated by electrostriction and magnetostriction, calculated as eq 2

$$\varepsilon_{ij}^0 = Q_{ijkl}P_kP_l \quad (2)$$

and

$$\varepsilon_{ij}^0 = \begin{cases} \frac{3}{2}\lambda_{100}\left(m_im_j - \frac{1}{3}\right), & i = j \\ \frac{3}{2}\lambda_{111}m_im_j, & i \neq j \end{cases}$$

in BFO and CFO phases, respectively; $\mathbf{Q}$ and λ are the electrostrictive coefficient of BFO and the saturation magnetostriction of CFO, respectively, taken as $Q_{11}= 0.032 \text{ C}^{-2}\text{m}^4$, $Q_{12}= -0.016 \text{ C}^{-2}\text{m}^4$, $Q_{44}= 0.020 \text{ C}^{-2}\text{m}^4$, $\lambda_{100}= -590 \text{ ppm}$ and $\lambda_{111}= 120 \text{ ppm}$.³⁵

On applying an OOP magnetic field of $H= 100 \text{ kA/m}$, our simulation finds a $\sim 34\%$ enhancement of polarization response from 0.068 to 0.091 C/m² through removing the substrate clamping in a membrane nanocomposite, which is attributed to the cooperative effect of IP and OOP elastic interactions between the CFO and BFO phases (Figure 1c). The significant enhancement of ME coupling coefficient in the BFO-CFO composite as shown in Figure 1d highlights the importance of reducing the substrate clamping effect. Thus, one can expect that the minimal substrate clamping effect in the BFO-CFO/mica heterojunction mediated *via* the weak vdW bonds can greatly enhance the ME coupling of BFO-CFO bulk heterojunction.

Structural Characterization. The samples were prepared by pulsed laser deposition (PLD). The growth conditions can be found in the methods section. The structural features were investigated by a combination of x-ray diffraction (XRD) and transmission electron microscopy (TEM). Typical XRD pattern of the sample shown in Figure 2a shows only (*lll*) reflections of BFO, CFO, and SrRuO₃ (SRO) bottom electrode together with (001)-oriented mica substrate without any other orientations or secondary phases. Moreover, Figure 2b shows the phi-scans of $\{200\}_{\text{SRO}}$, $\{200\}_{\text{BFO}}$, $\{400\}_{\text{CFO}}$ and $\{202\}_{\text{mica}}$ diffraction peaks. The peaks of SRO, BFO, and CFO phases exhibit six-fold symmetry with respect to three-fold symmetric mica peaks

corresponding to their cubic and hexagonal symmetries. The epitaxial relationship can be determined as $(001)_{\text{mica}}// (111)_{\text{CFO}}/ (111)_{\text{BFO}}/ (111)_{\text{SRO}}$ and $[010]_{\text{mica}}// [01\bar{1}]_{\text{CFO}}/ [01\bar{1}]_{\text{BFO}}/ [01\bar{1}]_{\text{SRO}}$. Furthermore, the heterostructure investigated by the reciprocal space mapping (RSM) in Figure 2c exhibits well-defined reciprocal diffraction peaks, showing the clear phase separation and good crystallinity of each constituent phase. By analyzing the relative d -spacings of all phases from their peak positions in the map, we can identify these reflections as CFO(400), BFO(200), and SRO(200). Because the reciprocal map is a vector space, we can further derive that the OOP and IP vector components should be along (111) and (3-1-1) due to the resembling included angle ($\sim 100^\circ$) with that in mica (202). The calculated OOP/IP d -spacings are 5.135 Å/2.472 Å, 2.376 Å/1.217 Å, and 2.335 Å/1.201 Å for CFO, BFO, and SRO, respectively. Compared with their bulk values (4.846 Å/2.531 Å for CFO, 2.286 Å/1.193 Å for BFO, and 2.265 Å/1.183 Å for SRO), the estimated OOP strains of -5.96 %, -3.94 % and -1.09 %, while the IP strains are -2.3 %, 2.01 %, and 1.52 % for CFO, BFO and SRO, respectively. The reversed sign of the IP strain states of CFO matrix and BFO pillars indicates a strong structural coupling between them. Further structural information is also made based on the results of Raman spectroscopy shown in the supplementary information Figure S1. The red shift of the vibration modes of BFO pillars on mica substrate indicates a substrate clamping release compared to the same structure on STO substrate.³⁶

The topography was examined by atomic force microscopy (AFM) as displayed in Figure 2d. The inset shows that the BFO nanopillars form as triangular islands embedded in the CFO matrix similar to that grown on STO(111).^{11,12} In the present study, as the constituent phases grow along $[111]$, perovskite BFO tends to form as pillars and emerges as triangular-like island in the BFO-CFO bulk heterojunction.¹¹ This is further confirmed in the microstructure examination by the

cross-sectional TEM depicted in Figure 2e showing the BFO nanopillars embedded in the CFO matrix on mica substrate with the CFO buffer layer and SRO bottom electrode. The high resolution (HR) TEM images displayed in Figures 2f,g also show a well-defined phase separation among the component phases with sharp interfaces between them. Moreover, the Fast-Fourier transform (FFT) patterns from the HRTEM images along [010] of the mica substrate shown in Figure 2h clearly indicate that the epitaxial relationships among the constituent phases in the composite as $[100]_{\text{mica}}//[111]_{\text{SRO}}//[111]_{\text{CFO}}//[111]_{\text{BFO}}$, in agreement with the XRD result. Thus, it is clear from overall Figure 2 that the BFO and CFO phases exhibit spontaneous phase-separation as well as strong structural coupling in BFO-CFO/mica heterojunctions with well-defined epitaxy and sharp interfaces inherent to the vdW epitaxy.

Electrical and Magnetic Properties. Having demonstrated the epitaxial growth of high quality BFO-CFO/mica heterojunction, the electric and magnetic properties were further examined. From Figure 3a, the OOP converse piezoelectric coefficient, d_{33} , of BFO-CFO bulk heterojunction on mica (76.5 pmV^{-1}) is higher than that on STO(111) (50 pmV^{-1}) grown under similar conditions. This value is also higher than the reported d_{33} in (100), (110), and (111)-oriented BFO-CFO/STO heterostructures (50 pmV^{-1} , 40 pmV^{-1} and 30 pmV^{-1} respectively),¹² suggesting the enhanced piezoelectric response of BFO pillars has been brought about by the release of the substrate constraint. The topographic and corresponding piezoresponse force microscopy (PFM) images in Figures 3b,c confirm that the electrical properties of BFO-CFO/mica are originated from the piezoelectric response of the BFO pillars, where the OOP component of the ferroelectric polarization in the BFO pillars can be switched between two stable states (bright and dark contrast inside and outside of the square area). On the other hand,

the magnetic properties in this system is dominated by ferrimagnetic CFO matrix as observed in (magnetic force microscopy) MFM measurement. The topographic and corresponding MFM images in Figures 3d,e shows a variation of contrast as the scanning area changes, indicating that the magnetization of the CFO matrix in the as-grown state is randomly distributed.

Furthermore, the magnetic hysteresis loops in Figure 3f exhibit isotropic magnetic behavior along the IP and OOP directions. This is attributed to the growth direction of CFO along [111], since the easy axis of CFO typically points to [001].^{9,25} The saturated magnetization (M_s) of CFO/mica is ~ 237 emu/cm³ with the coercivity field (H_c) of ~ 2 kOe, smaller than that obtained from epitaxial CFO/STO (~ 3 kOe),³⁷ possibly due to the effective relaxation of clamping from the mica substrate.³ Moreover, Figure 3g shows the magnetostriction of the sample probed through the deflection (Δz) of the sample under magnetic field by the conventional magnetostriction measurement using the digital holographic microscope (DHM) method.³⁸ The magnetostriction deflection profile ($\Delta z_{\parallel}$ or $\Delta z_{\perp}$) mapped out from the fixed end of the film plane with the magnetic fields applied parallel ($H_{\parallel}$, the longitudinal field) and perpendicular ($H_{\perp}$, the transverse field) to the IP-direction of the sample are represented in the inset of Figure 3g. Upon the application of magnetic field ($H = 2000$ Oe), the sample deflects up and down from the reference position ($H = 0$)³⁸ as shown in Figure 3g. From the deflection profile, the longitudinal and transverse magnetostriction coefficients of the sample can be determined by using eq 3.³⁹

$$\lambda_{\parallel,\perp} = \left(\frac{1}{3}\right) \left[\frac{\Delta Z_{\parallel,\perp}}{L^2}\right] K, \quad K = \left(\frac{E_s}{E_f}\right) \left(\frac{t_s^2}{t_f}\right) \left[\frac{(1 + \nu_f)}{(1 + \nu_s)}\right] \quad (3)$$

where L is the length, E_f is the Young's modulus of the film, E_s is the Young's modulus of the substrate, t_f is film thickness, t_s is substrate thickness, ν_f is the Poisson's ratio of the film, and ν_s is the Poisson's ratio of the substrate, respectively. The calculated longitudinal and transverse magnetostriction coefficients are -51 ppm and 61 ppm, respectively (with $\Delta\lambda = \lambda_{\parallel} - \lambda_{\perp} = -112$

ppm), slightly higher than that of CFO/mica ($\Delta\lambda = -104$ ppm),²⁰ which can be attributed to the strong antiferromagnetic-ferrimagnetic coupling of BFO-CFO.^{8,40} This result is also in agreement with the previous reports that CFO has negative longitudinal magnetostriction and positive transverse magnetostriction.^{1,25}

Magnetoelectric Properties. After realizing the manifestation of reduced substrate constraint in the improved electrical and magnetic properties of BFO-CFO/mica, it is important to ascertain whether the same gets reflected in the magnetoelectric response. To probe the magnetoelectric properties in nanoscale, the effect of magnetic field on the electrical properties was investigated by measuring hysteresis loops (d_{33} vs V) from individual switching of BFO pillars with ($H = 2000$ Oe) and without the applied magnetic field along the OOP-direction. The d_{33} decreases with the applied magnetic field from 76.5 pmV^{-1} to 42.5 pmV^{-1} as shown in Figure 4a. Such a behavior is attributed to that the CFO matrix together with BFO pillars are compressed along the OOP-direction *via* their strong structural coupling when the magnetic field is applied along the OOP-direction due to a negative longitudinal magnetostriction of CFO matrix. As a consequence, the d_{33} should decrease due to the rotation of P with decreasing length of the BFO pillars along the OOP-direction.^{1-3,25-27} It is also shown in the PFM map with spectroscopy in the supplementary information of Figure S2 where the piezo-response signal of BFO pillars get suppressed in the applied magnetic field of 2000 Oe along the OOP-direction. The associated magnetoelectric coefficient (α_{ME}) can be calculated by $\alpha_{\text{ME}} = \Delta E / \Delta H$ with the variation in the electric field ΔE induced by the magnetic field ΔH (2000 Oe), where $\Delta E = \Delta u / (d_{33} \cdot D)$, Δu is the piezo-response displacement with and without magnetic bias, D is the thickness of BFO-CFO nanocomposite (~ 200 nm), and the corresponding d_{33} without magnetic bias (76.5 pm/V).^{2,3,10}

The calculated α_{ME} of BFO-CFO/mica is ~ 11000 mV/cm·Oe, which is much higher than that found in the quasi (0-3) BFO-CFO nanocomposite on rigid STO substrate (338 mV/cm·Oe),² and comparable with the result from the unclamped PZT/CFO core-shell nanofiber structures (29500 mV/cm·Oe).¹⁰ This observation underscores the importance of substrate clamping release in the enhancement of the ME coupling of BFO-CFO nanocomposite.

However, this converse α_{ME} estimate based on microscopic measurements by PFM cannot reveal the direct ME response in the device level. To obtain better insights about the ME effect at the macroscopic level, the quantitative longitudinal and transverse magnetoelectric susceptibility (MES) studies that directly probe the ME effect were performed as shown in Figure S3a. Direct measurements of the MES based on a conventional scheme that employs small H_{ac} values with variations in the dc magnetic field (H_{dc}) would be useful for understanding the magnetoelectric coupling of numerous magnetoelectric films or nanostructures at the quantitative level.¹ The temperature evolution of longitudinal and transverse MES are presented in Figure 4b. The longitudinal MES (α_{33}) is slightly smaller than transverse MES (α_{31}) at all temperatures due to the fact that spontaneous polarization of BFO pillars point along the OOP direction while CFO matrix exhibits magnetic isotropy, and thus the negative sign is attributed from overall negative magnetostriction of CFO¹ consistent with the previous microscopic magnetoelectric measurement result. This is in stark contrast with anisotropic MES in BFO-CFO/STO where magnetic anisotropy of CFO plays a key role.¹ Notably, the room temperature MES of BFO-CFO/mica is about ~ 160 ps/m (~ 74 mV/cm·Oe) higher than BFO-CFO/STO (001) (~ 130 ps/m (~ 60 mV/cm·Oe))¹ displaying similar (1-3) nanostructure. The enhancement (24%) in MES of BFO-CFO/mica is in good agreement with the phase-field simulation prediction presented in Figure 1 confirming the reduced mica substrate clamping effect brought about by the vdW

epitaxy. Moreover, Table 1 compares the magnetoelectric coefficients from various magnetoelectric composites for various material combinations and different architectures aimed at achieving best magnetoelectric response. The enhancement in reported magnetoelectric coupling is mainly related to the substrate clamping release which strongly depends on the architecture and also the suitable composite components. The BFO-CFO/mica system shows a better magnetoelectric coefficient mainly due to the release of the mica substrate clamping to achieve an effective strain-coupling.

Flexibility. Finally, it is worthwhile to mention that, the magnetoelectric coefficient of BFO-CFO on mica is larger than the magnetoelectric coefficient reported on flexible substrate due to superior crystalline quality and nanoscale control of the interface connectivity.^{1,2,3} The effect of mechanical strain on the physical properties of the current flexible ME nanocomposite is tested further. The M-H loop remained unaltered under the different bending modes (bending radius ~ 2 mm) as shown in Figure 5a in agreement with the earlier work CFO/mica.²⁰ In contrast, the d_{33} of each selected individuals BFO pillars gets affected when the sample is under tensile and compressive bend as shown in Figure 5b, which is attributed to the rotation of P due to the variation of length of BFO pillars along c -axis under bending. The magnetic field of 0.1 and 0.2 T reduces the d_{33} coefficients further. The corresponding α_{ME} estimated from d_{33} ($H = 0, 0.1, 0.2$ T) as a function of bending are depicted in Figure 5c. It is noteworthy that the obtained microscopic α_{ME} values under bending are still comparable to those observed in unclamped magnetoelectric composites^{3,10} and higher than quasi (0-3) structure BFO-CFO/STO² calculated with similar method. The variation of local electric response of the BFO pillars under mechanical strain is responsible for the variation of α_{ME} . However, the α_{ME} varies much slower than local d_{33}

under mechanical strain. The transversal MES (α_{31}) variation as a function of bending radius is further tested, the α_{31} remains constant even under a small bending radius of 5 mm as shown in Figure S4. A permanent damage of the sample at the bending radius of 4 mm can be detected when the magnetoelectric coupling behavior vanishes. Furthermore, the microscopic magnetoelectric measurements for various bending cycles under a bending radius of ~7 mm have been carried out to check the recoverability of ME coefficient as displayed in Figure S5. The result shows a small variation of the α_{ME} up to 1000 bending cycles indicating that the ME coupling of this system is robust against mechanical bending. The insensitivity of magnetoelectric response under mechanically bending is attributed to the stability of magnetostriction of the CFO matrix (Figure 5a). The robust magnetoelectric behavior against mechanical strain makes this heterojunction a great candidate for flexible electronic devices applications.

CONCLUSIONS

In summary, we have successfully fabricated a high-quality BFO-CFO bulk heterojunction on mica substrate with minimal substrate clamping. Consistent with the phase-field simulations of the free clamping model, this nanocomposite exhibits the enhanced magnetic and electric properties. The most striking feature of such a flexible bulk heterojunction is the ME performance better than the conventionally reported of flexible ME nanocomposites. Our approach provides a great direction in the realization of highly sensitive yet flexible ME electronic devices application with optimized performance.

METHODS

Materials. The self-assembled BFO–CFO heterojunction with the thickness of 200 nm was grown on mica substrate *via* PLD technique using a mixed BFO-CFO target with the volume fraction ratio of 65:35. The mica substrate ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$), monoclinic structure with $a=5.253 \text{ \AA}$, $b=9.086 \text{ \AA}$, $c=10.159 \text{ \AA}$, $\beta=99.9^\circ$ (space group C12/c1) was heated up to 650°C and kept in an oxygen pressure of 100 mTorr during the growth. Prior to the deposition of BFO-CFO heteroepitaxy on mica, a CFO interfacial buffer layer was deposited. Then, the SRO bottom electrode was grown on top of CFO interfacial buffer layer for electrical and magnetoelectric measurements. In the meantime, a reference sample on $\text{STO}(111)$ substrate was also prepared in the same growth conditions.

Measurement. XRD with phi scan, RSM, AFM, and TEM were employed to study the details of the structure and morphology of the samples while the Raman spectroscopy is used to reveal the release of substrate clamping effect. The magnetic and magnetostrictive properties were investigated by a Quantum Design[®] magnetic property measurement system (MPMS), a superconducting quantum-interference device (SQUID) magnetometer, MFM, and DHM method. Furthermore, PFM has been used to characterize the piezoelectric response of samples by using a PtIr-coated tip with an AC voltage of 1.0 V modulated at 6.39 kHz. The macroscopic and microscopic ME responses were measured using a highly sensitive home-built magnetoelectric susceptometer operating inside the PPMS (Quantum Design) and PFM with applied magnetic field, respectively.

FIGURES

Figure 1. (a) Schematic of elasticity direction of the bulk and film (adopted from ref. [28]), shows that the elasticity of the film is limited due to clamping effect from the rigid substrate. (b) Crystal structure of the interface region between the CFO-BFO composite and MICA substrate, with 2D-3D bonding which exhibits the vdW heteroepitaxial relationship. (c) Phase structure of the BFO-CFO films in the phase-field model and simulated stress distribution on applying an out-of-plane (OOP) magnetic field of $H = 100 \text{ kA/m}$. (d) Longitudinal magnetoelectric coupling

coefficient α_{33} simulated using a phase-field model, which shows an enhancement of over 100% at low magnetic field bias (<500 kA/m) on removing the substrate clamping.

Figure 2. (a) XRD of BFO-CFO/SRO/CFO/mica. (b) Phi-scans of SRO{200}, BFO{200}, CFO{400} and mica{202}. (c) The RSM result shows incoherent epitaxy of BFO and CFO, evidencing no significant clamping effect from mica substrate. (d) The surface morphology of BFO-CFO/SRO/CFO/mica by AFM, indicates the BFO triangular pillars embedded in the CFO matrix. (e) The cross-sectional TEM image shows the BFO-CFO film, SRO and CFO layer and also the mica substrate. (f) and (g) are the HRTEM images of the BFO-CFO/SRO and CFO/mica interfaces, respectively. (h) The FFT patterns indicate the orientation relation between constituent phases and the substrate.

Figure 3. (a) Comparison of piezo-response from BFO-CFO grown on mica (brown) and STO (111) (purple) substrate. (b) and (c) show the topography and electric properties probed by PFM exhibit the ferro/piezoelectric response of BFO pillars. (d) and (e) show that the topography and MFM to illustrate that the magnetic properties are dominated by CFO matrix. (f) The M-H hysteresis loops show that the composite is magnetically isotropic. (g) The magnetostriction measurement to observe the magnetostriction of the sample in respect with the deflection behavior.

Figure 4. (a) d_{33} vs. V from the switching of BFO pillars with and without applied magnetic field along the OOP direction. (b) The MES variation at 10 K, 100 K, 200 K, and 300 K.

Figure 5. (a) The M-H loop of BFO-CFO with under bending modes. (b) The d_{33} of each selected individuals BFO pillars under different bending radius with and without applied magnetic field. (c) Calculated α_{ME} from Figure 5b.

TABLE

Table 1. Comparison of magnetoelectric coefficient from magnetoelectric composite materials

Microscopic α_{ME} measurements by PFM					
Architecture	Subst.	Component phases		α_{ME} (mV/cm·Oe)	Ref.
Quasi (0-3) structure	STO	BFO matrix	CFO particles	338	[2]
Well-ordered 0-0 nanodot	STO	BFO nanodot	CFO nanodot	12000	[3]

Core-Shell Nanofibers	-	PZT	CFO	29500	[10]
1-3 structure	Mica	CFO matrix	BFO pillars	11000	This work
Macroscopic α_{ME} measurements by magnetoelectric susceptometer					
Architecture	Subst.	Component phases		α_{ME} (mV/cm·Oe)	Ref.
2-2 structure	LAO	PZT layer	LSMO layer	4.2	[41]
2-2 structure	STO	BTO layer	CFO layer	66	[42]
2-2 structure	STO	PZT layer	NFO layer	20	[43]
0-3 structure	STO	PZT matrix	NFO particles	16	[44]
1-3 structure	STO	BFO matrix	CFO pillars	60	[1]
2-2 structure	Ni foil	BFO	Ni	3.5	[45]
2-2 structure	Metglass foil	BTO	Metglass	55	[46]
2-2 structure	flexible polyimide	CFO	P(VDF-TrFE)	12	[47]
1-3 structure	Mica	CFO matrix	BFO pillars	74	This work

ASSOCIATED CONTENT

Supporting Information Available: Additional Figures and data as described in the text. This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

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T. A., Y. B., and Y. H.C. designed the experiments. T. A. prepared all the samples in this study, performed XRD, AFM, and SQUID measurement and designed all schematic. K. S. and K. H. K. were responsible for MES measurement and analysis. T. Y. and L. Q. C. gave the phase field model and schematic. Y. H. H., Y. Y. C., and Y. C. C., carried out the PFM, MFM, and Raman measurement and analysis. H. J. L. performed the RSM measurement and analysis. D. T. H. performed the phi scan. D. S. responsible for TEM result. S. U. J. responsible for DHM result. T.

A., Y. B., J. Y. J., and Y. H. C. designed the study and wrote the manuscript with the help of all authors. All authors discussed the results and Y. H. C. directed the study.

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