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Supporting Information

Multi-material 3D printing-enabled multilayers for smart actuation via magnetic and thermal stimuli

Dharneedar Ravichandran,[a] Reza James Ahmed,[b] Rounak Banerjee,[c] Mahdi Ilami,[b] Hamid Marvi,[d] Guillaume Miquelard-Garnier,e Yuval Golan[f] and Kenan Song [g*]

a Systems Engineering, School of Manufacturing Systems and Networks, The Polytechnic School (TPS), Ira A. Fulton Schools of Engineering, Arizona State University, Mesa, AZ 85212, USA
b Mechanical Engineering, The School of Engineering of Matter, Transport and Energy (SEMTE), Ira A. Fulton Schools of Engineering, Arizona State University, Tempe, AZ 85281, USA
c Department of Physics, The College of Liberal Arts and Science, Arizona State University, Tempe, AZ 85281, USA
d The School of Engineering of Matter, Transport and Energy (SEMTE), Ira A. Fulton Schools of Engineering, Arizona State University, Mesa, AZ 85281, USA
e Laboratoire PIMM, UMR 8006, Arts et Métiers Institute of Technology, CNRS, CNAM, Hesam University, 151 boulevard de L'Hôpital, 75013, Paris, France
f Ilse Katz Institute for Nanoscale Science and Technology, Department of Materials Engineering, Ben-Gurion University of the Negev, Beer-Sheva 8410501, Israel
g The Polytechnic School (TPS), & The School of Engineering of Matter, Transport and Energy (SEMTE), Ira A. Fulton Schools of Engineering, Arizona State University, Mesa, AZ 85212, USA
** Corresponding author, Email: Kenan.song@asu.edu*

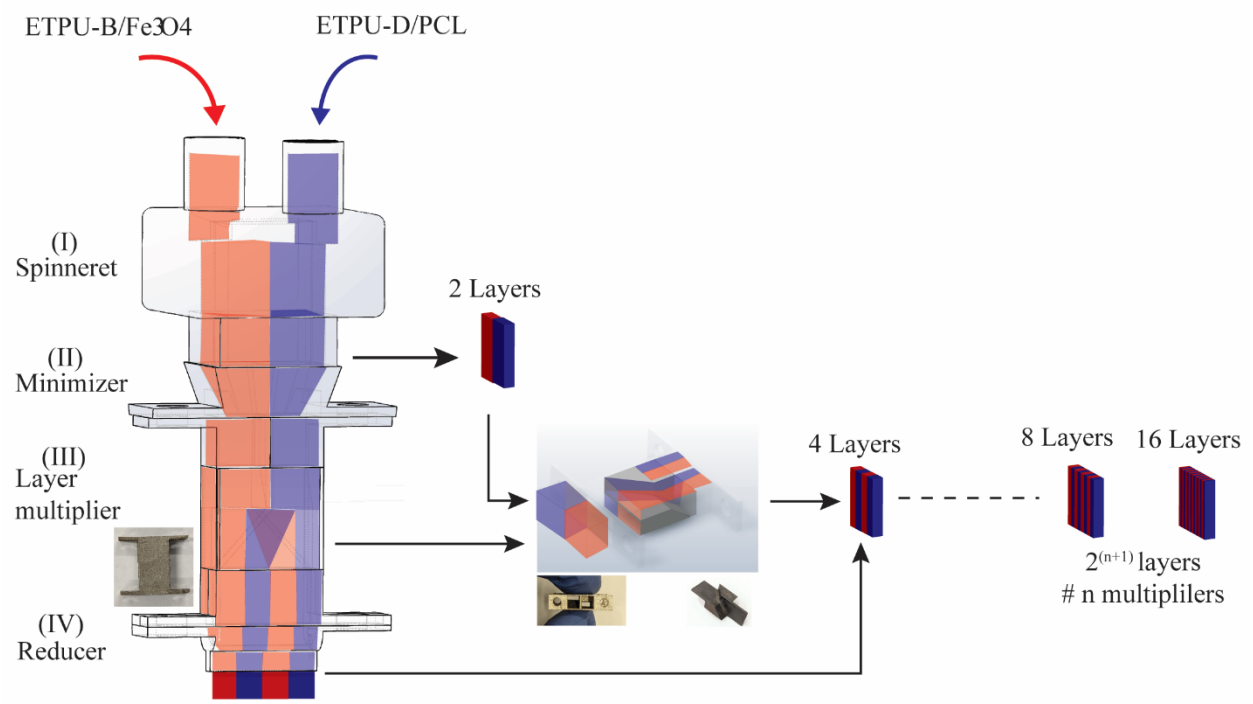

Figure S1. Illustrations of the printhead in-house developed for the feedstock flow through the MDIW nozzle, consisting of (I) the spinneret with the ability to take in two different feedstocks, (II) the minimizer to reduce the flow area with increased shear, (III) the layer multiplier with the ability to multiply and stack the incoming fluid in a vertical alternating fashion in the order of $2^{(n+1)}$, and (IV) the reducer which is the nozzle tip with a reduced dimension helping to deposit the feedstocks onto the printing substrate

Table S1: Nomenclature of the feedstocks

Solvent	Material A	Material B	Nanoparticle	Composition		Rational
				Feedstock A	Feedstock B	
DMF	TPU-B	--	Fe3O4	TPU-B/Fe3O4	--	Magnetic actuation control using Fe3O4 magnetic particles
DMF	TPU-D	PCL	--	--	TPU-D/PCL	Thermal actuation control using PCL as the switch element from the fixed shape

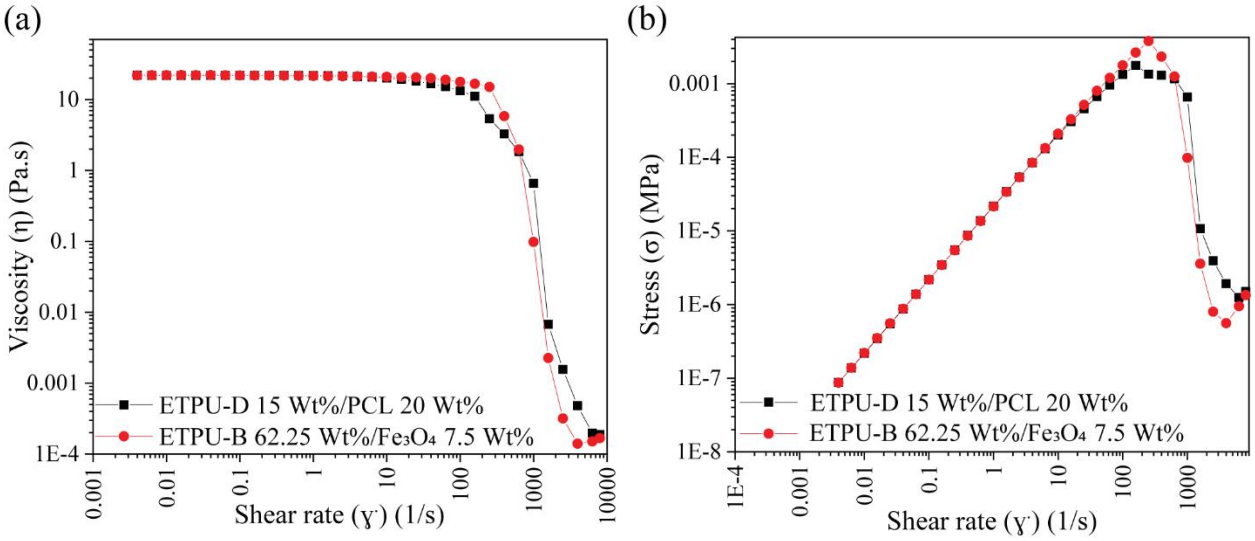

Figure S2. Rheology studies of both feedstocks (a) show the matching viscosity values and (b) similar shear-thinning properties essential for 3D printing with uninterrupted layers and smooth processing

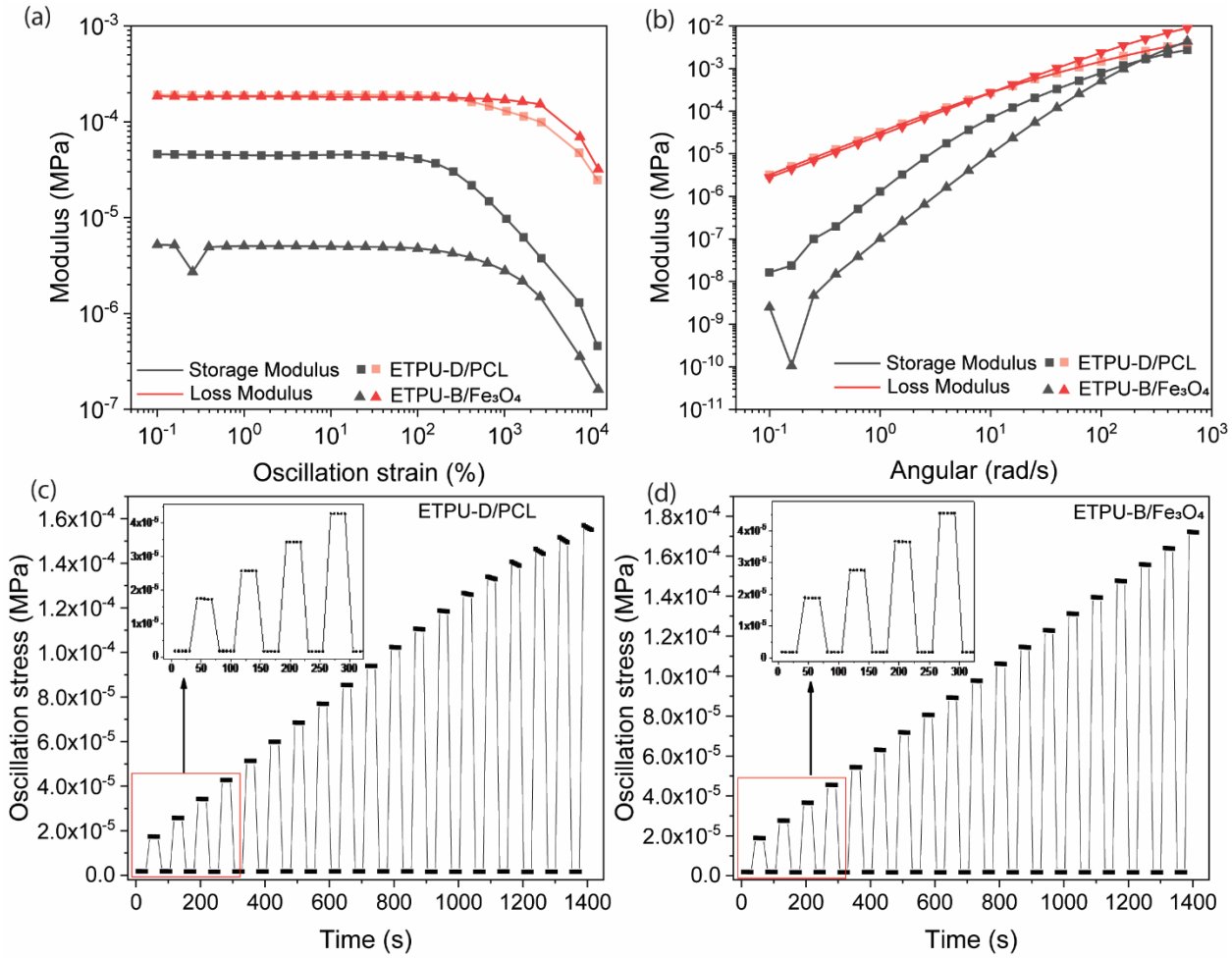

Figure S3. Rheology stability studies of both feedstocks (a) amplitude sweep, (b) frequency sweep, (c) step-strain cyclic analysis for ETPU-D/PCL, and (d) step-strain cyclic analysis for ETPU-B/Fe_3O_4.

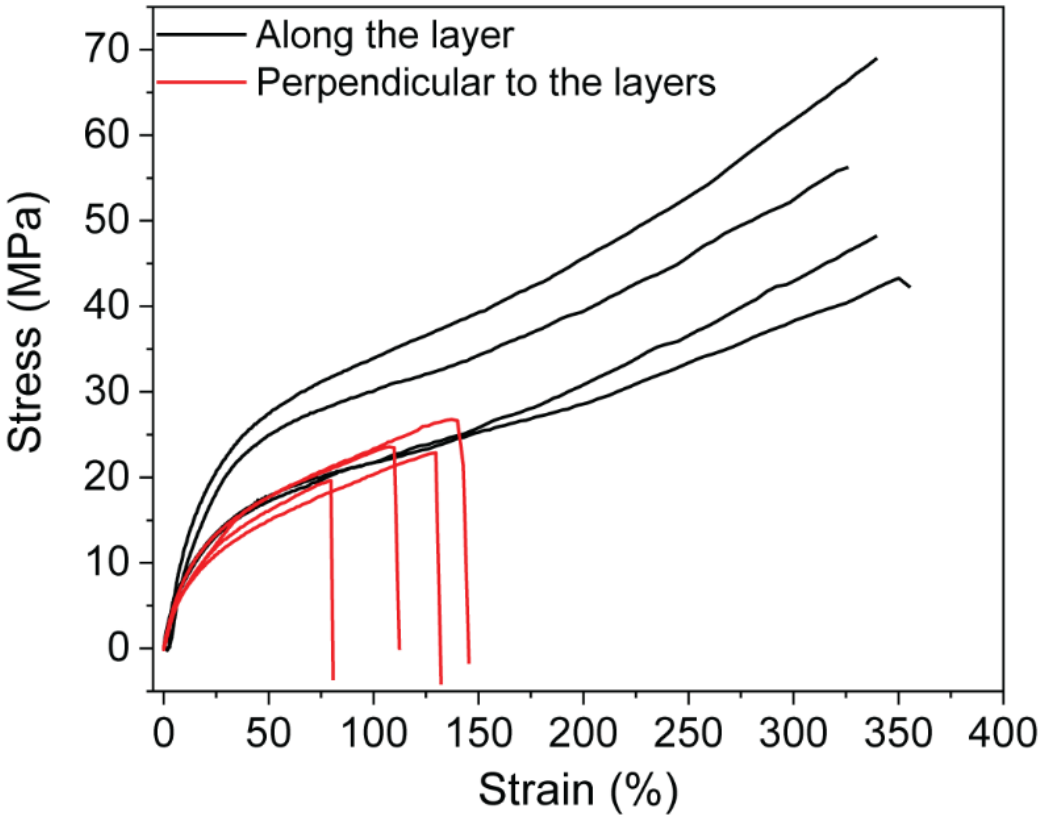

Figure S4. Tensile test on the 3L multiphase composites show the consistency of mechanical properties along and perpendicular to the layers, essential to form the thermal responsiveness

Table S2: Mechanical material properties of the 3L multiphase composite sample

Along the x-axis (i.e., along layer direction)		Along the y-axis (i.e., perpendicular to layer direction)			
Young's modulus	Max strain (i.e., no fracture observed at maximum instrument capability)	Young's modulus	Max strain (i.e., tensile strain at sample fractures)	Toughness	Fracture
MPa	%	MPa	%	MPa	MPa
126.30 ± 14.97	338.50 ± 8.74	85.75 ± 6.23	114.67 ± 12.5	21.40 ± 3.60	23.15 ± 2.50

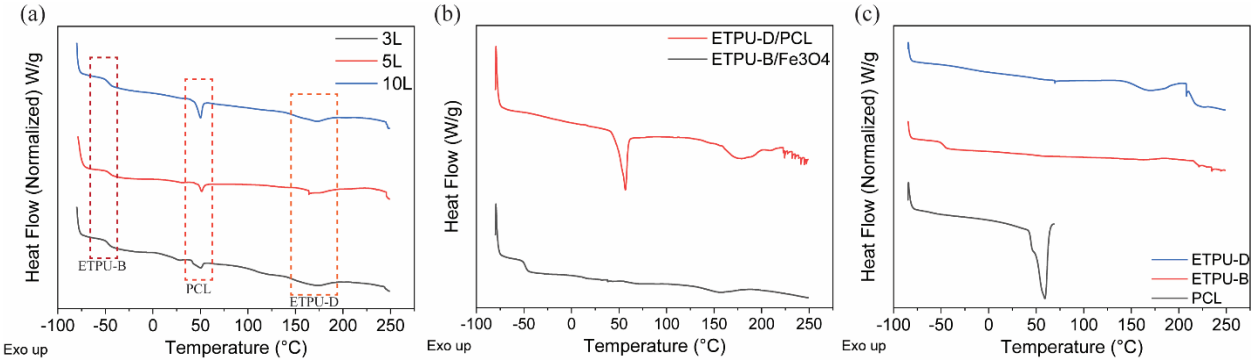

Figure S5. DSC thermal studies on the (a) multiphase layered composites, (b) the individual composites, and (c) the raw polymer used in the feedstock formulation

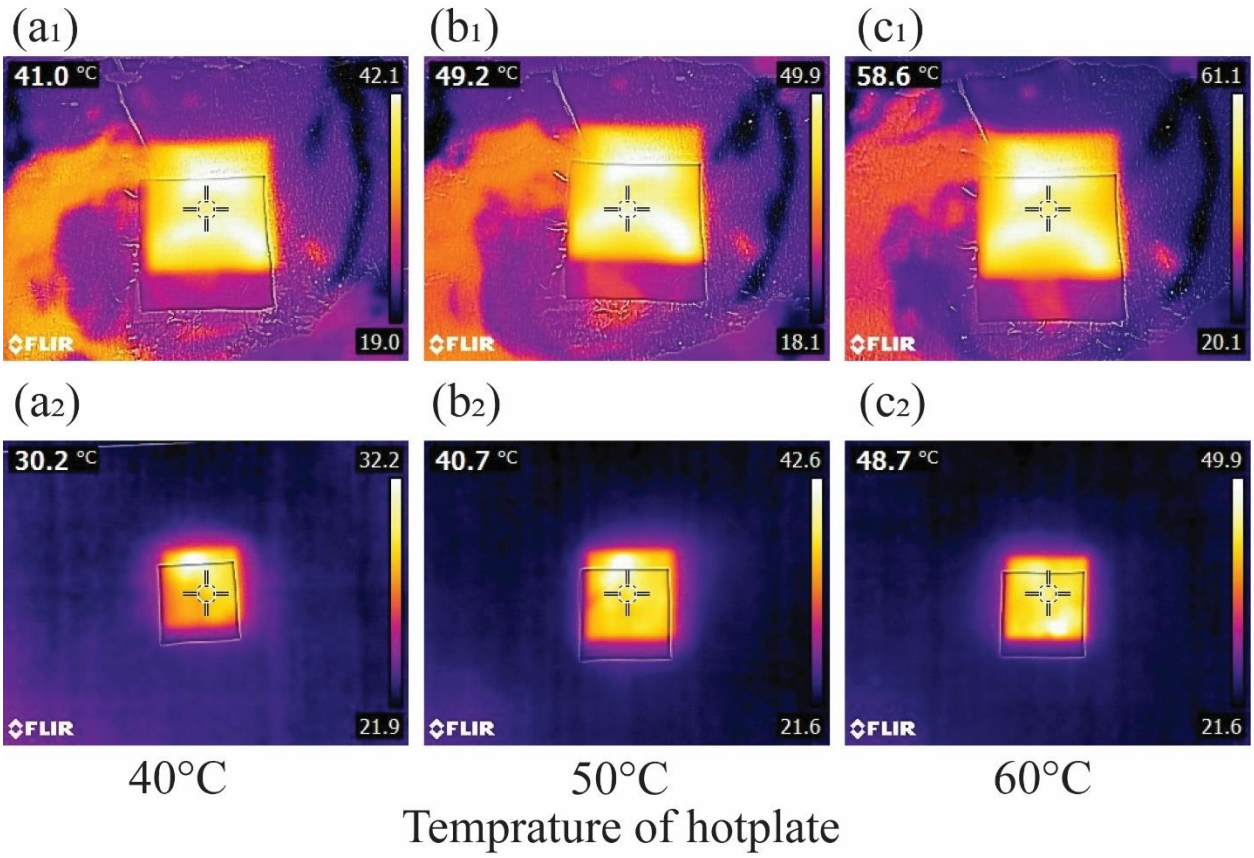

Figure S6. Thermal images of 5L sample post actuation at 40°C, 50°C, and 60°C (a1, b1, c1) on the hot plate and (a2, b2, c2) out of the hotplate.

Table S3: Examples from literature surveys of magnetic actuation of SMPs

Primary material	Magnetic particle	Particle size (µm)	Material system	Sample Fabrication	Magnetic system	Magnetic strength (mT)	Motion types	Ref
Silicon elastomer	NdFeB	5	Single/ composite	Casting	Electromagnetic coil	0 - 30	Walking, crawling, jumping, bending	1
TPU	Fe_3O_4	0.029	Single/composite	Casting	Permanent magnet	720	Attraction, repelsion	2
PEDGA	Fe_3O_4/SiO2 CNCs	0.01 Fe3O4 domain; 100-200 CNCs	Single/ composite	Lithography with particle orientation	Electromagnetic coil	60 - 300	Crawling, bending	3
Silicon resin	NdFeB; Silica	5; 20 - 30	Single/ composite	3D printing with magnetic orientation	Electromagnetic coil	200	Walking, rolling, bending, gripping	4
UV resin GC3D-EBE	NdFeB	5	Single/ composite	Lithography with particle orientation	Electromagnetic coil	20	Walking, crawling, swimming, twisting, bending, gripping	5
PDMS	Fe	5.1	Single/ composite	Two-step polymerization	Permanent magnet	100	Rolling	6
PDMS	CIPs/AgNWs	--	Single/ composite	substrate coating and vulcanization	Electromagnetic coil	27 - 130	Attraction, repelsion, crawling	7
Acrylate resin	NdFeB; Fe_3O_4	25;30	Single/ composite	Casting and curing	Electromagnetic coil	10 - 60	Twisting, gripping	8
PVP hydrogel	Fe_3O_4 coating	--	Single/ composite	4D laser printing - femtosecond laser direct writing	--	--	Swimming, gripping	9
Biofilm	Fe_3O_4	2	Single/ composite	Molding	Electromagnetic coil	3.4	Swimming	10
TPU	Fe_3O_4	0.016	Single/ composite	Hot pressing	Permanent magnet	30	Rotating	11
Two grades of TPU; PCL	**Fe_3O_4**	**0.3**	**Multi-material/ composite**	**3D printing - MDIW**	**Electromagnetic coil**	**12**	**Rotating, flipping, swimming, hovering**	**This work**

Table S4: Literature Reports on stimuli-responsive actuation

Material	System	Stimuli	Demonstration	Ref
Styrene based SMPs	Bilayer	Thermal	Self-deployed structures	12
Soft and elastic hydrogel	Bilayer	Thermal	Underwater gripper	13
Calcium alginate/polyacrylamide hydrogel	Bilayer	Solvent	Actuator	14
N-isopropylacrylamide/PCL	Bilayer	Solvent	Microfluidic and cell encapsulation	15
Vitrimer	Single	Thermal and light	Morphing electronics	16
Acrylate/PCL	Single	Thermal	Self-powered mechanosensing	17
Tert-butyl acrylate/PEG	Bilayer	Thermal and light	--	18
Acrylamide Hydrogel	Pseudo-double-network	Saline solution	Soft actuation	19
PEGDA resin	Single	Solvent	--	20
PDMS/CNTs/GO	Bilayer	NIR radiation	Weight-bearing robots and smart electronics	21
Nitrile butadiene rubber/ ZnCl2	Bilayer	Thermal	--	22
PLA/Fe3O4	Single	Thermal and magnetic	Restrictive shape recovery for intravascular stent	23
Silicon/CNTs	Bilayer	Thermal and NIR radiation	Gripper and smart electronics	24
Methylcellulose/ iron	Single	Magnetic	--	25
Verowhite/Tangoblack/polyurethane resin	Trilayer	Solvent and thermal	Weight-bearing structure	26
TPUs of two different grades in different combinations of PCL or Fe_3O_4	**Multi-material**	**Thermal and magnetic**	**Fish-mimicking moving forward/backward and rotation**	**This work**

Reference

1 W. Hu, G. Z. Lum, M. Mastrangeli and M. Sitti, *Nature*, 2018, **554**, 81–85.

2 S. R. Mishra, M. D. Dickey, O. D. Velev and J. B. Tracy, *Nanoscale*, 2016, **8**, 1309–1313.

3 J. Kim, S. E. Chung, S. E. Choi, H. Lee, J. Kim and S. Kwon, *Nat. Mater.*, 2011, **10**, 747–752.

4 Y. Kim, H. Yuk, R. Zhao, S. A. Chester and X. Zhao, *Nature*, 2018, **558**, 274–279.

5 T. Xu, J. Zhang, M. Salehizadeh, O. Onaizah and E. Diller, *Sci. Robot.*, 2019, **4**, eaav4494.

6 J. E. Park, J. Jeon, J. H. Cho, S. Won, H. J. Jin, K. H. Lee and J. J. Wie, *RSC Adv.*, 2019, **9**, 11272–11280.

7 L. Ding, J. Zhang, Q. Shu, S. Liu, S. Xuan, X. Gong and D. Zhang, *ACS Appl. Mater. Interfaces*, 2021, **13**, 13724–13734.

8 Q. Ze, X. Kuang, S. Wu, J. Wong, S. M. Montgomery, R. Zhang, J. M. Kovitz, F. Yang, H. J. Qi and R. Zhao, *Adv. Mater.*, 2020, **32**, 1–8.

9 C. Xin, D. Jin, Y. Hu, L. Yang, R. Li, L. Wang, Z. Ren, D. Wang, S. Ji, K. Hu, D. Pan, H. Wu, W. Zhu, Z. Shen, Y. Wang, J. Li, L. Zhang, D. Wu and J. Chu, *ACS Nano*, 2021, **15**, 18048–18059.

10 G. Hwang, A. J. Paula, E. E. Hunter, Y. Liu, A. Babeer, B. Karabucak, K. Stebe, V. Kumar, E. Steager and H. Koo, *Sci. Robot.*, 2019, **4**, eaaw2388.

11 S. Won, H. Je, S. Kim and J. J. Wie, *Adv. Intell. Syst.*, 2022, 2100269.

12 S. Ji, J. Wang, A. Olah and E. Baer, *J. Appl. Polym. Sci.*, 2017, **134**, 1–10.

13 Q. Wang, Z. Liu, C. Tang, H. Sun, L. Zhu, Z. Liu, K. Li, J. Yang, G. Qin, G. Sun and Q. Chen, *ACS Appl. Mater. Interfaces*, 2021, **13**, 10457–10466.

14 J. Wang, X. Zhang, A. Wang, X. Hu, L. Deng, L. Lou and H. Shen, *Polymer (Guildf).*, 2020, **204**, 122801.

15 G. Stoychev, S. Zakharchenko, S. Turcaud, J. W. C. Dunlop and L. Ionov, *ACS Nano*, 2012, **6**, 3925–3934.

16 X. Kuang, Q. Mu, D. J. Roach and H. Jerry Qi, *Multifunct. Mater.*, 2020, **3**, 045001.

17 R. Liu, X. Kuang, J. Deng, Y. C. Wang, A. C. Wang, W. Ding, Y. C. Lai, J. Chen, P. Wang, Z. Lin, H. J. Qi, B. Sun and Z. L. Wang, *Adv. Mater.*, 2018, **30**, 1–8.

18 C. Yuan, Z. Ding, T. J. Wang, M. L. Dunn and H. J. Qi, *Smart Mater. Struct.*, 2017, **26**, 105027.

19 S. Xiao, Y. Yang, M. Zhong, H. Chen, Y. Zhang, J. Yang and J. Zheng, *ACS Appl. Mater. Interfaces*, 2017, **9**, 20843–20851.

20 J. Wu, Z. Zhao, X. Kuang, C. M. Hamel, D. Fang and H. J. Qi, *Multifunct. Mater.*, 2018, **1**, 015002.

21 W. Wang, C. Xiang, Q. Zhu, W. Zhong, M. Li, K. Yan and D. Wang, *ACS Appl. Mater. Interfaces*, 2018, **10**, 27215–27223.

22 J. Zhang, X. Liu, W. Zao, H. Feng, Y. Hou and A. Huo, *ACS Appl. Mater. Interfaces*, 2021, **13**, 10376–10387.

23 H. Wei, Q. Zhang, Y. Yao, L. Liu, Y. Liu and J. Leng, *ACS Appl. Mater. Interfaces*, 2017, **9**, 876–883.

24 H. Li, Y. Liang, G. Gao, S. Wei, Y. Jian, X. Le, W. Lu, Q. Liu, J. Zhang and T. Chen, *Chem. Eng. J.*, 2021, **415**, 128988.

25 D. Podstawczyk, M. Nizioł, P. Szymczyk, P. Wiśniewski and A. Guiseppi-Elie, *Addit. Manuf.*, 2020, **34**, 101275.

26 Y. Mao, Z. Ding, C. Yuan, S. Ai, M. Isakov, J. Wu, T. Wang, M. L. Dunn and H. J. Qi, *Sci. Rep.*, 2016, **6**, 1–13.