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Proceeding Paper

The Synthesis of Anisotropic 3D Nanomagnets for Magnetic Actuation and Sensing in Piezoelectric Polyvinylidene Fluoride towards Magnetic Nanogenerator Device Fabrication †

Ojodomo J. Achadu [1,*], Gideon L. Elizur [2] and Owolabi M. Bankole [3]

[1] School of Health and Life Sciences, National Horizon Centre, Teesside University, Middlesbrough TS1 3BA, UK
[2] Institute of Pharmacy and Biomedical Sciences, University of Strathclyde, Glasgow G4 0RE, UK; gideon.elizur.2021@uni.strath.ac.uk
[3] Department of Chemical Sciences, Adekunle Ajasin University, Akungba 0901, Nigeria; bankolemutolib@yahoo.com
* Correspondence: o.achadu@tees.ac.uk
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Abstract: The geometry and anisotropic properties of 3D magnetic nanostructures have a direct impact on their magnetization properties and functionalities due to the presence of spatial coordinates. This has stimulated the exploration and synthesis of various types of nanosized magnetic materials for use in magnetic energy-harvesting technology. Herein, anisotropic 3D nanomagnets with cubic, spherical, and mixed truncated cubic/rod-like morphologies were prepared and embedded in a polyvinylidene fluoride (PVDF) polymer matrix to derive 3D nanomagnet–PDVF composites. The 3D nanomagnet–PDVF composites were found to exhibit the highly electroactive β-phase of PVDF, indicative of enhanced piezoelectric properties. Furthermore, the thin films of the 3D nanomagnet–PDVF composites displayed remarkable magnetic responsiveness and actuation capacity in the presence of a magnetic force. This work highlights the potential of the prepared 3D nanomagnet–PDVF composites as a magnetic sensing and actuator system towards the design of magnetic nanogenerators for harvesting ambient low-frequency magnetic noise.

Keywords: 3D nanomagnets; nanomagnet–PVDF composites; magnetic actuation and sensing; magnetic nanogenerators; energy harvesting

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1. Introduction

Magnetic noise from various electrical systems and electronic devices is a plentiful source of energy that is ubiquitous in the environment but rarely utilised. Like sunlight and wind energy, magnetic noise can be renewably harvested and converted into useful electricity using magnetic energy harvesters or generators [1–3]. However, this has not been sustainably feasible and/or achievable due to the technical limitations around the harvesting of ubiquitous magnetic noise with very low frequency in the region of 50/60 Hz [1–3]. This is coupled with the bulky nature of traditional magnetic generator systems [1,4]. State-of-the art magnetic energy harvesting technology utilises laminated magnetoelectric ceramic composites to convert low-frequency magnetic noise into electricity to power wireless sensors and minimise the dependence on batteries [5–8]. Meanwhile, ceramic-based magnetic energy generators are bulky (with heavy magnets used as cantilevers) and mechanically fragile with low power output [9,10]. To address these drawbacks, soft and flexible magnetic generators based on the combination of novel nanostructured magnetic materials with piezoelectric and/or magnetoactive polymers are required. This will not only make it easier to fabricate compact devices but will also result in low-cost and efficient

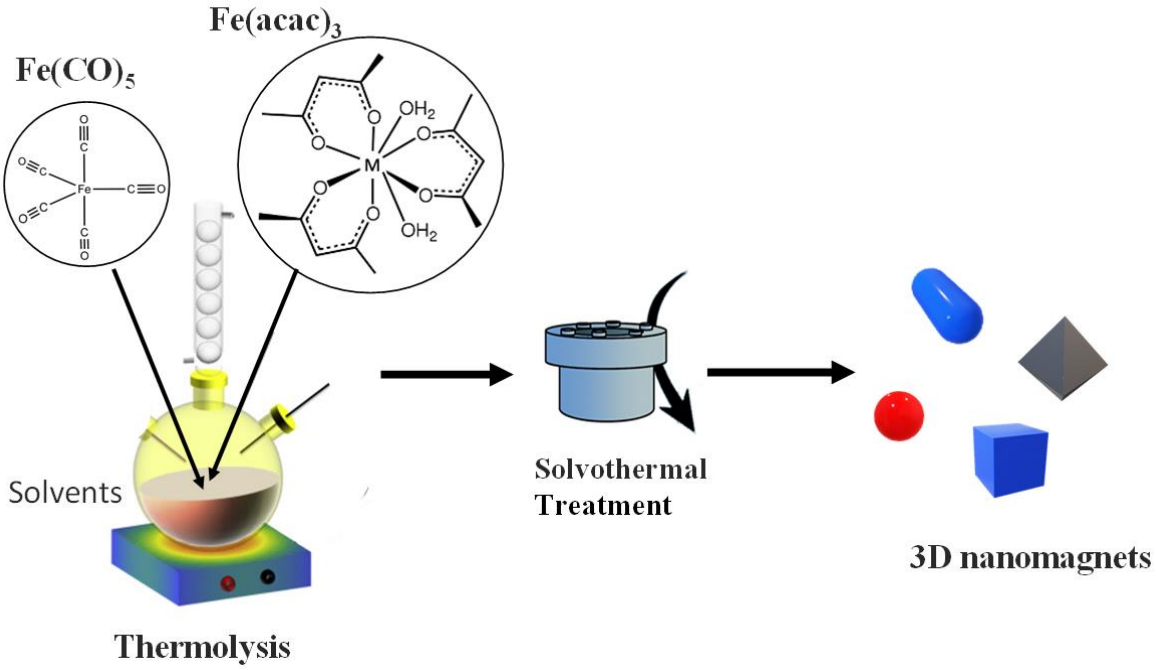
magnetic energy harvesting and conversion. Our hypothesis is that nanostructured magnetic materials that can respond to low-frequency magnetic fields [1,11] will be ideal for enabling high magnetoelectric responsiveness in piezoelectric and/or magnetoactive polymers for the magneto-mechano (piezo)-electric (MME) energy conversion of low-frequency magnetic noise. In this light, 3D nanomagnets are expected to outperform conventional bulk magnets and magnetic nanoparticles with a significant increase in magneto-electric performance due to the special magnetism induced by the 3D spatial coordinates [11–13].

In this work, we demonstrate the proof-of-concept of the magnetic actuation and sensing performance of novel anisotropic 3D nanomagnets when incorporated into piezoelectric polymers such as polyvinylidene fluoride (PVDF). The prepared magnetic nanostructures with different morphologies (mixed truncated cubic/rod-like shapes and cubic and spherical shapes) were characterised using high-resolution transmission electron microscopy (HR-TEM) and superconducting quantum interference device (SQUID) magnetometry. The 3D nanomagnets were subsequently embedded in a PVDF crystalline matrix for the fabrication of magnetic responsive and actuating thin films. The presence of the 3D magnetic nanostructures in the PVDF matrix induced the electroactive β-phase of the PVDF as well as imparting magnetic actuation of the 3D nanomagnet–PVDF composite thin films. We are currently developing propriety magneto-mechanical (piezo)-electric (MME) nanogenerators to realise magnetic energy to electric conversion using the prepared flexible 3D nanomagnet–PVDF composite thin films presented herein. The 3D nanomagnet–PVDF composites will reinforce magneto-restriction in the thin films, thus enlarging the magneto-mechanical coupling, which may lead to a higher magnetoelectric voltage coupling coefficient. With this system, an output voltage will be produced through a direct magnetoelectric electret effect. This paper highlights the exciting possibilities of 3D nanomagnet–PVDF composite thin films to serve as an alternative class of magnetic materials for constructing low-cost and compact magnetic nanogenerators as an upgrade over bulky ceramic-based and traditional magnetic energy harvesting technologies. The real-world applications of magnetic nanogenerator-based energy harvesting systems include providing an unlimited energy supply by recycling untapped magnetic energy for use in powering wearables, portable healthcare devices, and lighting up homes. This has the potential to change how low-power electronic devices, such as wireless sensors and smartphones, are operated and utilised in the future.

2. Materials and Methods

2.1. Synthesis of 3D Nanomagnets

The synthesis of the 3D nanomagnets with various morphologies ranging from cubic-, spherical-, and truncated cubic/rod-shaped was achieved by means of thermolysis–heterogeneous nucleation and the growth of precursor materials (Scheme 1). In a typical manner, iron (III) acetylacetonate, $Fe(acac)_3$ (1.3 mmol) or iron pentacarbonyl, $Fe(CO)_5$, 98%, and oleic acid (3 mL, 90%) (for the synthesis of cubic and truncated cubic/rod-shaped 3D nanomagnets) were mixed with oleylamine (0.956 g, 3 mmol) and 1-octadecene (5 mL) and then heated up to 310 °C for 1.5 h under nitrogen gas protection in a Schlenk line. The resulting nanomagnetic precursors were treated with triethylamine (5 mL, 99%) and poly (styrene-*co*-maleic anhydride), cumene-terminated, *PScMA* (M_n = 1900 g/mol) as a binder, followed by solvothermal heating in a Teflon-lined stainless steel autoclave at 150, 220, and 280 °C for 20 h. The products were cooled to room temperature and purified/collected by means of magnetic separation, followed by annealing at 500 °C to obtain solid 3D magnetic nanostructures.



Scheme 1. Synthetic routes for the 3D nanomagnetic materials with different morphologies.

2.2. Preparation of 3D Nanomagnet–PVDF Composites and Thin Films

The nanocomposites of 3D nanomagnet–PVDF were prepared by adding 0.1 g of the 3D nanomagnets to 10 mL of 15 wt % (*w*/*v*) PVDF-dimethyl formamide (DMF) solution. The mixture was mechanically stirred for 5 h. Thin films were prepared by means of a solution casting process on clean glass substrates and dried in vacuo at 70 °C for 10 h to obtain free-standing flexible films.

2.3. Morphological and Magnetic Characterisations

The as-synthesised 3D nanomagnets were characterised using high-resolution transmission electron microscopy (HRTEM)/selected area electron diffraction (SAED).

The magnetisation (M vs. H) and susceptibility (χ vs. T) of the 3D nanomagnets and PVDF composites/thin films were measured using a Quantum Design MPMS SQUID magnetometer. Fourier-transform infrared (FTIR) spectroscopy was used to elucidate the crystalline phase transformation and piezoelectric properties of the 3D nanomagnet–PVDF composites/thin films.

3. Results and Discussion

The synthesis process for the 3D nanomagnets is illustrated in Scheme 1. The adopted synthesis approach typically comprises thermal decomposition and a solvothermal process, which offers better-quality magnetic nanostructures in terms of size and morphology. The synthesis strategy was based on the choice of the precursors and most importantly the solvothermal reaction time and temperatures used to achieve both the size and anisotropic morphologies of the magnetic nanostructures [14]. The controlled synthesis to obtain anisotropic cubic and mixed truncated cubic/rod-like shapes was specifically dictated using Fe $(CO)_5$ as a precursor in the presence of oleic acid [15], which resulted in the formation of the mixed truncated cubic/rod-like and purely cubic morphologies. $Fe(acac)_3$ was used as the precursor for the spherical-shaped 3D nanomagnets in the absence of oleic acid. The 3D geometry of the nanomagnets was systematically engineered by the solvothermal clustering protocol [16] in the presence of the amphiphilic polymeric PScMA which was a factor that not only allowed for geometrical clustering but also the fine-tuning of the size.

Structural and morphological characterisation were carried out to evaluate the size and shapes of the synthesised nanomagnets. As shown by the HRTEM micrographs in Figure 1a,b, the cubic- and spherical-shaped nanomagnets were non-uniformly distributed, with sizes ranging between 20–30 nm and 15–25 nm, respectively. The HRTEM images also clearly revealed the distinctive adjacent crystal planes of (220) and (311) for the cubic morphology and (100), (111), (311), and (400) for the spherical nanomagnets. The various lattice fringes correspond to the typical magnetite crystalline phases of magnetic nanostructures [17]. The mixed truncated cubic/rod-like nanomagnets exhibited quite heterogeneous compositions with bigger size distributions and diameters in the range of 15–50 nm (Figure 1c).

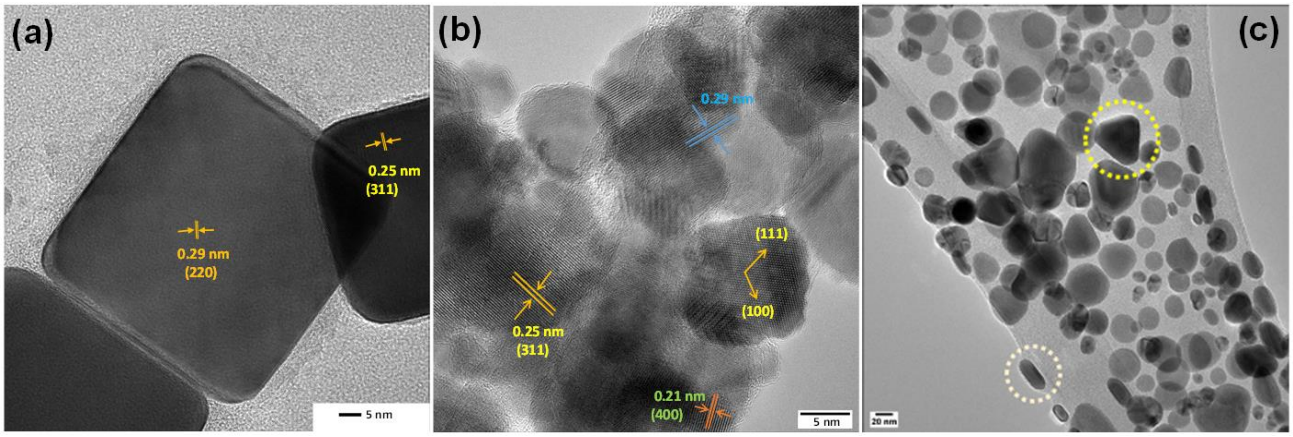


Figure 1. HRTEM images of the 3D nanomagnets showing cubic (**a**), spherical (**b**), and mixed truncated cubic/rod-like (**c**) morphologies. The crystalline planes of the cubic and spherical morphologies are shown in (**a**,**b**).

Furthermore, the various 3D nanomagnets were dispersed in commodity PVDF polymer to derive magnetically induced piezoelectric composites. Solution-processed 3D-nanomagnet-PVDF films were obtained with free standing, folding, and bending features, as shown in Figure 2a–c. PVDF film without incorporating the 3D nanomagnets was also prepared for comparison in terms of magnetic and piezoelectric susceptibility. The thin films were further characterised using scanning electron microscopy (SEM) to elucidate the structural differences between the 3D nanomagnets embedded and the neat PVDF films. The SEM images (Figure 2d,e) clearly show a difference in their surface morphologies (roughness) which may be ascribed to the encapsulation of the 3D nanomagnets into the PVDF polymer matrix. It is expected that the change in the surface morphology confirmed by SEM will equally result in a change in the surface, structural, and chemical properties of the PVDF such as its crystallinity and piezoelectric properties. It was envisaged that 3D nanomagnets would likely act as an agent for inducing the electroactive β-phase nucleation by aligning the -CH_2/-CF_2 molecular dipoles of PVDF [18]. This helps to achieve a high piezoelectric coefficient and sensitivity in addition to the magnetic responsiveness of the films.

To ascertain whether the produced films possess the desired magneto-piezoelectric properties towards MME nanogenerator fabrication, magnetic characterisation such as saturation magnetisation analysis of both the 3D nanomagnets and their PVDF films was carried out. Figure 3a,b shows the M-H hysteresis curve for the 3D nanomagnets (with the cubic shape shown as an example) and the 3D nanomagnet–PVDF film. The 3D nanomagnets generally exhibit very strong magnetic moments at 300 K with a ferromagnetic behaviour. Meanwhile, symmetric hysteresis and saturation magnetisation was observed in both the nanomagnets and their thin films, with saturation magnetisation values of ~80 and 45 emμ/g, respectively. Importantly, for the thin films, saturation magnetisation and remanent magnetization can be observed, which is one of the desired properties as

evident from the displayed remarkable magnetic responsiveness and actuation capacity in the presence of a magnetic force.

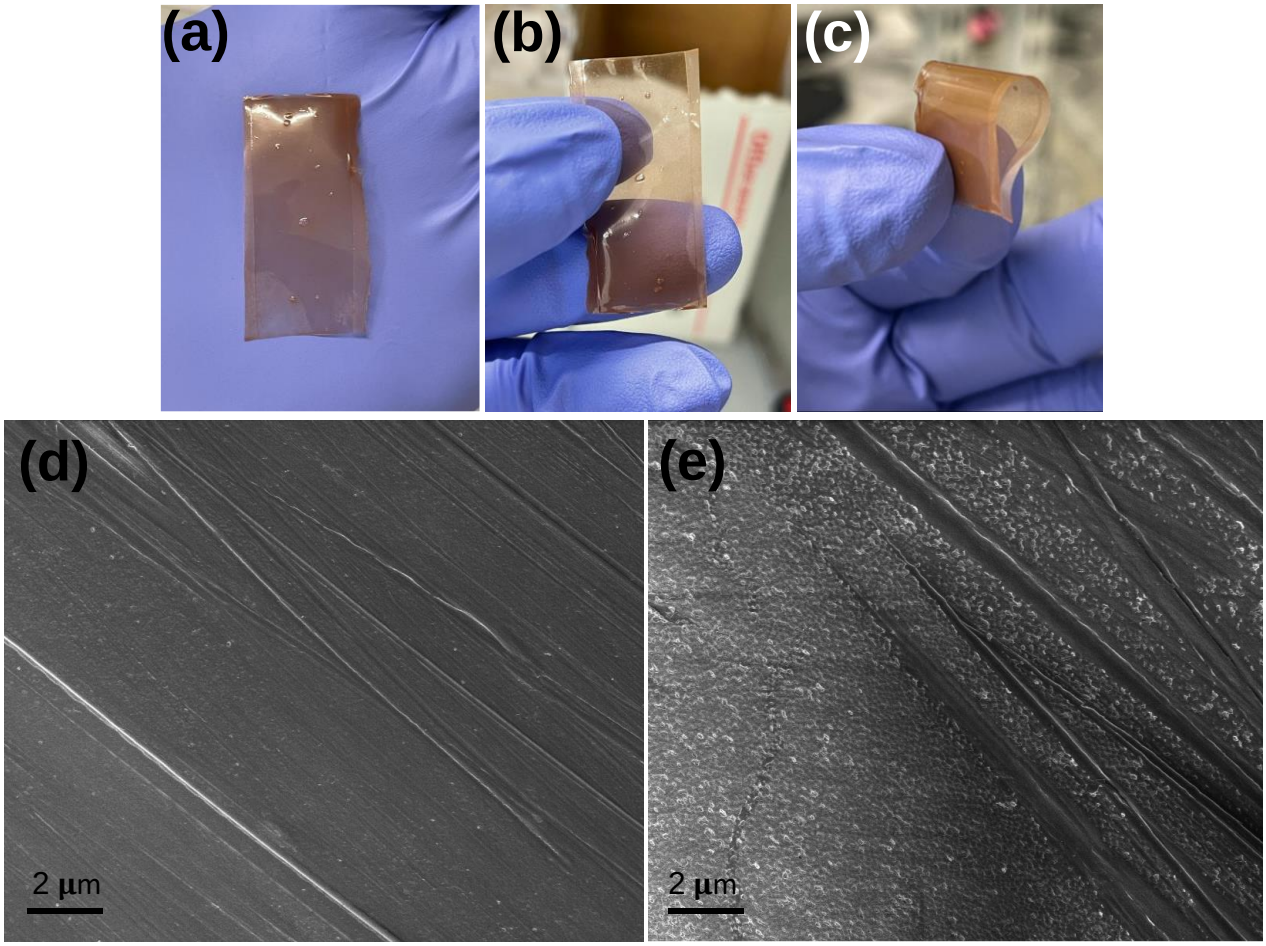


Figure 2. Thin films of the cubic-shaped 3D nanomagnet–PVDF composites displaying freestanding, stretching, and bending features (**a**–**c**). SEM images of the PVDF (**d**) and cubic-shaped 3D nanomagnet–PVDF (**e**) films.

FTIR spectroscopy was used to confirm the PVDF piezoelectric-favored -CH_2/-CF_2 dipolar alignments in the presence of the 3D nanomagnets. In Figure 3c, the FTIR results clearly show the induction of the extensive polar β-phase in the 3D nanomagnet–PVDF films. This is evident from the appearance of the intense vibrational peak at ~1190 cm^{-1}, which is non-existent in the pristine PVDF films [18]. The dual characteristic peaks at 705 cm^{-1} and 520 cm^{-1} correspond to the β- and γ-phases, which is an indication of the β-phase [18], suggesting that its induction is the result of the 3D nanomagnets. Similar characterisation trends and results were observed for all of the synthesised anisotropic 3D nanomagnets. However, the cubic morphology of the 3D nanomagnets exhibited superior magnetic properties alone and in the PVDF thin films. The results of all the characterisations illustrate the remarkable properties and motivation for using 3D nanomagnet–PVDF films as an MME generator component.

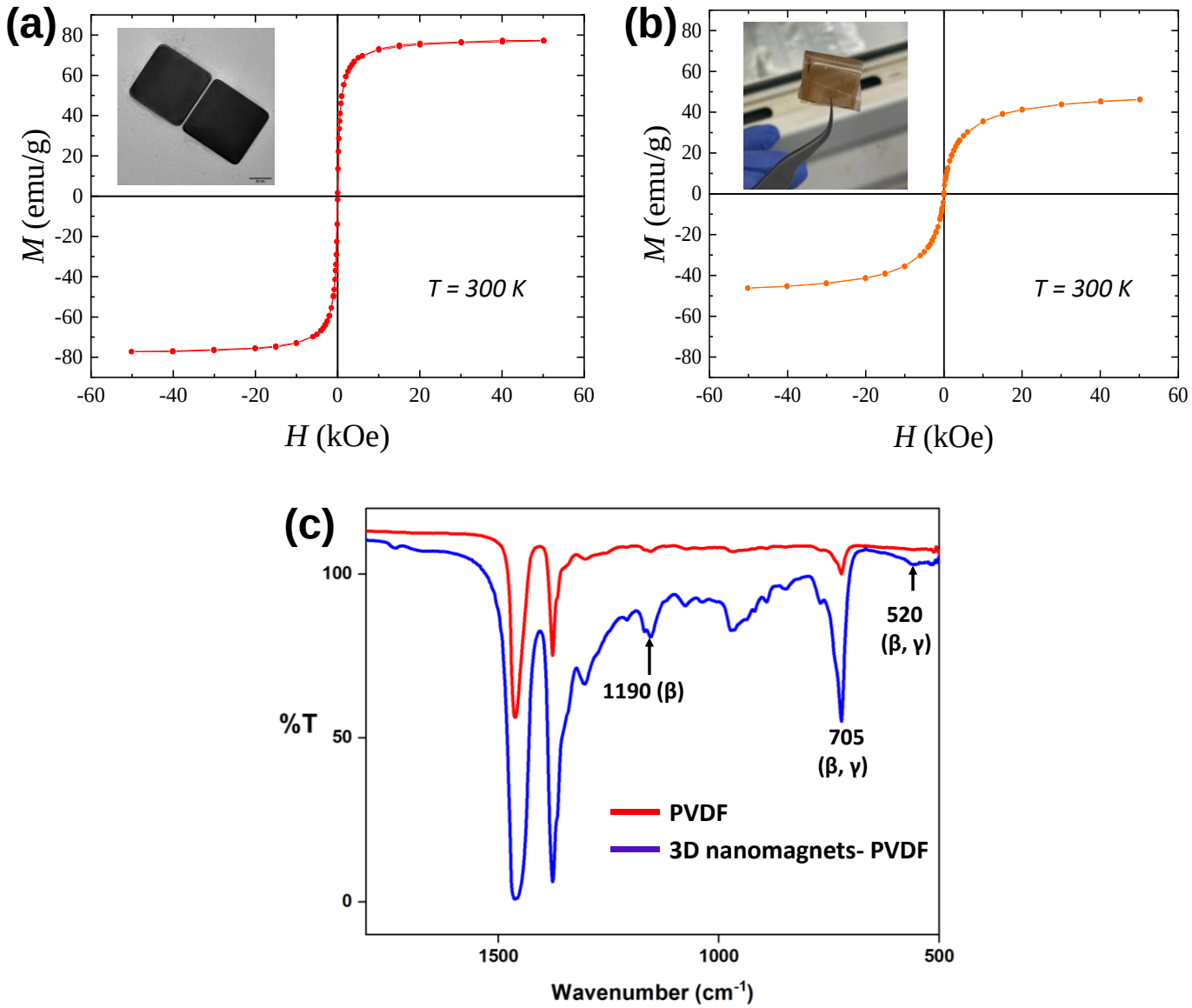


Figure 3. Magnetometry plots (hysteresis curves) for the cubic-shaped 3D nanomagnets (**a**) and their PVDF thin films (3D nanomagnets–PVDF) (**b**). FTIR spectra of the thin films of PVDF (pristine) and 3D nanomagnets–PVDF (**c**).

4. Conclusions

In summary, advanced 3D magnetic nanostructures with distinctive anisotropic features such as cubic, spherical, and mixed truncated cubic/rod-like morphologies have been prepared and subsequently embedded in the polymeric matrix of piezoelectric PVDF to induce an electrically active β phase of the PVDF. The fabricated thin films displayed excellent formability features with better adaptability. The flexible films of 3D nanomagnet–PVDF composites with their attractive properties in terms of cost-effectiveness and excellent electroactive properties, as well as the induced large spontaneous polarizability, piezoelectricity, and magnetic responsiveness by incorporating 3D nanomagnets, make them innovative materials for not just magnetic nanogenerator device fabrication but also various magnetic applications such as sensing and actuation. This will facilitate the development of self-powered and portable wireless communication systems and medical and diagnostic devices by harvesting the ambient waste stray magnetic noise and minimising the dependence on batteries, benefitting the fast-growing industry automation and the Internet of Things (IoT).

Author Contributions: O.J.A.: conceptualization, methodology, validation, execution of experiments, and manuscript preparation; G.L.E. and O.M.B.: validation, data curation, review, and editing. All authors have read and agreed to the published version of the manuscript.

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