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## Induced magneto-electric coupling in ferroelectric/ferromagnetic heterostructures

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Using an external magnetic field, we have demonstrated room temperature control of the electric polarization of a ferroelectric polymer, polyvinylidene fluoride (PVDF), in an artificial multiferroic structure. For ferroelectric PVDF polymer thin films in an iron-PVDF-iron heterostructure, both the ferroelectric coercivity and polarization display a hysteresis dependence on the external magnetic field. We also find that the thickness of the PVDF layer has an effect on the magnetoelectric coupling in our samples. We observe a giant magnetoelectric coupling with values as large as 3700 V/cm Oe to 41700 V/cm Oe. © 2013 AIP Publishing LLC.

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Materials with combined ferroelectric and ferromagnetic properties or magneto-electric (ME) coupling effects<sup>1–3</sup> are promising candidates for information technology and device fabrication.<sup>4</sup> Preparation and characterization of multiferroic materials in which ferroelectricity and ferromagnetism coexist have attracted much interest in research for functionalized materials and devices. They present the possibility of electrically controlled magnetic memory devices<sup>5,6</sup> and, conversely, magnetically manipulated electric devices.<sup>7</sup> Room temperature manipulation of magnetically ordered states by electrical means is among the most promising approaches towards developing novel spintronics devices.<sup>8–16</sup> The reported values for the magneto-electric coupling sensitivity range from 1 V/(cm Oe)<sup>17</sup> to 6 V/(cm Oe),<sup>18</sup> 21 V/(cm Oe),<sup>19</sup> and up to 720 V/(cm Oe) at resonance.<sup>20</sup> More reports show that magneto-electric heterostructures display both large magneto-electric voltage coefficients<sup>21</sup> and extreme low magnetic noise.<sup>22</sup> For a more practical high sensitivity magnetic sensor or voltage control of magnetization, the coupling at room temperature has to be optimized and increased for device applications.

Using organic ferroelectrics, in combination with ferromagnetics, could lead to revolutionary device applications due to their intrinsic low-cost, lightweight, and flexible features. The magneto-electric coefficients in organic structure have been reported to be 5.45 V/(cm Oe) for the organic ferroelectric elemental ferromagnetic heterostructures.<sup>23,24</sup> The magneto-electrical response of the organic ferroelectric polyvinylidene fluoride trifluoroethylene (PVDF-TrFE) matrix composite, with dispersed magnetic ferromagnetic CoFe<sub>2</sub>O<sub>4</sub> (CFO) nanoparticles, had a magneto-electric coefficient of ~40 mV/(cm Oe).<sup>25</sup> A relatively large magneto-electric response is reported in multiferroic nanocomposite films

composed of magnetic Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> (NZFO) nanoparticles embedded into a poly(vinylidene-fluoride) copolymer matrix.<sup>26</sup> Promisingly, a much larger direct magneto-electric coupling of 300 V/(cm Oe) has been reported in laminated composites of polyvinylidene fluoride (PVDF) and Metglas.<sup>27</sup>

Here, we report the discovery of a giant ME coupling effect at room temperature, which is larger than the reported values, in multiferroic heterostructures by sandwiching a layer of PVDF ferroelectric polymer between two ferromagnetic iron thin films. This giant ME coupling effect is not due to simple strain effects alone. Our new results of the organic multiferroic heterostructures have potential applications for low cost high sensitivity magnetic sensors and nonvolatile memory elements without the large current densities and power consumption. To study artificial multiferroics that are based on organic ferroelectrics, we synthesized multiferroic heterostructures, shown as Fig. 1, consisting of a ferromagnetic iron layers sandwich with ferroelectric PVDF polymer layer, i.e., Fe/PVDF/Fe. Very thin Al layers (with thickness of only 3 nm) were added to avoid interdiffusion between Fe and PVDF layers with the goal of improving the magneto-electric coupling. Samples were fabricated using physical vapor deposition for magnetic layers and the Langmuir-Schaefer film fabrication method for PVDF layers as described in previous experiments.<sup>28,29</sup> The thickness of each sample is precisely controlled and calibrated. A Radiant Technology Precision ferroelectric measurement system was used to measure the polarization versus electric field hysteresis loops of all the samples. Each sample was placed between the pole pieces of an electromagnet with the external magnetic field applied parallel to the sample surface. By applying an external magnetic field, we were able to control the electric polarization of the ferroelectric PVDF layer.

Fig. 2(a) shows a set of polarization versus electric field (P-E) hysteresis loops measured under different magnetic

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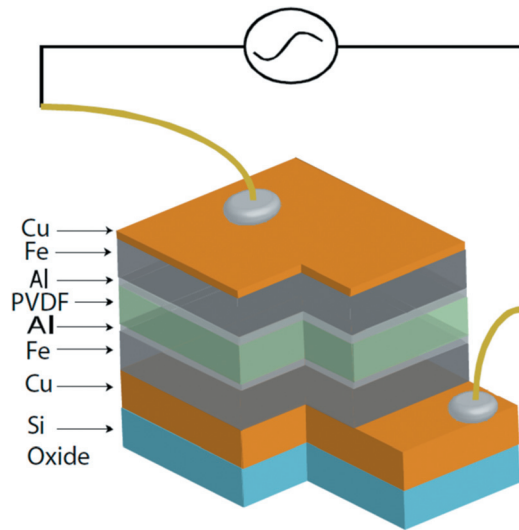


FIG. 1. Schematic of multilayer ferromagnetic Fe/ferroelectric PVDF/ferromagnetic Fe heterostructure sample. The magnetic field used to magnetize magnetic layers was applied in parallel with the sample. The electric field used to characterize the ferroelectric properties of PVDF layer was applied perpendicular to the sample as shown in the graph.

fields for a multilayer sample with the key structure of Fe(80 nm)/PVDF(52 nm)/Fe(26 nm). Here the external magnetic field was varied from  $-930$  Oe to  $930$  Oe and then returned from  $930$  Oe to  $-930$  Oe. Under this magnetic field, the ferromagnetic Fe layer can be fully saturated based on our magnetometer measurements on Fe thin films. Each P-E loop was recorded under a constant magnetic field applied in parallel to the sample, as noted. It is clear that the ferroelectric properties of the PVDF polymer thin film strongly depend upon the applied magnetic field.

This dependence of the PVDF thin film ferroelectric properties is not simply on the magnitude of the external magnetic field, but also on the direction of the magnetic field. The energy product (area under P-E loop) shows a minimum at  $-930$  Oe which then increases with external magnetic field. When the magnetic field is applied at  $-930$  Oe, as shown in Fig. 2(a), the polarization can be saturated at  $6.8$  MV/m, while the polarization switches with a characteristic coercivity of  $4.3$  MV/m. As the applied magnetic approaches to zero, the electric polarization of the PVDF polymer layer saturates at electric field of  $8.4$  MV/m, and the characteristic coercivity is then seen to occur with a  $5.5$  MV/m field (labeled as 0 up).

The PVDF polymer polarization becomes hard to saturate and flip with magnetic field changed from  $-930$  Oe to  $930$  Oe. The P-E loop taken at  $930$  Oe magnetic field shows that the polarization can be saturated at an electric field of  $10.8$  MV/m and it can be flipped at  $7.9$  MV/m. While this influence of the external magnetic field is extremely reproducible over many cycles, after the initial cycle, as described above, when the applied magnetic field is returned to zero from maximum field, the electric polarization saturates at electric field of  $8.9$  MV/m and the coercivity is at  $6.9$  MV/m electric field. The P-E loop taken at this zero magnetic field (labeled as 0 down in Fig. 2(a)) is different from the results taken at the zero magnetic field following an  $-930$  Oe applied field (labeled as 0 up). This training effect means that the P-E loop taken at zero magnetic field depends on history. In order to characterize the magneto-electric coupling of the sample, at a bias electric field of  $6.0$  MV/m, we studied the polarization versus magnetic field, shown in Fig. 2(b). It can be clearly seen that the electric polarization shows hysteresis with the applied external magnetic field.

Because of the fabrication methodology for these Fe/PVDF/Fe heterostructures, the top and bottom PVDF interfaces differ significantly. The difference between the two Fe/PVDF/Fe interfaces is also evident in the difference in the coercive field that indicates that the ferroelectric dipoles do have a slightly favored asymmetry in the favored dipole direction. This is a common observation, especially with thin organic ferroelectric layers, and it is also expected on theoretical grounds given differences in the two Fe/PVDF/Fe interfaces.<sup>30</sup> From Fig. 2(a), it is evident that the polarization hysteresis at  $-930$  Oe results in a smaller coercive field than  $+930$  Oe indicating the polarity dependence of ferroelectric properties on external magnetic field. To better understand this feature, we have plotted the ferroelectric coercivity of the PVDF polymer in the Fe(80 nm)/PVDF(52 nm)/Fe(26 nm) heterostructure under different magnetic fields as shown in Fig. 3(a). The ferroelectric coercivity shows hysteresis that very clearly depends upon the applied external magnetic field. It is also clear that there is significant magneto-electric coupling presented in our Fe/PVDF/Fe heterostructures, and it is also evident that the coupling strength depends upon the PVDF film thickness. The variation in the magneto-electric coupling strength in each of the samples is evident from,  $\Delta E_C$  (labeled as the black arrow in Fig. 3(a), the width of the hysteresis curve of  $E_C$  versus magnetic field

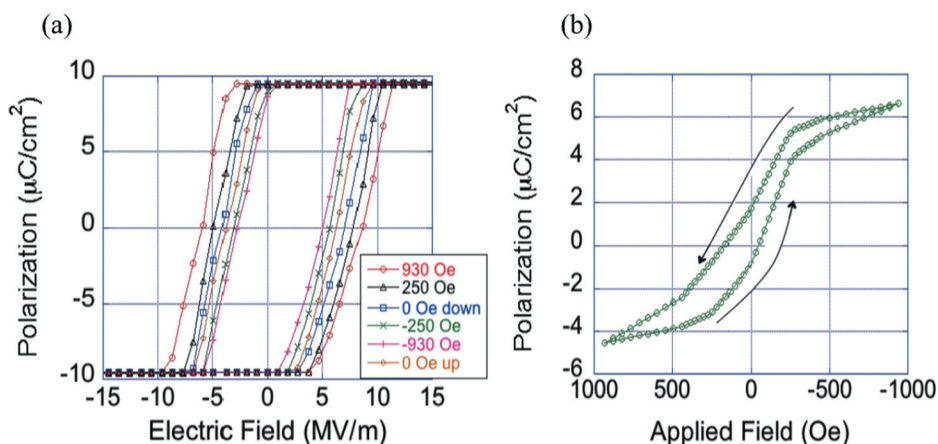


FIG. 2. (a) P-E hysteresis loops of the Fe (80 nm)/PVDF (52 nm)/Fe (26 nm) heterostructure measured under different applied magnetic fields. (b) The polarization of the PVDF polymer as a function of the applied magnetic field at an electric bias field of  $6.0$  MV/m.

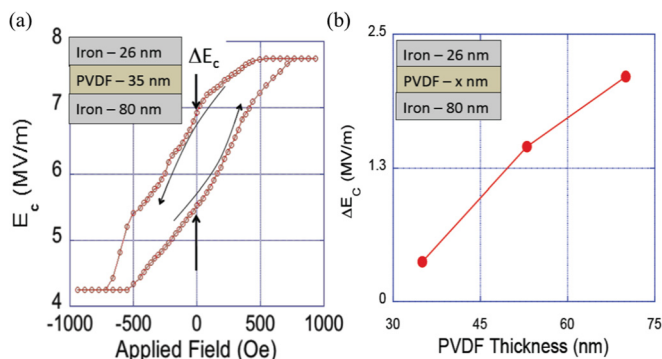


FIG. 3. (a) Electric coercivity of the Fe (80 nm)/PVDF (52 nm)/Fe (26 nm) heterostructure as a function of the applied magnetic field, showing that the coercivity of the PVDF layer hysterically depends on the magnetic field. Figure (b) shows,  $\Delta E_C$  (indicated with arrows in (a)), the width of the coercivity hysteresis under magnetic field as a function of PVDF layer thickness.

graph evaluated at  $H = 0$  field. This width  $\Delta E_C$  indicates the effect of the magnetic field on the ferroelectric properties and it has been plotted as a function of PVDF thickness as Fig. 2(b).  $\Delta E_C$  displays a strong dependence on the PVDF thickness, as shown in Fig. 3, where  $\Delta E_C$  increased by 4 times when the thickness of PVDF is doubled. The comparable results for fixed PVDF thickness, exhibits a relatively smaller dependence of  $\Delta E_C$  on the thickness of Fe layer, as shown in Fig. 4, where  $\Delta E_C$  decreased about twice when the thickness of Fe layer is doubled.

The magneto-electric coupling strength is evident in the width of  $\Delta E_C$ : the wider  $\Delta E_C$ , the stronger the magneto-electric coupling strength. It can be seen that as the PVDF thickness increases, the width  $\Delta E_C$  from the  $E_C$ - $H$  hysteresis loops also increases, so the magneto-electric coupling strength increases as the PVDF thickness increases. This cannot be explained by the simple strain effect. A magnetostriction stress is kept the same for all our samples by keeping the iron layers thickness unchanged. When this same stress (or pressure) is applied to a thicker PVDF layer, the magneto electric coupling effect is expected to be smaller which contradicts our observed data. Second, and more importantly, magnetostriction does not depend on the polarity of magnetic field, however, our data shows clearly dependence on the polarity of the magnetic field. We believe the magneto-electric coupling effect is charge related. The

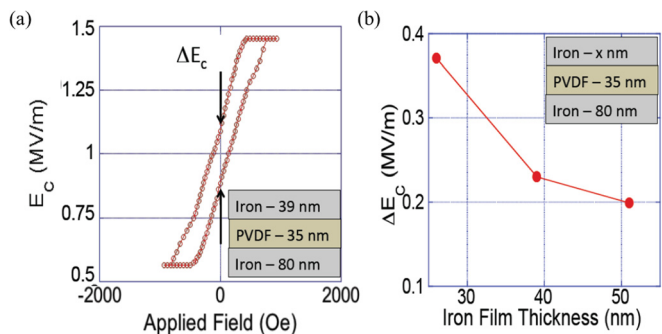


FIG. 4. (a) Electric coercivity of the Fe (80 nm)/PVDF (35 nm)/Fe (39 nm) heterostructure as a function of the applied magnetic field. We vary the top ferromagnetic Fe layer thickness, and (b) shows,  $\Delta E_C$  (indicated with arrows in (a)), the width of the coercivity hysteresis under magnetic field as a function of Fe layer thickness.

magnetic field generated by magnetized Fe is much larger than the external applied magnetic field and we estimated it is around 2 Tesla based on the complete magnetization of Fe layer. This generated magnetic field can exert a Lorenz force on rotating dipoles of PVDF and affect the rotation speed of those dipoles, while the electric dipoles of PVDF can influence the magnetization in the iron layers, as suggested by prior work.<sup>23–26</sup> The direction of this force is either long centripetal or centrifugal direction and it does depend on the polarity of the magnetic field. So the magnetic field could either hinder or stimulate the rotation of electric dipoles, leading to an increase or a decrease of the electric coercivity when the external magnetic field direction is flipped. As a result of that, this additional force can affect and tune the polarization properties of the PVDF layer.

Interdiffusion of iron into the PVDF at the other Fe/PVDF interface is possible,<sup>28,29</sup> so we have added Al layers to minimize the diffusion in order to improve the magneto-electric coupling effect. To verify our study, we have performed similar measurements on reference samples which are PVDF layers sandwiched by Al layers with Fe magnetic layers absent and samples which are PVDF layers sandwiched by Fe magnetic layers with Al layers absent. We noticed that for samples with Fe layers absent the ferroelectric properties of PVDF of those samples do not depend on the external magnetic field at all. For samples with Al layers absent, the ferroelectric properties of PVDF show less magneto-electric coupling strength. Our observed magneto-electric coupling is absolutely due to the heterostructure. Because Fe magnetic layers generate a huge local magnetic field at the interface and this field is much larger than the external magnetic field, this is why the giant magneto-electric coupling can be observed at room temperature with relatively small magnetic field. The added thin Al layers can produce native  $Al_2O_3$  which could minimize the leakage and pinholes in our samples. The results on the reference samples suggest that the observed magneto-electric coupling cannot be due to the deflection of leakage current.

The linear term for the magneto-electric coupling is often used to characterize the performance of a magneto-electric material, and is defined as<sup>31,32</sup>

$$\alpha_E = \frac{\Delta E}{\Delta H} \quad (1)$$

and this quantifies the response of a ferroelectric layer, such as in our heterostructures, to the applied magnetic field. The linear magneto-electric coefficient  $\alpha_E$  has been estimated as a function of the PVDF ferroelectric layer thickness. According to Fig. 2(b) showing the polarization dependence on external magnetic field, we calculated the electric field change due to polarization change with applied magnetic field. The values of magneto-electric coupling coefficient  $\alpha_E$  for our samples are estimated to be  $3700 \pm 400$  V/(cm Oe),  $30\,000$  V/(cm Oe), and  $41\,700 \pm 2200$  V/(cm Oe), for samples with a PVDF layer thickness of 35 nm, 52 nm, and 70 nm, respectively. These giant  $\alpha_E$  values for the magneto-electric coefficient are almost 50 times higher than previously reported.<sup>20,27</sup> This points a way to increasing the magneto-electric effect: construct multiferroics from organic

multilayer structures or metal organic frameworks (MOFs). We have now shown that a large electrical response for only a small applied magnetic field change is also possible—ideal for magnetic sensors.

In summary, we have been able to create multiferroic ferromagnetic/ferroelectric heterostructures by sandwiching a layer of PVDF polymer between ferromagnetic iron thin films. We found that both the coercivity and polarization for the PVDF polymer display hysteretic features as the applied magnetic field is changed. Our experimental results have shown significant advances to prior studies of organic ferromagnetic multilayer studies where an electric field induced change in magnetic anisotropy was demonstrated but here the magneto-electric coupling is seen to be extremely strong by comparison. A giant magneto-electric coupling with values as large as 3700 V/(cm Oe) to 41700 V/(cm Oe) have been observed at room temperature.

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