Supporting Information

Magnetoelastoelectric coupling in core-shell nanoparticles enabling directional and mode-selective magnetic control of THz beam propagation

Moumita Dutta, Kamaraju Natarajan, Soutik Betal, Rohit P. Prasankumar, Amar S. Bhalla and Ruyan Guo*

S1. Nanoparticle Fabrication: To fabricate $CoFe_2O_4$ (CFO) - $BaTiO_3$ (BTO) core-shell nano-particles with a molar mass proportion of 60CFO-40BTO, a citrate solution containing 10 mg (~$0.04288x10^{-3}$ mol) of BTO was prepared for 15 mg of CFO nanoparticles (~$0.00639x^{10-3}$ mol). The citrate solution was prepared by using a polymerized solution of Barium and Titanium ions as the precursor, with citric acid ($C_6H_8O_7$) and ethylene glycol ($C_2H_4(OH)_2$) added in a molar ratio of 1:1:3:30, to form a transparent resin. 8.5 mg of $BaCaO_3$ (molar mass ~197.34g/mol) and 0.0117 ml of ($Ti[OCH(CH_3)_2]_4$) (density ~0.96g/ml and molar mass ~284.215g/mol), along with 24.7mg of $C_6H_8O_7$ (molar mass ~192.124 g) were used to prepare the citrate solutions containing the Ba and Ti ions. Both the citrate solutions were prepared separately by constant stirring and heating at 90^o for ~20 mins, and then mixed thoroughly and heated at 100^{o}C to form a homogeneous gel. The solution was then dissolved in 2 ml of DI water and 0.0886ml of $C_2H_4(OH)_2$ (having a density of 1.11g/ml and molar mass of 62.07g/mol).

The as acquired CFO nano-particles were then dispersed in the above solution (the citrate-gel precursor containing BTO), with simultaneous stirring and heating to form a gelatine. They were then sintered at 800^{o}C for 8 hours for the crystallization process to take place, in a low supply of oxygen to avoid any unwanted oxidation of CFO (the ferromagnetic phase). The resulting particles were then processed through several rounds of washing with ethanol and de-ionized water and were sonicated to extract the fabricated ferromagnetic-ferroelectric core-shell nanocomposites.

S2. Average size analysis of the CFO-BTO nanoparticles: A wide range (3µm x 3µm) Atomic Force Microscopic (AFM) topographical scan was performed using a standard SCM tip by Bruker and Bruker multimode V, configured in tapping mode.[1]

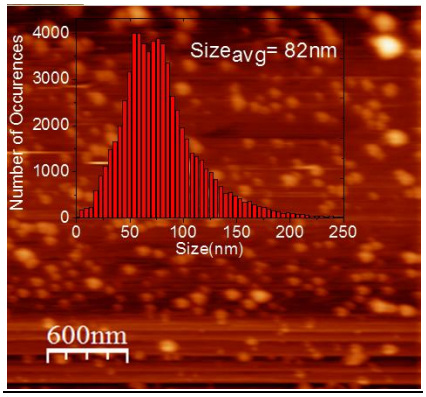

Figure S2. AFM topographical scan showing the average size of the nano-particles to be 80±5 nm.

S3. Piezo-force Microscopic (PFM) measurements: PFM measurements were performed in contact mode. A freshly cleaved mica substrate was used with the nanoparticles immobilized at the surface, by pre-treating the substrate with (1:5) Poly-L-Lycin: DI water.[2]

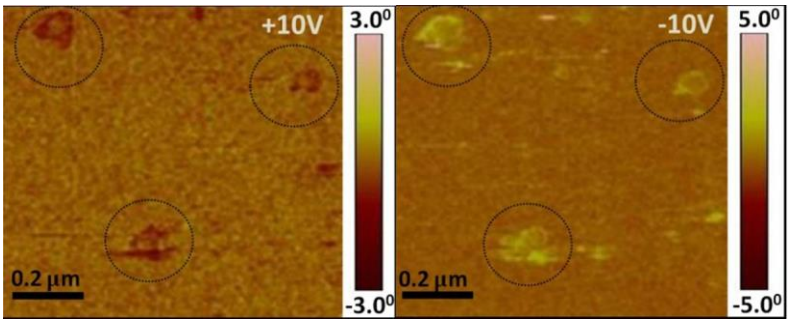

Figure S3. The phase switching (for applied bias field ± 10v) confirms the existence of the ferroelectric (FE) phase of the nano-particles (recreated from one of our previous works, ref.2 for better understanding of the material characteristic).

S4. The magnetization hysteresis: The magnetic measurements were performed at room temperature, by placing the nanoparticles in a small Teflon cuvette in a vibrating sample magnetometer mounted between the electromagnets (GWM-3473). The measurements were obtained using a highly sensitive gauss meter (Lakeshore-425) and a Hall probe.[2]

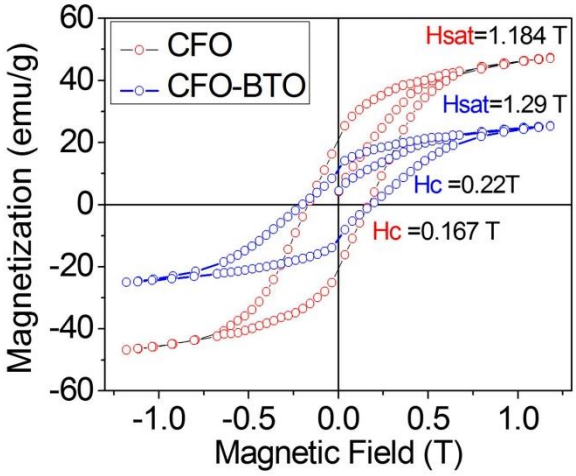

Figure S4. The magnetic hysteresis measurements for CFO (in red) and CFO-BTO (in blue) shows CFO-BTO being non-magnetic, the effective magnetisation gets reduced with the coercive fields (H_c) and saturation fields (H_{sat}) for CFO and CFO-BTO measured as 0.167 T and 0.22 T, 1.184 T and 1.29 T (recreated from ref.2 for better understanding of the material characteristic).

S5. Zetapotential measurements of the CFO nanoparticles: Zeta potential measured using a Malvern zeta-potentiometer shows that CFO nanoparticles have a (-) ve surface potential.

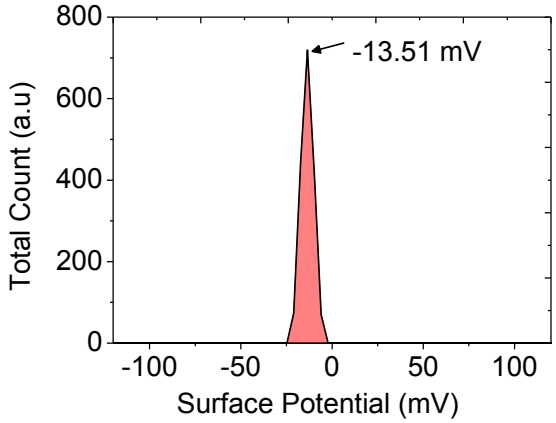

Figure S5: Surface potential measurement of CFO nanoparticles.

S6. Orientation dependent magnetostrictive coefficient of CFO: As a pseudo-cubic material, CFO has the easy axis of magnetization either along <100> or <111>. Thus, a tensorial computation of its magnetostrictive coefficient matrix N' has been performed using its two saturation strain coefficients λ_{100} and λ_{111}, to derive its orientation dependence along and transverse to the applied magnetic field direction. Saturation strain coefficients λ_{100} and λ_{111} have been used as follows to compute the magneto-strictive coefficient matrix $N_{[6 \times 6]}$, where I_s is the saturation current.

$$N_{11}=\frac{8*\lambda_{100}}{{I_s}^2}, N_{12}=-\frac{8*\lambda_{100}}{3{I_s}^2}, N_{44}=\frac{3*\lambda_{111}}{{I_s}^2}$$

$$N = \begin{pmatrix} -3.67\times10^{-8} & 1.22\times10^{-8} & 1.22\times10^{-8} & 0 & 0 & 0 \\ 1.22\times10^{-8} & -3.67\times10^{-8} & 1.22\times10^{-8} & 0 & 0 & 0 \\ 1.22\times10^{-8} & 1.22\times10^{-8} & -3.67\times10^{-8} & 0 & 0 & 0 \\ 0 & 0 & 0 & 3.30\times10^{-9} & 0 & 0 \\ 0 & 0 & 0 & 0 & 3.30\times10^{-9} & 0 \\ 0 & 0 & 0 & 0 & 0 & 3.30\times10^{-9} \end{pmatrix} \text{[m/A]}$$

Eulers transformational equation $N' = a.N.\beta_I$ has been used to compute the orientation dependency where the direction matrix (a) and the corresponding condensed form (β) are expressed as below (β_I refers to inverse of β):

$$a = \begin{pmatrix} \text{Cos}[\varphi]\text{Cos}[\psi] - \text{Cos}[\theta]\text{Sin}[\varphi]\text{Sin}[\psi] & \text{Cos}[\psi]\text{Sin}[\varphi] + \text{Cos}[\theta]\text{Cos}[\varphi]\text{Sin}[\psi] & \text{Sin}[\theta]\text{Sin}[\psi] \\ -\text{Cos}[\theta]\text{Cos}[\psi]\text{Sin}[\varphi] - \text{Cos}[\varphi]\text{Sin}[\psi] & \text{Cos}[\theta]\text{Cos}[\varphi]\text{Cos}[\psi] - \text{Sin}[\varphi]\text{Sin}[\psi] & \text{Cos}[\psi]\text{Sin}[\theta] \\ \text{Sin}[\theta]\text{Sin}[\varphi] & -\text{Cos}[\varphi]\text{Sin}[\theta] & \text{Cos}[\theta] \end{pmatrix}$$

$$\beta = \begin{pmatrix} \text{a11}^2 & \text{a21}^2 & \text{a31}^2 & 2\text{a21a31} & 2\text{a11a31} & 2\text{a11a21} \\ \text{a12}^2 & \text{a22}^2 & \text{a32}^2 & 2\text{a22a32} & 2\text{a12a32} & 2\text{a12a22} \\ \text{a13}^2 & \text{a23}^2 & \text{a33}^2 & 2\text{a23a33} & 2\text{a13a33} & 2\text{a13a23} \\ \text{a12a13} & \text{a22a23} & \text{a32a33} & \text{a23a32} + \text{a22a33} & \text{a13a32} + \text{a12a33} & \text{a13a22} + \text{a12a23} \\ \text{a11a13} & \text{a21a23} & \text{a31a33} & \text{a23a31} + \text{a21a33} & \text{a13a31} + \text{a11a33} & \text{a13a21} + \text{a11a23} \\ \text{a11a12} & \text{a21a22} & \text{a31a32} & \text{a22a31} + \text{a21a32} & \text{a12a31} + \text{a11a32} & \text{a12a21} + \text{a11a22} \end{pmatrix}$$

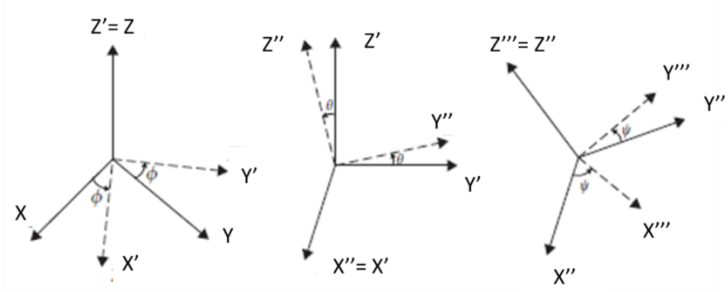

Figure S6(i). Angular rotations used for direction cosine matrices

The direction cosine matrix (a) was derived using the general Eulerian (θ, φ, ψ) rotations, where the first rotation was made by an angle of φ along Z, followed by a rotation of θ along X' and then by ψ along Z''. All the (+) ve rotations were considered counterclockwise in nature with (θ, φ) specifying the orientation of a single direction in space and ψ fixing the remaining two axes of the orthogonal system.[3]

Considering the applied magnetic field to be along the z direction H//z, N'_{33} (using Voigt notations) is along the field and $\sqrt{((N_{31})^2 + (N_{32})^2)}$, transverse to the field. The negative magnetostrictive effect of CFO is demonstrated, where it is all negative (yellow referring to (-) ve value of (-3.5x10^{-8} m/A), see the following Fig(a)) along the direction of field resulting in contraction and all positive (blue referring to (+) ve value (1.75x10^{-8} m/A), see the following Fig(b)) i.e. exhibiting expansion in the transverse direction.

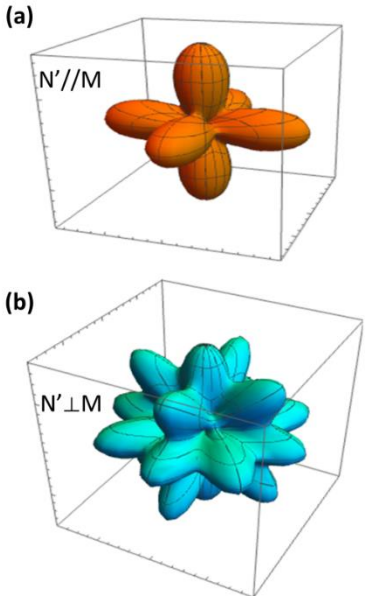

Figure S6(ii). Three-dimensional plot of orientation dependent of magnetostrictive coefficient of CFO, parallel (a) and transverse (b) to the direction of the field.

S7. Orientation dependent piezoelectric coefficients (of BTO) and magnetoelastoelectric coefficients (of CFO-BTO): Orientation dependent piezoelectric coefficient $d_{mjk}{}'(\theta, \varphi, \psi)$ of BTO, has been derived by similar use of Eulers transformation matrix as described above (for further details see ref. 4). The piezoelectric coefficient matrix (d) used for the derivation is as follows.

$$dmjk'(\theta, \varphi, \psi) = a.\, dmjk.\beta_I$$

$$d = \begin{pmatrix} 0 & 0 & 0 & 0 & 392 & 0 \\ 0 & 0 & 0 & 392 & 0 & 0 \\ -34.5 & -34.5 & 85.6 & 0 & 0 & 0 \end{pmatrix} \text{ [pC/N]}$$

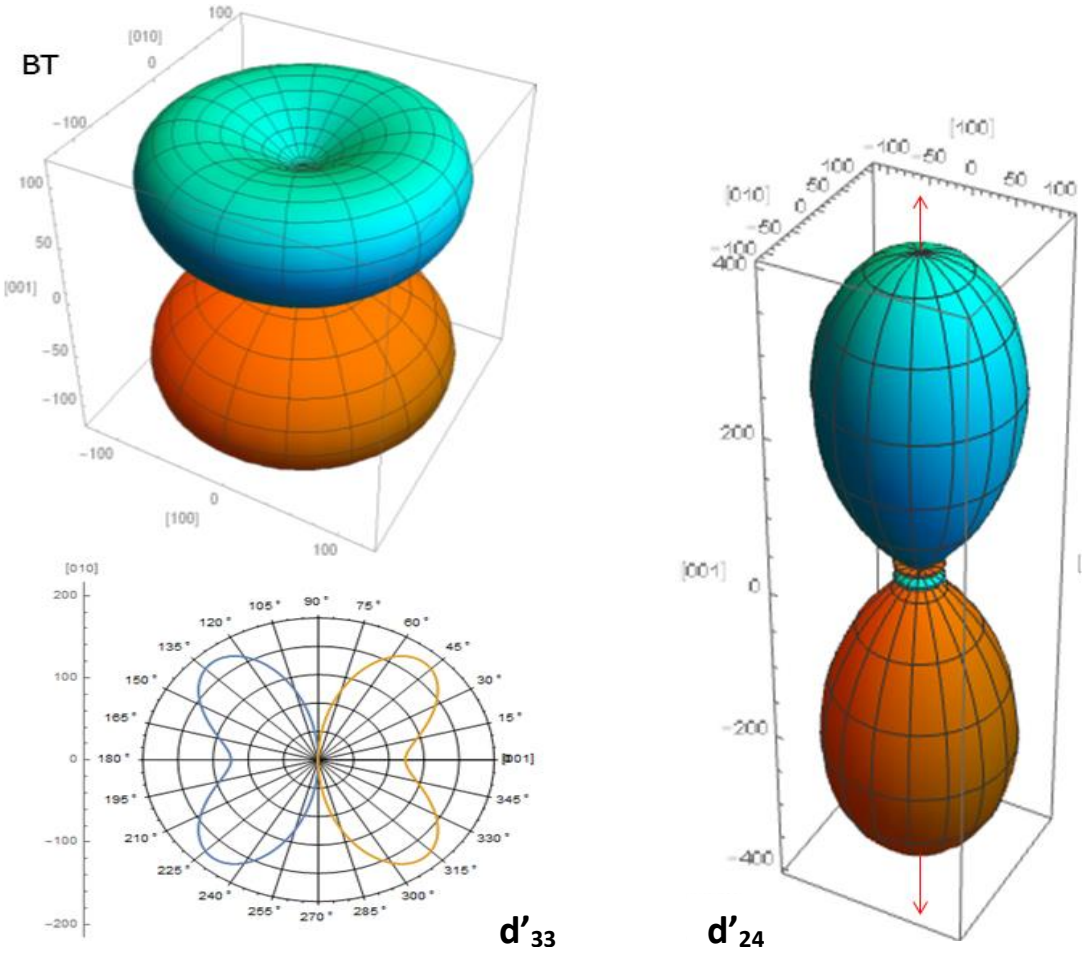

Figure S7: Three-dimensional plots of d'_{33} , d'_{24} and polar plot of d'_{33} for BTO

To evaluate the induced magnetoelastoelectric coupling coefficient α_{ijk}, a matrix multiplication is performed between the above derived N' matrix (of CFO) and d' (of $BaTiO_3$).

$$\alpha_{ijk_{[3X6]}} = d_{iop_{[3X6]}} . N_{lmjk_{[6X6]}}$$

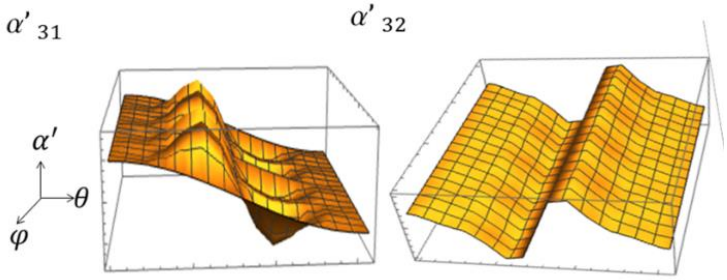

Figure S8: Three-dimensional representation of coupled magneto-elasto-electric coefficients of CFO-BTO, α'_{31}(-2x10^{-6} - 2x10^{-6} V/Oe.m) and α'_{32}(-5x10^{-6} - 5x10^{-6} V/Oe.m) as a function of parametric angles θ (0-π) and φ (0-2π)

References

1 M. Dutta, S. Betal, X. G. Peralta, A. S. Bhalla, R. Guo, *Sci. Rep.*, 2016, **6**, 38041.

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4 M. Dutta, A.S. Bhalla, R. Guo, *Integrated Ferroelectrics.*, 2016, **174**, 26-33.