

Proceeding Paper

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, and National Horizon Centre, Teesside University, Middlesbrough TS1 3BA, UK

² Institute of Pharmacy and Biomedical Sciences, University of Strathclyde, Glasgow, UK; email1@email.com

³ Department of Chemical Sciences, Adekunle Ajasin University, Akungba, Nigeria; email2@email.com

* Correspondence: o.achadu@tees.ac.uk

[†] Presented at the 10th International Electronic Conference on Sensors and Applications (ECSA-10), 15–30 November 2023; Available online: <https://ecsa-10.sciforum.net/>.

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/rods-like morphologies were prepared and embedded in a polyvinylidene fluoride (PVDF) polymer matrix to derive 3D nanomagnets-PVDF composites. The 3D nanomagnets-PVDF composites were found to exhibit the highly electroactive β -phase of PVDF, indicative of enhanced piezoelectric properties. Further, the thin films of the 3D nanomagnets-PVDF composites displayed remarkable magnetic responsiveness and actuation capacity in the presence of a magnetic force. This work highlights the potential of the prepared 3D nanomagnets-PVDF composites as a magnetic sensing and actuator system towards the design of magnetic nanogenerators for harvesting ambient low-frequency magnetic noise.

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

Citation: Achadu, O.J.; Elizur, G.L.; Bankole, O.M. Synthesis of Anisotropic 3D Nanomagnets for Magnetic Actuation and Sensing in Piezoelectric Polyvinylidene Fluoride towards Magnetic Nanogenerator Device Fabrication. *Eng. Proc.* **2023**, *56*, x. <https://doi.org/10.3390/xxxxx>

Academic Editor(s): Name

Published: 15 November 2023



Copyright: © 2023 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

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 harvester or generators [1–3]. However, this has not been sustainably feasible and/or achievable due to the technical limitations around the harvesting of the 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]. The state-of-the-art magnetic energy harvesting technology utilise laminated magnetolectric ceramic composites to convert low-frequency magnetic noise to electricity to power wireless sensors and minimising the dependence on batteries [5–8]. Meanwhile, ceramic-based magnetic energy generators are bulky (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 it will also result in low-cost and efficient magnetic energy harvesting and conversion. Our hy-

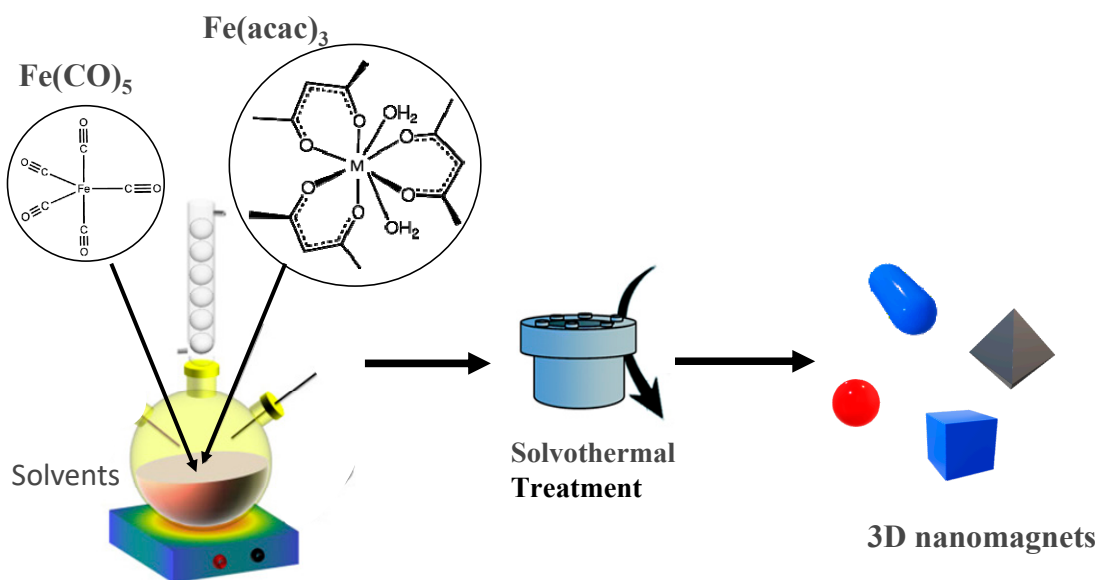
pothesis is that nanostructured magnetic materials that can respond to low-frequency magnetic fields [1,11] will be ideal for enabling high magnetoelectric responsiveness in piezoelectric and/or magnetoactive polymers for a magneto-mechano (piezo)-electric (MME) energy conversion of low-frequency magnetic 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 have demonstrated 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/rods, 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 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 nanomagnets-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 nanomagnets-PVDF composite thin films presented herein. The 3D nanomagnets-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 nanomagnets-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 thermolytic-heterogeneous nucleation and growth of precursor materials (Scheme 1). Typically, iron (III) acetylacetonate, $\text{Fe}(\text{acac})_3$ (1.3 mmol) or iron pentacarbonyl, $\text{Fe}(\text{CO})_5$, 98% and oleic acid (3 mL, 90%) (for the synthesis of cubic and truncated cubic/rod-shaped 3D nanomagnets) was mixed with oleylamine (0.956 g, 3 mmol) and 1-octadecene (5 mL), then heated up to 310 °C for 1.5 h under nitrogen gas protection in a Schlenk line. The resulting nanomagnetic precursors was 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 stain-less steel autoclave at 150, 220 and 280 °C for 20 h, respectively. The products were cooled to room temperature and purified/collected by magnetic separation, followed by annealing at 500 °C to obtain solid 3D magnetic nanostructures.



Thermolysis

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

2.2. Preparation of 3D Nanomagnets-PVDF Composites and Thin Films

The nanocomposites of the 3D nanomagnets-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 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-synthesized 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 nanomagnets-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 comprised of thermal decomposition and solvothetical synthesis process which offered better quality of the magnetic nanostructures in terms of size and morphology. The synthesis strategy was based on the choice of the precursors and most importantly the solvothetical reactions time and temperatures used to achieve both 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 $\text{Fe}(\text{CO})_5$ 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. $\text{Fe}(\text{acac})_3$ 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 solvothetical clustering protocol [16] in the presence of the amphiphilic polymeric PScMA which was a factor that not only allowed for geometrical clustering, but also for 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 size ranging between 20–30 nm and 15–25 nm, respectively. The HRTEM 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 magnetic nanostructures [17]. The mixed truncated cubic/rod-like nanomagnets exhibited quite heterogeneous compositions with bigger size distribution and diameter in the range of 15–50 nm (Figure 1c).

Further, the various 3D nanomagnets were dispersed in commodity PVDF polymer to derive magnetically induced piezoelectric composites. A 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 were 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 difference between the 3D nanomagnets embedded and the neat PVDF films. The SEM images (Figure 2d,e) clearly showed 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 change in the surface, structural and chemical properties of 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 $-\text{CH}_2/-\text{CF}_2$ molecular dipoles of PVDF [18]. This help to achieve a high piezoelectric coefficient and sensitivity in addition to the magnetic responsiveness of the films.

To ascertain that 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 were carried out. Figure 3a,b show that M-H hysteresis curve for the 3D nanomagnets (the cubic shape shown as an example) and 3D nanomagnets-PVDF film. The 3D nanomagnets generally exhibit very strong magnetic moment at 300 K with a ferromagnetic behaviour. Meanwhile, symmetric hysteresis and saturation magnetisation was observed in both nanomagnets and their thin films with saturation magnetisation values of ~ 80 and 45 emu/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 displayed remarkable magnetic responsiveness and actuation capacity in the presence of a magnetic force.

FTIR spectroscopy was used to confirm the PVDF piezoelectric-favored $-\text{CH}_2/-\text{CF}_2$ dipolar alignments in the presence of the 3D nanomagnets. In Figure 3c, the FTIR results clearly showed the induction of the extensive polar β phase in the 3D nanomagnets-PVDF films. This is evident from the appearance of the intense vibrational peak at $\sim 1190 \text{ cm}^{-1}$, 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, is an indication of the β -phase [18] suggesting it's induction as result of the 3D nanomagnets. Similar characterisation trends and results were observed for all the synthesised anisotropic 3D nanomagnets. However, the cubic morphology of the 3D nanomagnets exhibited more superior magnetic properties alone and in the PVDF thin films. The results of all the characterisations illustrated the remarkable properties and motivation for using the 3D nanomagnets-PVDF films as an MME generator component.

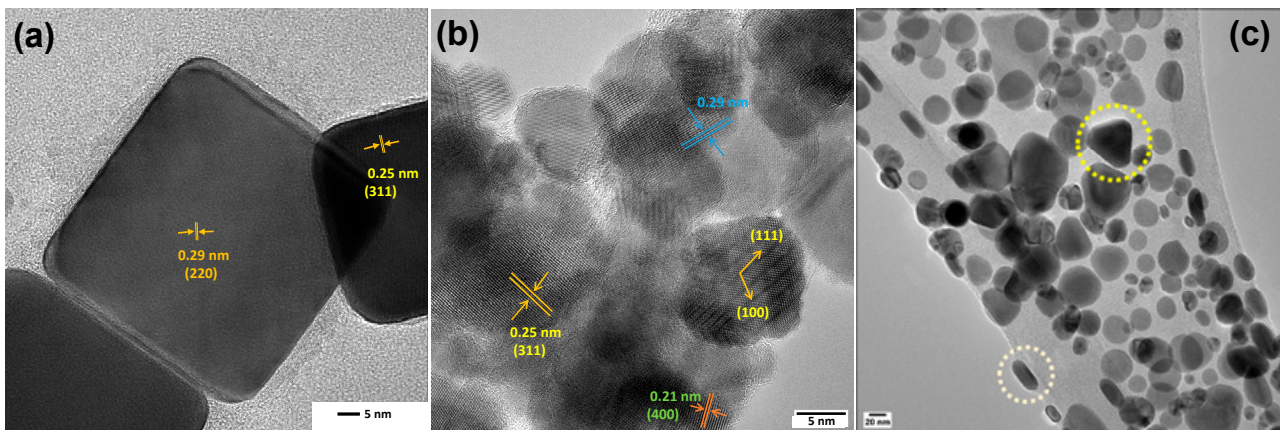


Figure 1. HRTEM of the 3D nanomagnets showing cubic (a); spherical (b) and mixed truncated cubic/rod (c) morphologies. The crystalline planes of the cubic and spherical morphologies are shown in (a,b).

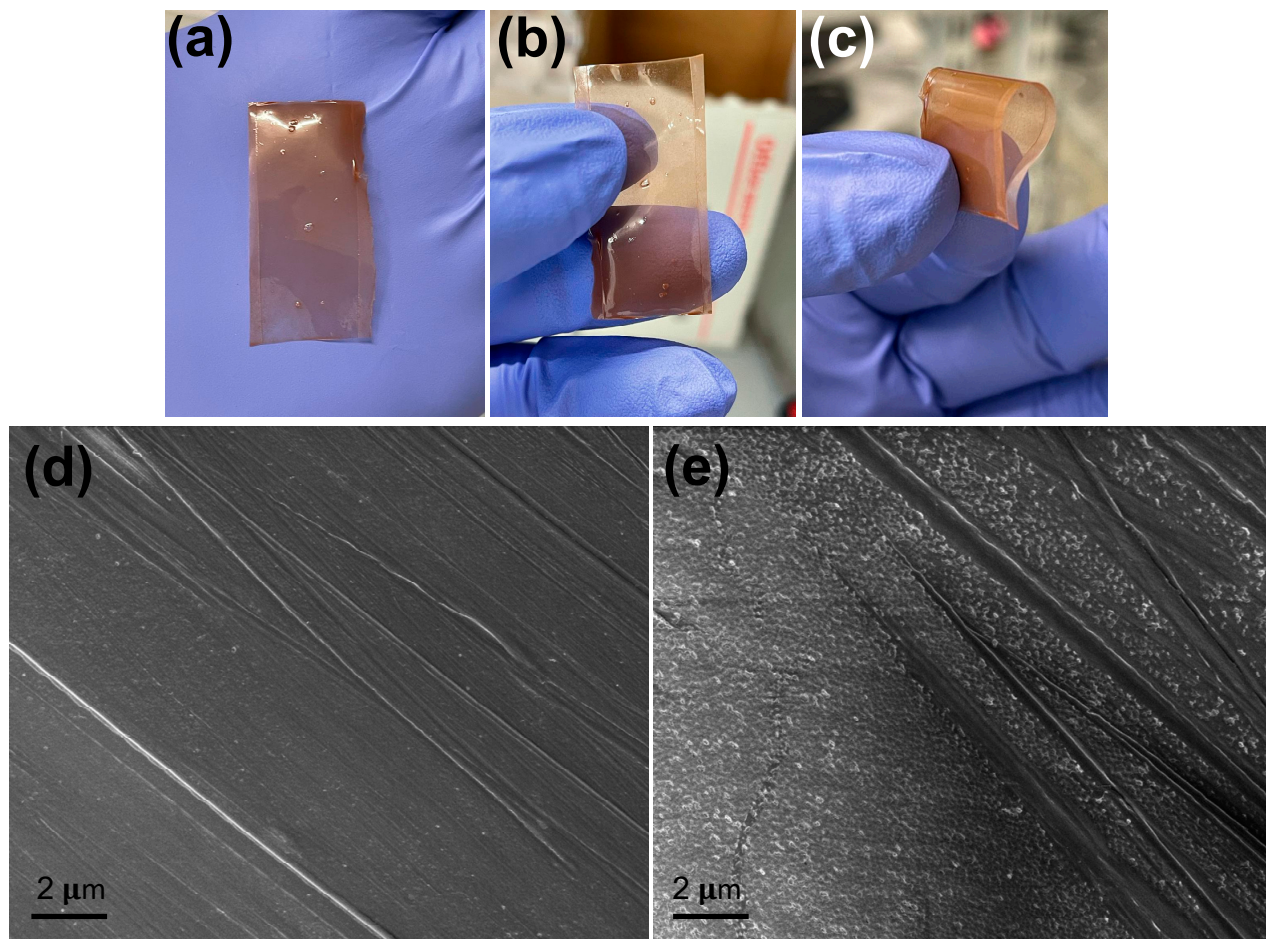


Figure 2. Thin films of the cubic-shaped 3D nanomagnets-PVDF composites displayed freestanding, stretching, and bending features (a–c). SEM images of PVDF (d) and cubic-shaped 3D nanomagnets-PVDF (e) films.

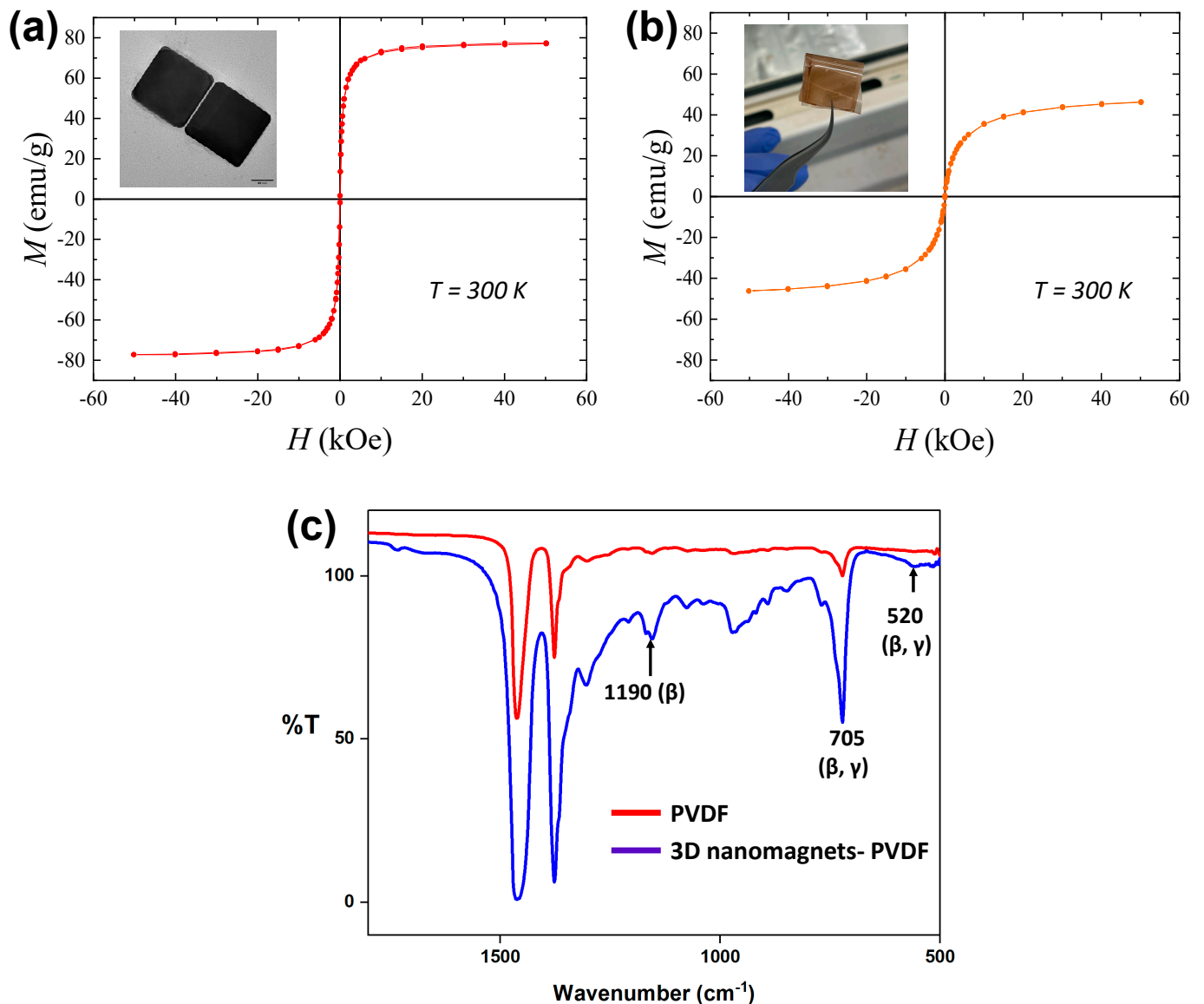


Figure 3. Magnetometry plots (hysteresis curves) for the cubic-shaped 3D nanomagnets (a) and their PVDF thin film (3D nanomagnets-PVDF) (b). FTIR spectra of the thin films of PVDF (pristine) and 3D nanomagnets-PVDF (c).

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 nanomagnets-PVDF composites with its 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 only magnetic nanogenerators device fabrication, but also for various magnetic applications such as sensing and actuation. This will facilitate the development of self-powered and portable wireless communication systems, 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 Internet of Things (IoT).

Author Contributions: O.J.A.; conceptualization, methodology, validation, execution of experiments, 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.

Funding: Funding supports from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement no. 945380 for the project to develop sustainable magnetic nanogenerators is gratefully acknowledged.

Data Availability Statement: Available on request.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Annapureddy, V.; Palneedi, H.; Hwang, G.T.; Peddigari, M.; Jeong, D.Y.; Yoon, W.H.; Kim, K.H.; Ryu, J. Magnetic energy harvesting with magnetoelectrics: An emerging technology for self-powered autonomous systems. *Sustain. Energy Fuels* **2017**, *1*, 2039–2052.
2. Ryu, J.; Kang, J.E.; Zhou, Y.; Choi, S.Y.; Yoon, W.H.; Park, D.S.; Choi, J.J.; Hahn, B.D.; Ahn, C.W.; Kim, J.W.; et al. Ubiquitous magneto-mechano-electric generator. *Energy Environ. Sci.* **2015**, *8*, 2402–2408.
3. Lee, H.; Sriramdas, R.; Kumar, P.; Sanghadasa, M.; Kang, M.G.; Priya, S. Maximizing power generation from ambient stray magnetic fields around smart infrastructures enabling self-powered wireless devices. *Energy Environ. Sci.* **2020**, *13*, 1462–1472.
4. Dai, X.; Wen, Y.; Li, P.; Yang, J.; Li, M. Energy harvesting from mechanical vibrations using multiple magnetostrictive/piezoelectric composite transducers. *Sens. Actuators A-Phys.* **2011**, *166*, 94–101.
5. Hu, X. Increased effective piezoelectric response of structurally modulated P(VDF-TrFE) film devices for effective energy harvesters. *Mater. Des.* **2020**, *192*, 108700.
6. Annapureddy, V.; Na, S.M.; Hwang, G.T.; Kang, M.G.; Sriramdas, R.; Palneedi, H.; Yoon, W.H.; Hahn, B.D.; Kim, J.W.; Ahn, C.W.; et al. Exceeding milli-watt powering magneto-mechano-electric generator for standalone-powered electronics. *Energy Environ. Sci.* **2018**, *11*, 818–829.
7. Lim, K.W.; Peddigari, M.; Park, C.H.; Lee, H.Y.; Min, Y.; Kim, J.W.; Ahn, C.W.; Choi, J.J.; Hahn, B.D.; Choi, J.H.; et al. A high output magneto-mechano-triboelectric generator enabled by accelerated water-soluble nano-bullets for powering a wireless indoor positioning system. *Energy Environ. Sci.* **2019**, *12*, 666–674.
8. Al-Ashtari, W.; Hunstig, M.; Hemsell, T.; Sextro, W. Frequency Tuning of Piezoelectric Energy Harvesters by Magnetic Force. *Smart Mater. Struct.* **2012**, *21*, 035019.
9. Narita, F.; Fox, M. A review on piezoelectric, magnetostrictive, and magnetoelectric materials and device technologies for energy harvesting applications. *Adv. Eng. Mater.* **2018**, *20*, 1700743. <https://doi.org/10.1002/adem.201700743>
10. Ahn, C.-W.; Choi, C.-H.; Park, H.-Y.; Nahm, S.; Priya, S. Dielectric and Piezoelectric Properties of (1-x)(Na_{0.5}K_{0.5})NbO₃-xBaTiO₃ Ceramics. *J. Mater. Sci.* **2008**, *43*, 6784–6797.
11. Fernández-Pacheco, A.; Streubel, R.; Fruchart, O.; Hertel, R.; Fischer, P.; Cowburn, R.P. Three-dimensional nanomagnetism. *Nat. Commun.* **2017**, *8*, 15756.
12. Faure, B.; Wetterskog, E.; Gunnarsson, K.; Josten, E.; Hermann, R.P.; Brückel, T.; Andreassen, J.W.; Meneau, F.; Meyer, M.; Lyubartsev, A.; et al. 2D to 3D crossover of the magnetic properties in ordered arrays of iron oxide nanocrystals. *Nanoscale* **2013**, *5*, 953–960.
13. Anagnostopoulou, E.; Grindi, B.; Lacroix, L.M.; Ott, F.; Panagiotopoulos, I.; Viau, G. Dense arrays of cobalt nanorods as rare-earth free permanent magnets. *Nanoscale* **2016**, *8*, 4020–4029.
14. Ma, Z.; Mohapatra, J.; Wei, K.; Liu, J.P.; Sun, S. Magnetic Nanoparticles: Synthesis, Anisotropy, and Applications. *Chem. Rev.* **2023**, *123*, 3904–3943.
15. Soran-Erdem, Z.; Sharma, V.K.; Hernandez-Martinez, P.L.; Demir, H.V. Tailored Synthesis of Iron Oxide Nanocrystals for Formation of Cuboid Mesocrystals. *ACS Omega* **2021**, *6*, 20351–20360.
16. Niculaes, D.; Lak, A.; Anyfantis, G.C.; Marras, S.; Laslett, O.; Avugadda, S.K.; Cassani, M.; Serantes, D.; Hovorka, O.; Chantrell, R.; et al. Asymmetric assembling of iron oxide nanocubes for improving magnetic hyperthermia performance. *ACS Nano* **2017**, *11*, 12121–12133.
17. Achadu, O.J.; Nwaji, N.; Lee, D.; J.Lee; Akinoglu, E.M.; Giersig, M.; Park, E.Y. 3D hierarchically porous magnetic molybdenum trioxide@gold nanospheres as a nanogap-enhanced Raman scattering biosensor for SARS-CoV-2. *Nanoscale Adv.* **2022**, *4*, 871–883.
18. Tamang, A.; Ghosh, S.K.; Garain, S.; Alam, M.M.; Haeberle, J.; Henkel, K.; Schmeisser, D.; Mandal, D. DNA-Assisted β -phase Nucleation and Alignment of Molecular Dipoles in PVDF Film: A Realization of Self-Poled Bioinspired Flexible Polymer Nanogenerator for Portable Electronic Devices. *ACS Appl. Mater. Interfaces* **2015**, *7*, 16143.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.