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Positive temperature coefficient of magnetic anisotropy in polyvinylidene fluoride (PVDF)-based magnetic composites

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The magnetic anisotropy is decreased with increasing temperature in normal magnetic materials, which is harmful to the thermal stability of magnetic devices. Here, we report the realization of positive temperature coefficient of magnetic anisotropy in a novel composite combining β-phase polyvinylidene fluoride (PVDF) with magnetostrictive materials (magnetostrictive film/PVDF bilayer structure). We ascribe the enhanced magnetic anisotropy of the magnetic film at elevated temperature to the strain-induced anisotropy resulting from the anisotropic thermal expansion of the β-phase PVDF. The simulation based on modified Stoner-Wohlfarth model and the ferromagnetic resonance measurements confirms our results. The positive temperature coefficient of magnetic anisotropy is estimated to be 1.1×10^2 J m^{-3} K^{-1}. Preparing the composite at low temperature can enlarge the temperature range where it shows the positive temperature coefficient of magnetic anisotropy. The present results may help to design magnetic devices with improved thermal stability and enhanced performance.

Magnetic anisotropy is a fundamental property of magnetic materials determining the easy magnetization axis[1], which is essential for their application in many devices such as magnetic recording systems, magnetic sensors, microwave devices, and so on[2–4]. Magnetic anisotropy is known to decrease as temperature increases showing a negative temperature coefficient[5,6], which is harmful to the performance of most magnetic devices. For example, the decrease of magnetic anisotropy may lead to the reversal of magnetization resulting in the failure of magnetic recording media[7]. The resonant frequency of a microwave device is decreased with increasing temperature because of the decrease of magnetic anisotropy[8]. In general, from application point of view, zero or positive temperature coefficient of magnetic anisotropy is desirable. It has been well established that magnetocrystalline anisotropy, strain-induced anisotropy, shape anisotropy and Zeeman energy together determine the total magnetic anisotropy energy[9,10]. The intrinsic magnetocrystalline anisotropy is proportional to saturation magnetization (M_S^n, n depends on correlation and crystal symmetry), which decreases with increasing temperature[10,11]. Therefore, magnetocrystalline anisotropy usually shows a negative temperature coefficient. For the extrinsic magnetic anisotropy, it can be changed by the outside stimuli, such as stress/strain, shape change. The strain-induced anisotropy is proportional to the magnetostrictive coefficient[12,13]. As the magnetostrictive coefficient decreases with increasing temperature, the strain-induced anisotropy (for a constant strain) also shows a negative temperature coefficient[14]. The magnitude of shape anisotropy depends on the saturation magnetization, which exhibits a negative temperature coefficient as well[15,16]. Thus, it is very difficult to obtain a zero or positive temperature coefficient of magnetic anisotropy in normal magnetic materials[17].

It is well known that, in strain-mediated ferromagnetic/ferroelectric (FM/FE) bilayers, a uniaxial strain produced through converse piezoelectric effect when an electric field applied on FE layer can be transferred to FM layer to manipulate the magnetic anisotropy[18,19]. Thus, if a functional layer can generate a uniaxial strain when changing the temperature, the positive temperature coefficient of magnetic anisotropy can be realized in bilayers structure through strain-induce anisotropy. β-phase polyvinylidene fluoride (PVDF) and its copolymer, i.e.

PVDF-trifluoroethlene (PVDF-TrEE) are well-known ferroelectric materials showing widely applications in information storage, field-effect transistors, sensors and actuators[20–22]. Besides the ferroelectric properties, PVDF also has an anisotropic thermal expansion, which can generate a uniaxial strain when changing the temperature[23]. We report here the realization of positive temperature coefficient of magnetic anisotropy in magnetic film/PVDF bilayers. The enhanced magnetic anisotropy with increasing temperature originates from the strain-induced anisotropy resulting from the anisotropic thermal expansion of β-phase PVDF substrate (Figure 1a).

Results

Structure and magnetic properties at room temperature. $Co_{40}Fe_{40}B_{20}$ (CoFeB) films of 60 nm were deposited on 30 μm thick PVDF substrate by magnetron-sputtering at room temperature, followed by a 5 nm Pt layer to protect the film against oxidation. X-ray diffraction (XRD) measurement reveals a peak around 21°, which confirms that PVDF is ferroelectric β-phase (Figure 1b)[24]. No diffraction peaks from CoFeB were observed. The CoFeB film shows a diffuse electron diffraction pattern under transmission electron microscope (TEM) reflecting the expected amorphous structure (inset of Figure 1b). Superconducting quantum interference device-vibrating sample magnetometer (SQUID-VSM) was employed to measure the magnetic hysteresis loops of the CoFeB/PVDF composite. Figure 1c shows the loops with magnetic field H parallel (along x direction) and perpendicular to the plane of the CoFeB film at 300 K. It is clearly seen that the CoFeB film is easier to saturate when H is parallel to the film plane. So the easy axis lies in the plane of film. In order to check the in-plane anisotropy, angular

dependence of the magnetic hysteresis loop was measured at 300 K. During the measurements, H is rotated within the xy plane with φ being the angle between H and x direction. Figure 1d shows the angular dependence of normalized remanent magnetization (M_r/M_s), which oscillates with 180° periodicity showing a uniaxial symmetry with easy axis along x direction.

Temperature dependence of magnetic properties for CoFeB/PVDF composite. In order to study the temperature coefficient of magnetic anisotropy in the CoFeB/PVDF composite, we measured the magnetic hysteresis loops along the easy (x direction) and hard axis (y direction) at different temperatures. Figure 2a shows the in-plane magnetic hysteresis loops measured with H along x direction ($\varphi = 0°$). It is quite surprising to observe that the loop becomes squarer as the temperature is increased. On the other hand, the hard axis magnetic hysteresis loop along y direction ($\varphi = 90°$) becomes more slanted (Figure 2b). Figure 2c shows the M_r/M_s versus temperature for H along x and y directions, respectively. With temperature increasing from 250 to 350 K, the M_r/M_s increases from 0.32 to 0.86 and decreases from 0.68 to 0.16 for H along x and y directions, respectively (Figure S1). The crossover occurs at about 298 K, which means that the sample is magnetically isotropic at around 298 K. When the temperature decreases from above 298 K to below 298 K, the easy axis is switched from x to y direction. When the temperature is higher than 298 K, the M_r/M_s difference between the easy and hard axes is increased with increasing temperature. That is, the easy axis becomes easier while the hard axis becomes harder, indicating an abnormal enhanced magnetic anisotropy with increasing
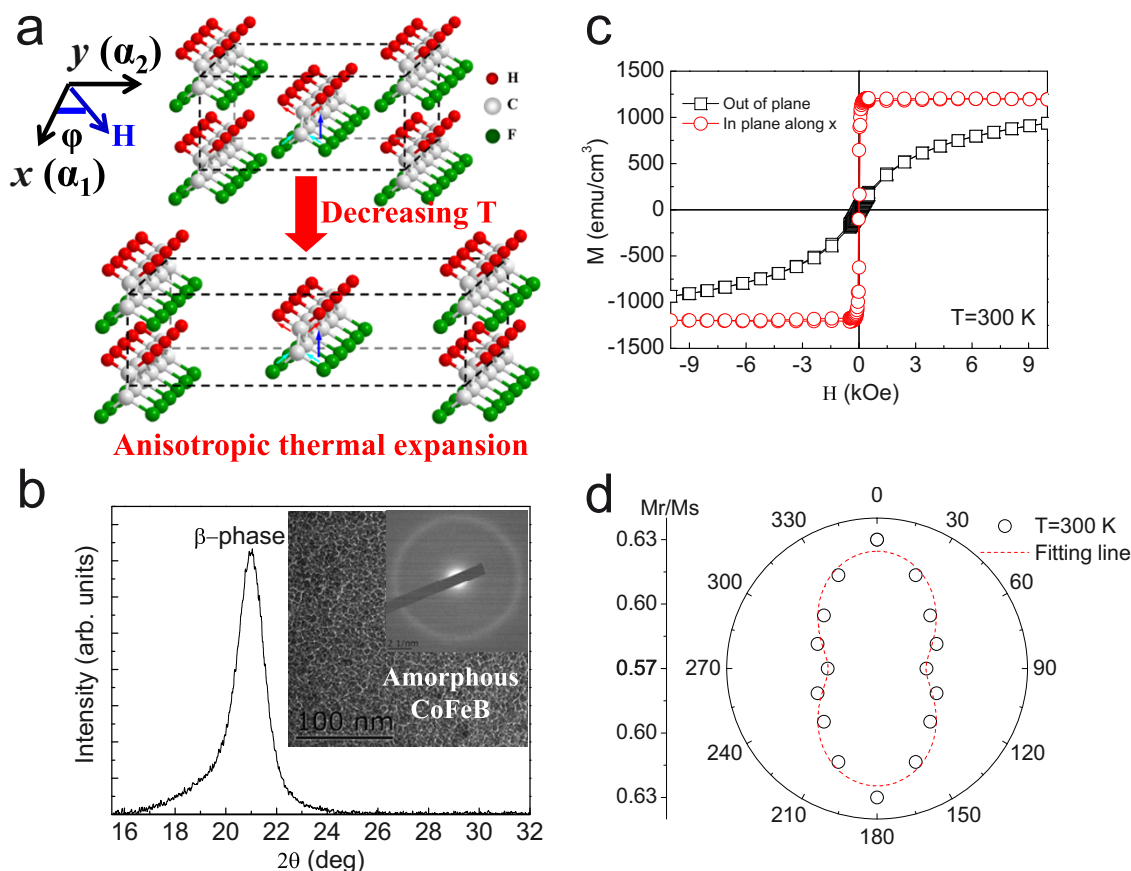

Figure 1 | **The structure and magnetic properties of CoFeB/PVDF at room temperature.** (a) Schematic view of the PVDF substrate. (b) XRD pattern of PVDF substrate. Inset: TEM results for CoFeB films. (c) The magnetic hysteresis loops of CoFeB/PVDF with H parallel (along x direction) and perpendicular to the plane of CoFeB film at 300 K (d) The angular dependence of normalized remanent magnetization M_r/M_s with fitting line at 300 K. The dashed line is $\cos^2\varphi$ fitting.
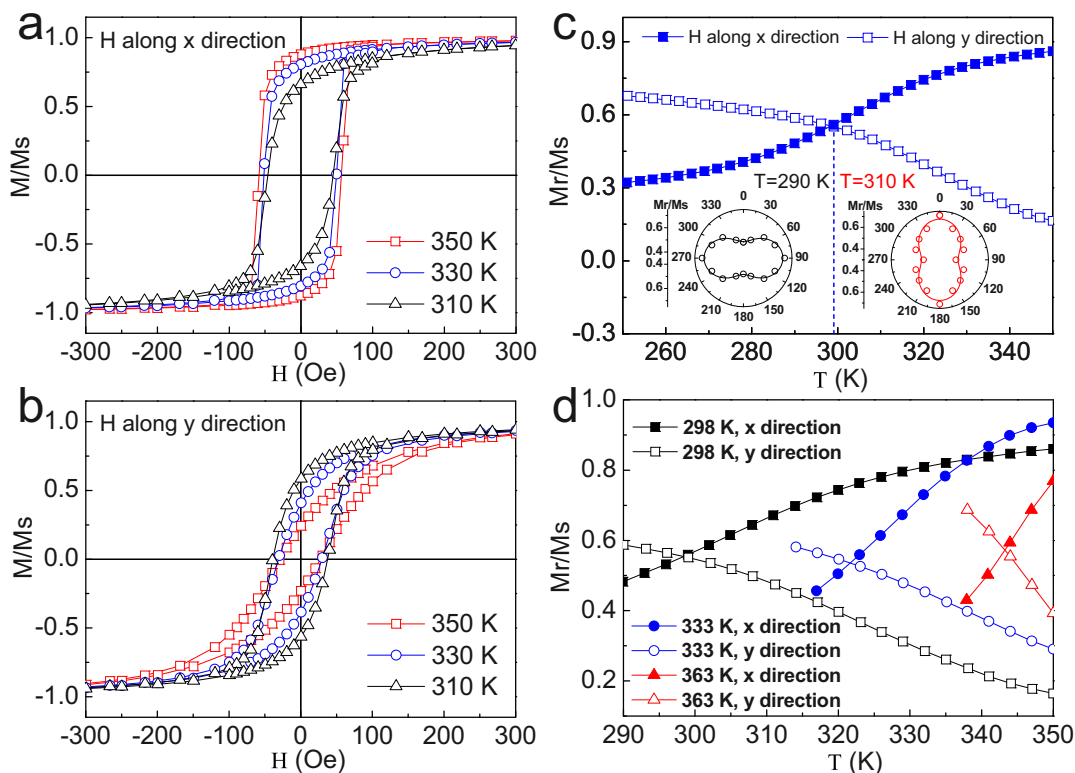
Figure 2 | Temperature dependence of magnetic properties of CoFeB/PVDF. (a) In-plane magnetic hysteresis loops measured along x direction at various temperatures (b) In-plane magnetic hysteresis loops measured along y direction at various temperatures. (c) Temperature dependence of the remanent magnetization with H along x and y directions. The inset: angular dependence of M_r/M_s at 290 and 310 K. (d) Temperature dependence of the remanent magnetization with H along x and y directions for the samples prepared at different temperatures.

temperature. Thus, we can conclude that the CoFeB/PVDF composite possesses a positive temperature coefficient of magnetic anisotropy. The behavior of composites with CoFeB of different thickness (10 nm, 100 nm, and 200 nm) was also studied (Figure S2). All of them show similar temperature dependence of magnetic anisotropy as CoFeB (60 nm)/PVDF. However, when the thickness of CoFeB is too large (i.e. 200 nm), the temperature tunability of M_r/M_s decreases (Figure S2). Figure 2d shows the temperature dependence of M_r/M_s for the samples prepared at 298, 333 and 363 K. The results show that the temperature at which isotropic magnetic behavior is observed to increase with increasing deposition temperature (the small discrepancy is likely due to the difference between the actual sample temperature and the thermal couple reading, which is located behind the heater). After this point, all the samples exhibit an increase of magnetic anisotropy with temperature.

Temperature dependence of magnetic properties of other PVDF-based magnetic films. In order to know the temperature dependence of magnetic anisotropy for different magnetostrictive films, we prepared two other composites by depositing different magnetic materials on PVDF: one is positive magnetostrictive FeGa and the other is negative magnetostrictive Ni. Figure 3a and 3b show the temperature dependence of magnetic hysteresis loops measured with H along x direction for FeGa/PVDF and Ni/PVDF, respectively. For FeGa/PVDF, the slanted loop is changed to a square one with increasing temperature from 280 to 320 K, which is similar to that observed for CoFeB/PVDF. However, for Ni/PVDF, the square loop is changed to a slanted one with increasing temperature. Figure 3c and 3d show the temperature dependence of the remanent magnetization along both x and y directions for FeGa/PVDF and Ni/PVDF, respectively. Both FeGa/PVDF and Ni/PVDF show easy axis reorientation. The temperature dependence of M_r/M_s for FeGa/PVDF is similar to that for CoFeB/PVDF. But the change of

M_r/M_s with H along x is about 0.62, which is larger than that observed for CoFeB/PVDF. This is likely due to the fact that FeGa possess a larger magnetostrictive coefficient than CoFeB. On the other hand, the temperature dependence of M_r/M_s for Ni/PVDF shows an opposite behavior. With increasing temperature from 280 to 320 K, M_r/M_s decreases from 0.45 to 0.08 and increases from 0.26 to 0.48 for H along x and y direction, respectively. The change of M_r/M_s with H along x for Ni/PVDF is about 0.37, which is similar to the value of CoFeB/PVDF due to the comparable magnetostrictive coefficients for CoFeB and Ni. Nevertheless, both FeGa/PVDF and Ni/PVDF composites show enhanced magnetic anisotropy with increasing temperature. The only difference is the direction of easy axis at high temperature. The results confirm that it is possible to design PVDF-based magnetic films with specific temperature dependence of magnetic anisotropy by combining the positive and negative magnetostrictive films (Figure S3).

Ferromagnetic resonance studies at different temperatures. To characterize the temperature dependence of magnetic anisotropy in PVDF-based magnetic composites quantitatively, ferromagnetic resonance (FMR) spectroscopy was measured at 9.5 GHz under different temperatures. It is well known that ferromagnetic resonance frequency f can be expressed by Kittel's equation[25]:

$$2\pi f/\gamma = \sqrt{(H_{res}+H_K)(H_{res}+H_K+4\pi M_S)} \quad (1)$$

where H_{res} is the field where FMR signal is zero, H_K is the in-plane magnetic anisotropy field, M_S is the saturation magnetization, and γ is the gyromagnetic ratio. When the direction of magnetic field is changed from easy axis to hard axis, the FMR line is shifted to the high field region. By observing the shift of H_{res}, H_K can be quantitatively determined[26,27]. Figure 4a shows the field dependence of FMR signal with H along x and y directions at different
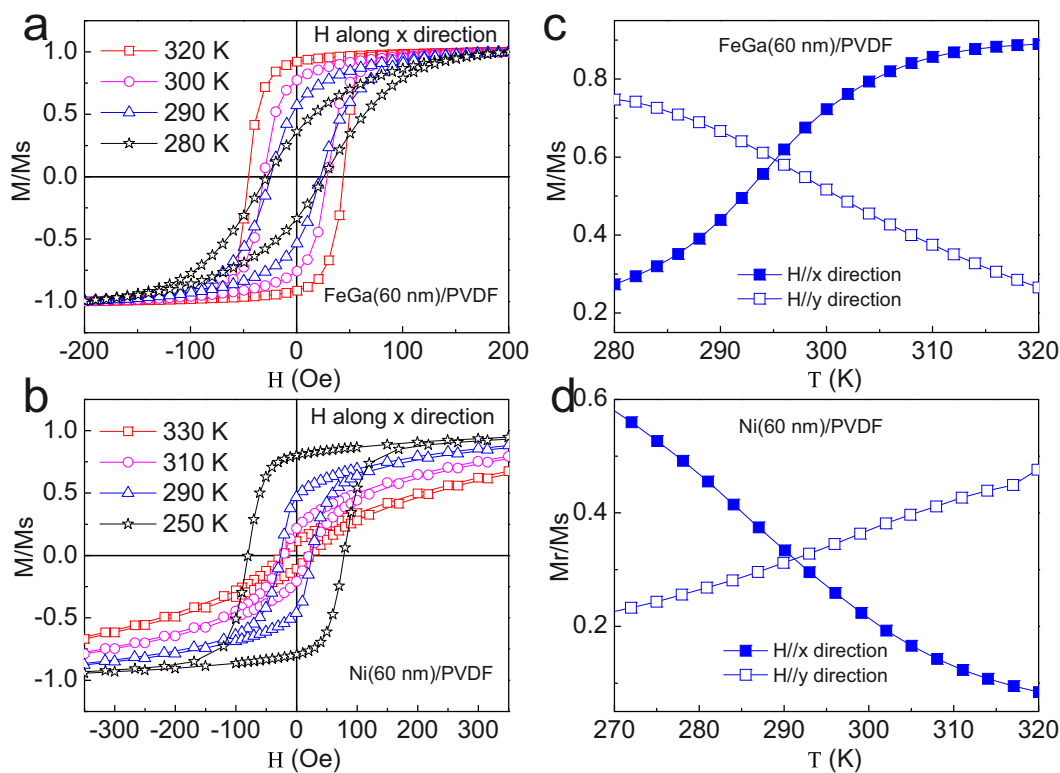
Figure 3 | Temperature dependence of magnetic properties of other PVDF-based magnetic films. In-plane magnetic hysteresis loops measured along x direction at various temperatures for (a) FeGa/PVDF and (b) Ni/PVDF. The temperature dependence of the remanent magnetization with H along x and y directions for (c) FeGa/PVDF and (d) Ni/PVDF.

temperatures for CoFeB/PVDF. FMR line is shifted to the high field region for H along y compared with that of H along x at the same temperature. This indicates that hard axis is along y direction, which is consistent with the result from magnetometry measurements. When the temperature is increased from 290 to 310 K, FMR line with H along y (x) direction is shifted to the high (low) field region. Therefore, the difference of H_{res} between H along x and y directions at 310 K is larger than that at 290 K. In other words, magnetic anisotropy field is enhanced at 310 K compared with 290 K. Figure 4b shows the temperature and angle dependence of H_{res}. The angular dependence of H_{res} oscillates with 180° periodicity showing a uniaxial symmetry about the easy axis ($\varphi = 0°$, x direction). With increasing temperature, H_{res} is increased along y direction (hard axis) and decreased along x direction (easy axis), which means that the uniaxial symmetry is enhanced reflecting an increased magnetic anisotropy. It is clearly seen that the H_K increases linearly from 160 Oe at 290 K to 260 Oe at 350 K [inset of Figure 4a], which indicates that the samples possess a positive temperature coefficient of magnetic anisotropy. For comparison, the temperature dependence of the H_K for 60 nm CoFeB prepared on Kapton substrate is also shown in the inset of Figure 4a. The H_K decreases with increasing temperature showing a negative temperature coefficient of magnetic anisotropy in this sample. This confirms the role of anisotropic thermal expansion to produce the positive temperature coefficient of magnetic anisotropy in PVDF-based magnetic composites. It is well known that the effective uniaxial magnetic anisotropy energy K_{eff} can be expressed by the following formula[28]:

$$K_{eff} = \frac{M_S H_K}{2} \qquad (2)$$

According to above results, K_{eff} is increased from 9.6×10^3 J m^{-3} to 1.6×10^4 J m^{-3} when temperature is increased from 290 to 350 K.

Therefore, the positive temperature coefficient of magnetic anisotropy is estimated to be 1.1×10^2 J m^{-3} K^{-1}.

Discussion

To understand the abnormal positive temperature coefficient of magnetic anisotropy in the CoFeB/PVDF composite, we turn to the properties of the β-phase PVDF substrate. It is well known that ferroelectric PVDF has pyroelectric effect[29]. When the temperature is changed, charges accumulate at the interface between PVDF and magnetic layer. Then, the interface charges can influence the magnetic anisotropy through charge-mediated magnetoelectric coupling when changing the temperature[30–32]. However, the screening length of magnetic metal is smaller than several nanometers[30–32]. As the thickness of our sample (CoFeB, Ni or FeGa) is larger than 10 nm, the charges cannot dominate the control of magnetic anisotropy. So, we can rule out the contribution from the pyroelectric effect to the abnormal positive temperature coefficient of magnetic anisotropy.

On the other hand, we consider the contribution from the anisotropic thermal expansion of β-phase PVDF. It is a non-conjugated linear fluorinated hydrocarbon with a local polarization pointing from fluorines (F) to hydrogens (H) on each monomer (Figure 1a)[33,34]. A tensile strain is applied along x direction during the preparation, the zigzag carbon chains are formed along the same direction[34,35]. Therefore, the dipole chain-chain interaction along y direction is weaker than the carbon atomic interaction along x direction[36], and the thermal expansion coefficient along y direction ($\alpha_2 = -145 \times 10^{-6}$ K^{-1}) is larger than that along x direction ($\alpha_1 = -13 \times 10^{-6}$ K^{-1})[37]. An in-plane anisotropic strain can be generated in PVDF by changing temperature as shown in Figure 1a. The anisotropic strain is transferred from PVDF to the magnetostrictive film resulting in a strain-induced anisotropy. The M_r/M_s difference between two directions increases with increasing (decreasing) temperature above (below) 298 K (sample preparation temperature).
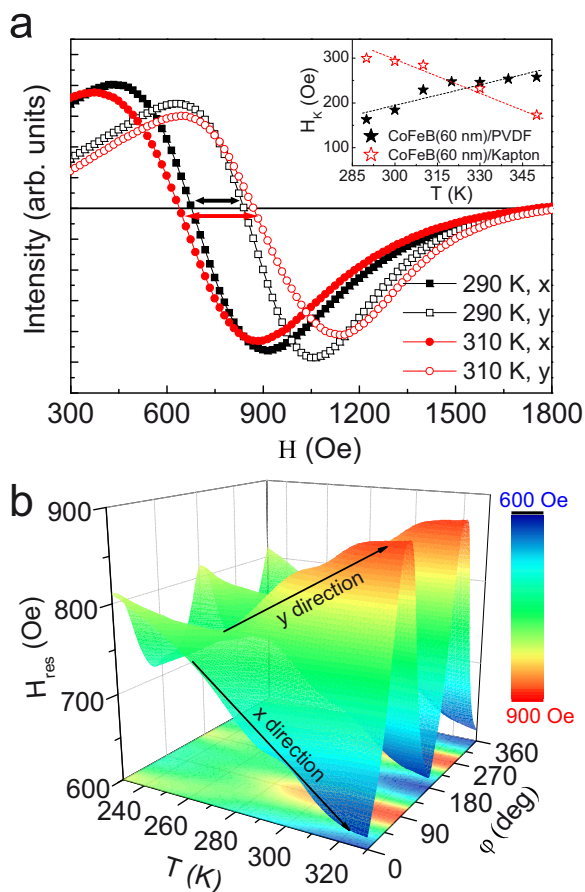
Figure 4 | Ferromagnetic resonance studies at different temperatures.
(a) The magnetic field dependence of FMR signals with H along x and y directions at different temperatures. Inset: temperature dependence of the effect magnetic anisotropy field for 60 nm thick CoFeB prepared on PVDF and Kapton. (b) Temperature and angle dependence of H_{res}.

Note that the easy axis changes direction around 298 K. To further understanding the phenomenon, we perform simulations based on the modified Stoner-Wohlfarth model[13,38]. The total free energy F of CoFeB film can be written as: $F = -K_T\cos^2(\theta-\delta) - MH\cos(\theta-\varphi)$, where K_T is the uniaxial magnetic anisotropy induced by the thermal field through anisotropic thermal expansion effect, δ is the angle between the average easy axis and x/y direction considering the distribution of the uniaxial magnetic anisotropy (Figure 5a), θ is the angle between the magnetization M and x direction. Thus, $K_T = 3\varepsilon_T\lambda_S E_f/2(1-v^2)$, where the thermal induced strain ε_T is $\varepsilon_T = (\alpha_1 - \alpha_2)\Delta T$, λ_S is the magnetostriction constant of amorphous CoFeB film estimated to be 35 ppm[39], Young's modulus E_f of CoFeB film is about 162 GPa[39], Poisson ratio v of CoFeB film is chosen to be 0.3, a typical value for metals[40]. When decreasing or increasing the temperature, effective tensile or compressive strain is generated along y direction due to the anisotropic thermal expansion of PVDF. Therefore, the initial distribution of the magnetizations is squeezed along y and x direction for decreasing and increasing temperature, respectively (Figure 5a). When $\Delta T = 0$ K, the magnetic moments orient randomly due to the distribution of the magnetic anisotropy. Therefore, the angle δ is chosen to be 45° when $\Delta T = 0$ K. The angle δ is estimated to decrease 5° when ΔT changes by 6 K. According to the above hypothesis, we can simulate the magnetic hysteresis loops at different temperatures as shown in Figure 5b and 5c. The simulated results match very well with the experimental observation (Figure 5d), indicating an enhanced magnetic anisotropy with increasing temperature.

When the temperature is higher than 298 K ($\Delta T = 0$), PVDF contracts due to its negative thermal expansion coefficient, which generates an effective compressive strain along y because of the larger thermal expansion coefficient along this direction. The effective compressive strain results in the hard axis of CoFeB being along y direction due to its positive magnetostrictive coefficient. Similarly, an effective tensile strain along y direction is applied to CoFeB if the temperature is lower than 298 K. Hence, the hard axis is changed from y to x direction. The inset of Figure 2c shows the angular dependence of M_r/M_s at 290 and 310 K, respectively. It is clearly seen that the easy axis at 290 and 310 K are perpendicular to each
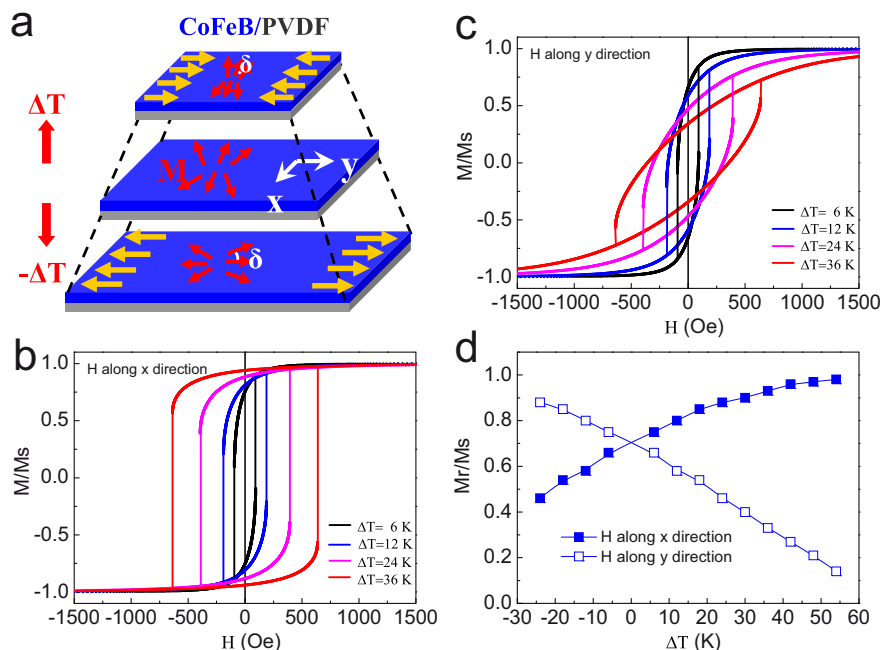

Figure 5 | Simulation of thermal field induced magnetic anisotropy in CoFeB/PVDF samples. (a) Schematic view of the magnetization distribution when changing the temperature. (b) and (c) Simulated magnetic hysteresis loops when increasing temperature with H along x and y direction, respectively. (d) Simulated temperature dependence of M_r/M_s for H along x and y direction.

other. Moreover, the model predicts that the temperature above which positive temperature coefficient of magnetic anisotropy occurs is determined by the sample preparation temperature (Figure S4). We can thus test the model by varying the CoFeB deposition temperature intentionally using a heater. The results are shown in Figure 2d, which is consistent with the model. The method presented here is clearly universal. As long as the substrate has an anisotropic thermal expansion coefficient, we can always obtain a positive temperature coefficient of magnetic anisotropy for any magnetostrictive films.

In conclusion, we have demonstrated that positive temperature coefficient of magnetic anisotropy can be realized in PVDF-based magnetic composites, which has been verified by both magnetometry and FMR measurements. PVDF generates an increasing uniaxial strain with increasing temperature, which transfers to the magnetic films and induces the increase of their magnetic anisotropy. It is demonstrated that the positive temperature coefficient of magnetic anisotropy can be realized in both positive and negative magnetostrictive materials deposited on β-phase PVDF. The positive temperature coefficient of magnetic anisotropy is estimated to be 1.1×10^2 J $m^{-3} K^{-1}$. Preparing the magnetic materials at different temperatures can design the temperature range where the composites show the positive temperature coefficient of magnetic anisotropy. Our results are meaningful for designing the magnetic devices with highly thermal stability.

Methods

Sample preparation. PVDF-based magnetic films were prepared by magnetron sputtering method. The base pressure of the vacuum chamber was in the range of 10^{-5} Pa. During sputtering, the argon flow was kept at 50 sccm (standard cubic centimeter per minute) and the pressure was set at 0.5 Pa. The growth rate for growing CoFeB, $Fe_{81}Ga_{19}$ and Ni films is 12, 10, and 11 nm/min, respectively. The thickness of the magnetic layer (CoFeB, FeGa or Ni) is about 60 nm with 5 nm Pt as the protection layer. We also deposited 60 nm CoFeB film on the NaCl substrates for the transmission electron microscope (TEM) measurement. CoFeB/PVDF samples were also prepared at 333 and 363 K. At first, PVDF substrate was fixed on the holder with high temperature Kapton tape. Then PVDF was heated to 333 or 363 K at high vacuum. At this temperature, PVDF contracted along α_2 direction. After the deposition of CoFeB film on PVDF at 333 or 363 K, CoFeB/PVDF sample was cooled down to room temperature. Therefore, PVDF is back to the original state and a tensile strain is transferred to CoFeB film along y direction.

Measurement. The structure of PVDF was analyzed by using X-ray diffraction (XRD, D8 Advance, Bruker, Germany) with Cu K_α radiation. TEM was used to observe the structure of CoFeB films. A quantum design superconducting quantum interference device-vibrating sample magnetometer (SQUID-VSM) was employed to measure the magnetic hysteresis loops and the angular dependence of the magnetic hysteresis loops for PVDF-based magnetic film in the temperature range from 200 to 350 K. Ferromagnetic resonance (FMR) spectroscopy were measured at 9.5 GHz using a BRUKER EMXplus 10112 spectrometer in the temperature region of 200–300 K by sweeping magnetic field parallel to the film plane.

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Author contributions

Y.L., B.W. and R.L. conceived the experiments; Y.L., Z.T. and H.Y. carried out experiments; Q.Z. did modeling; G.L., Z.Z., X.Zhang, Y.X., X.Zhu., B.C. and J.W. discussed the results and commented the manuscript; Y.L., B.W. and R.L. wrote the manuscript.

Additional information

Supplementary information accompanies this paper at http://www.nature.com/scientificreports