Three dimensional printed nanogenerators

Xinran Zhou1,2 | Pooi See Lee1,2

1School of Materials Science and Engineering, Nanyang Technological University, Singapore, Singapore
2Singapore-HUJ Alliance for Research and Enterprise (SHARE), Nanomaterials for Energy and Water Nexus (NEW), Campus for Research Excellence and Technological Enterprise (CREATE), Singapore, Singapore

Correspondence
Pooi See Lee, School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore. Email: pslee@ntu.edu.sg

Funding information
National Research Foundation, Grant/Award Number: NRF-CRP13-2014-02

Abstract
In the dawn of energy crisis and rising challenges in powering distributed low energy portable devices, nanogenerators, a class of mechanical energy harvesters is gaining increasing interest in fundamental research and commercial applications. Nanogenerators harvest energy by transducing mechanical energy into electric energy, the performance is highly related to the mechanical and electrical properties of the materials and devices. A typical nanogenerator consists of a substrate, a functional triboelectric active layer, electrode, and separator, which overall built-up a three dimensional (3D) structure. 3D printing with its ability to form complex 3D structures possess coveted advantages in the development of nanogenerators. In this review, we introduce the importance of 3D structures for nanogenerators and explicitly discuss the different 3D printing methods and the ink formulation to tackle the challenges in 3D structured nanogenerators. Additionally, the principle and application of 4D printing in nanogenerator fabrication are critically highlighted.

KEYWORDS
3D printing, 3D structure, 4D printing, nanogenerator, piezoelectric, triboelectric

1 | INTRODUCTION

One of the biggest challenges in the coming decade is the energy crisis and climate change due to the combustion of fossil fuels. There is a dire need for long-term sustainable energy resources to replace the existing nonsustainable fossil fuel energy. In addition, the rise of big data requires the collection of distributed data in which numerous sensing devices are used, leading to the emerging need for portable energy sources for these distributed devices. The disordered energy from the environment is considered an alternative energy source for these distributed autonomous devices. Mechanical energy is the most widely distributed energy in the environment, it has a stable supply regardless of the weather condition. Nanogenerators, which transfer mechanical energy to electrical energy based on the displacement current in the Maxwell equation, has emerged as a promising candidate for harvesting energy for distributed autonomous devices.1-3 According to the working principles, mechanical nanogenerator can encompass two categories, namely, the triboelectric nanogenerator (TENG) that is based on triboelectric effect and electrostatic induction, and piezoelectric nanogenerator (PENG) that is based on the changes in dipole moment in piezoelectric materials to harvest mechanical energy.

Three dimensional (3D) printing is a promising additive manufacturing approach in the fabrication of nanogenerators attributed to its ability to fabricate complex structures in a simple bottom-up manner according to...
the designed 3D model. 3D printing can be used in fabricating every part of a nanogenerator. For example, for nanogenerators that involve deformation by external force or vibration, the structure design of the device becomes important and can determine its functioning mode. Forming these structural components with traditional methods is time-consuming, therefore 3D printing is highly suited in making the structural components, especially those related to rotors, relative motion, and separators. Not only can 3D printing be applied in fabricating the structural components, but it is also beneficial for depositing the functional materials. It is proven that with special design in 3D printing model and parameters, the surface area of triboelectric materials can be increased so that the surface charge of the device can be improved for improved output.4,5 Also, stacking of devices to construct a device matrix, which contains vertical and horizontal stacking of multiple triboelectric pairs, is necessary for many applications that require high output or multi-force-direction activated energy harvesting. More importantly, 3D printing can easily form regular 3D structures with repeating units for better volumetric energy density.

2 | 3D PRINTING OF NANOGENERATORS

2.1 | Printing method

3D printing can be categorized according to printing materials and forming principles. Fused deposition modeling (FDM) is the most commonly used 3D printing method in nanogenerator fabrication due to its convenience and low cost. In FDM, a thermoplastic filament is heated at the nozzle above its glass transition temperature in order for it to be extruded to the substrate. After extrusion, as the temperature decreases, the printed part solidifies to build up the 3D shape (Figure 1A). It can print common thermoplastics such as polylactic acid (PLA) and acrylonitrile butadiene styrene (ABS), as well as shape memory polymers (SMPs) and polymer composites including conductive polymer composite.6 The second commonly used 3D printing method for nanogenerator fabrication is direct ink writing (DIW).7-10 In DIW, ink in liquid or paste form is filled in a syringe. The nozzle of the syringe moves in x, y, and z directions controlled by a computer program. At the same time, the ink is extruded (Figure 1B). The shape of the liquid ink is maintained by shear thinning and followed by one of the curing methods such as thermal cure, UV cure, solvent evaporation, and others. Comparing with FDM, more various forms of ink can be applied in DIW, and it can be used to print a wide range of materials, including polymers, ceramics, and composites. For example, our group has developed a 3D printable extremely stretchable (2500% strain) and self-healing TENG, with DIW printed self-healing polyurethane acrylate (PUA) as triboelectric material and silver flakes and liquid metal particles embedded in the PUA as electrodes.11 Additionally, UV curing-based stereolithography (SLA) and digital light processing (DLP) have also been applied in the fabrication of nanogenerators (Figure 1C).12-15 In DLP, liquid form monomers or oligomers with a photoinitiator are mixed as the printing ink. During printing, the ink is either placed into a tank with a UV window on the bottom or spread layer by layer onto the UV window. The UV light is projected through the UV window onto the

Figure 1 Schematics of general printing methods. (A) FDM. Reproduced with permission. Copyright 2017, Wiley-VCH.47 (B) DIW. Reproduced with permission. Copyright 2019, Elsevier.9 (C) SLA. Reproduced with permission. Copyright 2019, Elsevier12
stage to cure each layer, while the stage moves upward with the printed parts to allow the formation of the next layer. Besides, selective laser melting (SLM) and selective laser sintering (SLS) 3D printing have also been occasionally used in nanogenerator fabrication.

2.2 | Ink formulation

To 3D print triboelectric or piezoelectric materials, the ink formulation process is important. It determines whether a material can be successfully built up into a 3D structure. Different type of 3D printing requires different ink properties. For example, for the most commonly used FDM printing, materials are required to be thermoplastic. Yu et al16 and Chen et al17 have demonstrated making triboelectric materials into filament to get them 3D printed by FDM (the performance, size, and material comparison of these works and all below-mentioned works are shown in Table 1). However, most FDM printed nanogenerator uses the commercial filaments PLA and ABS, so this review will focus on the ink formulation for DIW. In DIW, the viscosity and shear thinning behavior of the ink is essential. Viscosity controls the form of the extruded ink. For example, if the viscosity is too low, the ink will spread on the substrate after printing before it is cured. If the viscosity is too high, the ink will have a response delay during the printing process, which means it keeps flowing out when extrusion stops and it cannot be extruded immediately at the next starting point of the printing. Although common DIW printers can print a wide range of ink, the viscosity for the best printing result is around 20 cPs. Common ways to adjust the viscosity of ink include adjusting solids loading, polymer loading, polymer chain length, pH, and solvent percentage. On the other hand, shear thinning behaviour is the key principle in DIW printing. It means the reduction of viscosity of a non-Newtonian fluid under shear strain. When the ink passes through the narrow needle during extrusion, the ink experiences shear strain, under which the viscosity of the ink decreases. After the ink is extruded, the shear strain is released, and the viscosity suddenly increases to fix the shape of the extruded ink and prevent it from spreading. Thus, a shear thinning ink is essential for high resolution DIW printing by reducing the spreading or deformation of the printed materials and reduce the line dimension and shape change to better follow the designed model.7,9 The printing parameters are also important, which controls the solidification process of the material to achieve unique property. For example, Li et al printed silicone elastomer with different morphology with DIW by controlling film thickness and space distance.9 The different morphology of the triboelectric material can affect the surface roughness to improve the triboelectricity and energy harvesting performance. Besides, adjusting the curing process of the ink can control the mechanical property and thermal behaviors of the printed material. Chen et al has demonstrated a multilevel TENG by controlling the curing process in DIW printing.7 In that work, a UV curable monomer is mixed with a thermally curable monomer to form the ink. During printing, a photomask is used to selectively UV cure the material at certain positions, followed by a thermal cure of the whole object. Thus, at different positions of the printed object, the polymer has different cross-linking conditions, which leads to variations in glass transition temperature, buckling behaviour with compression, and failure stress under stretching, so that the crack propagation pathways can be controlled.

3 | 3D STRUCTURE DESIGN FOR NANOGENERATORS

The most attractive feature for 3D printing is to form complex structures that are difficult to be formed with traditional fabrication methods. The functioning of nanogenerators is highly dependent on the structure of the device, such as the rotary mode TENG requires design in the rotating structures. For example, the FDM printing method is used to print rotating sleeves in Cao et al’s work.19 Other works use FDM to print the rotating wheels.20,21 Rotating axis with a special design which can also be achieved with the FDM method, as shown in Figure 2A.22 Besides, structures for vibration and moving-part-restriction also benefited from 3D printing. Lee et al used FDM to print the body of TENG to realize the moving-ball system for noise-cancelling TENG, as shown in Figure 2B.23 Yoon et al printed a biomimetic villus structure with ABS to increase the surface area of the triboelectric surface in contact with the polytetrafluoroethylene (PTFE) powder so that the power output can be improved to 4-5 folds (Figure 2C).12 Xiao et al also used 3D printed structures for restricting moving parts. PTFE balls are contained in each honeycomb holes for harvesting vibration energy (Figure 2D).24

Not only can the performance of TENG be affected by the 3D structure, but the mechanical response of PENG is also dependent on the 3D structure. It was proven that the honeycomb structure can affect the response frequency of PENG.25 Cui et al have designed unique 3D structures that can affect the value and direction of the piezoelectric coefficient and printed the structures with a high-resolution DLP printer using functionalized lead zirconate titanate (PZT) nanoparticle (3 vol%) and
| Section of this article | Mechanism   | Maximum peak power density | Size                                  | Functional material                                                                 | 3D printed parts                  | References |
|-------------------------|-------------|----------------------------|---------------------------------------|-------------------------------------------------------------------------------------|----------------------------------|------------|
|                         | FDM         | TENG                       | 5.93 W/m²                             | 4 cm × 4 cm                                                                         | Polyamide/lignin; polyethylene/polydimethylsiloxane (PDMS) | Triboelectric material | [16]      |
|                         | TENG        |                            | 1.11 W/m²                             | 3 cm × 3 cm × 0.5 cm                                                                | Poly(glycerol sebacate), carbon nanotubes | Triboelectric material & electrodes | [17]      |
|                         |              |                            | 0.6085 W/m²                           | 3 cm × 3 cm                                                                         | Silicone rubber                  | Triboelectric material | [9]       |
|                         | TENG        |                            | 0.196 W/m²                            | 1.4 cm² area                                                                        | PTFE, multimaterial resin        | One of the triboelectric materials | [7]       |
|                         | DIW         | TENG                       | 1.11 W/m²                             | 3 cm × 3 cm                                                                         |                                |                        |            |
|                         |              |                            | 0.6085 W/m²                           | 3 cm × 3 cm                                                                         |                                |                        |            |
|                         |              |                            | 0.196 W/m²                            | 1.4 cm² area                                                                        |                                |                        |            |
|                         |              |                            | 5.93 W/m²                             | 4 cm × 4 cm                                                                         |                                |                        |            |
|                         |              |                            | 1.11 W/m²                             | 3 cm × 3 cm × 0.5 cm                                                                |                                |                        |            |
|                         |              |                            | 0.6085 W/m²                           | 3 cm × 3 cm                                                                         |                                |                        |            |
|                         |              |                            | 0.196 W/m²                            | 1.4 cm² area                                                                        |                                |                        |            |
|                         | 2           | FDM TENG                   | 5.93 W/m²                             | 4 cm × 4 cm                                                                         | Polyamide/lignin; polyethylene/polydimethylsiloxane (PDMS) | Triboelectric material | [16]      |
|                         |             | TENG                       | 1.11 W/m²                             | 3 cm × 3 cm × 0.5 cm                                                                | Poly(glycerol sebacate), carbon nanotubes | Triboelectric material & electrodes | [17]      |
|                         |             | TENG                       | 0.6085 W/m²                           | 3 cm × 3 cm                                                                         | Silicone rubber                  | Triboelectric material | [9]       |
|                         |             | TENG                       | 0.196 W/m²                            | 1.4 cm² area                                                                        | PTFE, multimaterial resin        | One of the triboelectric materials | [7]       |
|                         |             |                            | 5.93 W/m²                             | 4 cm × 4 cm                                                                         |                                |                        |            |
|                         |             |                            | 1.11 W/m²                             | 3 cm × 3 cm × 0.5 cm                                                                |                                |                        |            |
|                         |             |                            | 0.6085 W/m²                           | 3 cm × 3 cm                                                                         |                                |                        |            |
|                         |             |                            | 0.196 W/m²                            | 1.4 cm² area                                                                        |                                |                        |            |
|                         | 3           | Rotating TENG&EM            | 14.9 W/m³ (TENG)^a                     | 9.6 cm diameter × 13 cm height                                                      | Fluorinated ethylene propylene (FEP) | Rotating structure | [19]      |
|                         |             | TENG                       | 2.54 W/m³                             | 13.4 cm diameter × ~5 cm height                                                     | Kapton, PTFE                    | Rotating structure | [20]      |
|                         |             | TENG                       | 7.9 W/m³a                             | 13 cm × 12 cm × 13 cm                                                              | FEP                            | Rotating structure | [21]      |
|                         |             | TENG&EM                    | 0.6 mW/g (TENG)                        | 9.5 cm diameter × ~3 cm height                                                     | Porous PTFE                     | Rotating structure | [22]      |
|                         | Shaking     | TENG                       | 804 W/m³a                             | 8 cm² area × 7 cm height                                                          | PDMS                           | Containing structure | [23]      |
|                         |             | TENG                       | 0.000046 W/m³                          | 4.2 cm diameter × 3.8 cm height                                                     | PTFE powder, ABS                | One of the triboelectric materials | [12]      |
|                         |             | TENG                       | 50 W/m³                               | 6.2 cm × 5.4 cm                                                                   | PTFE                           | Containing structure | [24]      |
|                         |             | PENG                       | N.A. (sensor application)              | 8 mm × 8 mm × 2 mm                                                                 | PZT/PEGDA                      | Piezoelectric material | [26]      |
|                         | Piezo-electric Stacking | TENG                       | 0.0055 W/m³                           | 17.5 cm × 5 cm × 4.9 cm                                                             | Polyethersulfone (PES)/As₂Se₃ core-shell nanostructure | Stacking structure | [27]      |
|                         |             | TENG                       | 6.7 W/m²                              | 7.2 cm × 4 cm                                                                      | PTFE                           | Folding structure | [28]      |
|                         |             | TENG                       | 10.98 W/m³                            | 3.5 cm × 3.5 cm × 3.5 cm                                                           | Composite resins                | Triboelectric materials | [29]      |
|                         |             | TENG                       | 12.4 W/m³                             | 10 cm diameter sphere                                                              | FEP                            | Folding structure | [30]      |
|                         |             | N.A.                       |                                        |                                                                                      |                                | N.A.                  | [31]      |
|                         | Origami     | TENG                       | 0.14 W/m²                             | ~5 cm × 5 cm × changing thickness                                                  | PTFE                           | Folding structure | [28]      |
|                         |             | TENG                       | 5.42 W/m²                             | 3 cm × 3 cm × ~2 cm                                                                | PTFE                           | Triboelectric materials | [29]      |
|                         |             | TENG                       | 8.39 W/m³a                             | 16 cm diameter sphere                                                              | FEP                            | N.A.                  | [33]      |
|                         |             | PENG                       | 3000 W/m³                             | 4.5 cm × 4 cm                                                                      | PVDF                           | N.A.                  | [34]      |
|                         | Kirigami    | PENG                       | 0.014 W/m³                            | 1 cm × 1 cm                                                                        | BaTiO₃/P(VDF-TrFE)              | Piezoelectric material & electrodes | [8]       |
|                         |             | PENG                       | 0.48 W/m³a                             | 2 cm × 2 cm                                                                        | PZT                            | N.A.                  | [35]      |
|                         |             |                            | 0.8 W/m³a                             | 4 cm × 2.5 cm                                                                       |                                |                        |            |
|                         |             | TENG                       | 12.8 W/m³a                            | 2 cm × 2 cm                                                                        |                                |                        |            |
|                         | 4           | TENG                       | 0.8 W/m³a                             | 4 cm × 2.5 cm                                                                       |                                |                        |            |
|                         |             | TENG                       | 12.8 W/m³a                            | 2 cm × 2 cm                                                                        |                                |                        |            |

^aValue calculated by the authors from the output power and the dimension from the original articles.
poly(ethylene glycol) diacrylate (PEGDA) monomer ink. This work introduces the 3D printed metamaterial into the nanogenerator, and the 3D printed structure can be applied to realize the self-powered sensor with multidirectional sensing ability.

3D structures can also be designed as special separators in TENG. In the typical contact and separation mode TENG, separators are usually an additional layer at the edge of the device. Without structure optimization, the separator is easy to lose its separating function after a long cycling time. The single separating function is also a waste of volume. With 3D printing, the separating structure can be printed together with the triboelectric material or substrate material, which reduces the chance of losing the separating function comparing with the adhered separators. The 3D printed separating structure can at the same time act as the structure for stacking of multiple devices, either layer by layer like traditional

---

**FIGURE 2** 3D printed nanogenerators. (A) A linear-to-rotary hybrid triboelectric and electromagnetic nanogenerator with 3D printed spiral rotating axis (0.6 mW/g). Reproduced with permission. Copyright 2019, Elsevier. (B) A 3D printed noise-cancelling triboelectric nanogenerator by shaking (804 W/m³). Reproduced with permission. Copyright 2017, Elsevier. (C) A 3D-printed biomimetic-villus structure TENG by shaking (46 μW/m²). Reproduced with permission. Copyright 2019, Elsevier. (D) A 3D printed honeycomb structure inspired TENG by shaking (50 W/m³). Reproduced with permission. Copyright 2019, Wiley-VCH. (E) A 3D printed motion- and sound-activated TENG with stacking structure (5.5 mW/m²). Reproduced with permission. Copyright 2015, Wiley-VCH. (F) A 3D printed triboelectric nanogenerator with folding structure for more triboelectric contact pairs (6.7 W/m²). Reproduced with permission. Copyright 2019, Elsevier. (G) A three-dimensional ultraflexible TENG made by 3D printing with conductive hydrogel as electrode (10.98 W/m²). Reproduced with permission. Copyright 2018, Elsevier.
device stacking, or with tilting angles to create more triboelectric contact and separation pairs in limited volume. Moreover, complex 3D interconnecting structures can be created with 3D printing for more uniform separation. For example, Kanik et al. printed a framework to separate and stack multiple TENGs to improve the output (Figure 2E). Similarly, Gao et al. printed a series of complicated structures with similar elastic supporting substrates, with PTFE as triboelectric material and copper film as electrode assembled on a different surface of the framework. The 3D printed structures help to form more pairs of triboelectric contact and separation pairs, and increase the active surface area in one device, and achieve the excellent ability of rehabilitation (Figure 2F).

Moreover, complex 3D interconnecting structures can be created with 3D printing for more uniform separation. For example, Kanik et al. printed a framework to separate and stack multiple TENGs to improve the output (Figure 2E). Similarly, Gao et al. printed a series of complicated structures with similar elastic supporting substrates, with PTFE as triboelectric material and copper film as electrode assembled on a different surface of the framework. The 3D printed structures help to form more pairs of triboelectric contact and separation pairs, and increase the active surface area in one device, and achieve the excellent ability of rehabilitation (Figure 2F).

Also, Chen et al. reported an ultra-flexible TENG, with a 3D printed ultra-flexible framework and 3D printed composite resin and 3D printed hydrogels to fill into the framework (Figure 2G). Not only can the 3D printed separating structure be used in compression-induced contact and separation mode TENG, but it can also be used in blue energy harvesting, which harvests the wave energy from the ocean. An et al. has reported a 3D printed whirling-folding structure to separate different triboelectric contact pairs and transfer the vibration from the wave to the device to make different surfaces contact and separate to generate electric energy.

Metamaterials are attractive because they can change the macroscopic structure of the material, to achieve new properties that do not exist in natural materials, such as negative Poisson’s ratio and manipulation of electromagnetic waves. A good way to fabricate metamaterial is the kirigami and origami techniques, which can turn a flexible film into a stretchable function. The original meaning of kirigami is “the art of cutting.” By cutting certain patterns on flexible film materials, the local deformation of the material under stretching can be changed from unidirectional tensile deformation along the force direction, to bending, rotating, or a combination of bending and rotating in different directions. In this way, the mechanical deformation of the material can be changed, and the flexible film material can be multi-directional stretchable. While origami originates from “the art of paper folding.” By folding film materials, the material changes from 2D to a 3D structure so that the deformation under compression or stretching can be changed. Since both kirigami and origami structures require structural design and fabrication, 3D printing is a good way to fabricate kirigami and origami structures. For example, Yang et al. has reported an origami TENG made with paper folding (Figure 3A). The origami structure increased the number of layers of the TENG, and it enables more function modes such as stretching mode, lifting mode, or twisting mode. It also eliminates the separator since the self-unfolding behaviour of the origami structure can separate the contacting surfaces. Xia et al. also used origami

![Figure 3](image-url)
structure to create a paper-based TENG, for more triboelectric contact surface pairs and eliminate the separator (Figure 3B).32 In addition, Yi et al utilized the stretchable and compressible property of origami structure to make the origami TENG as a spring between the container wall and vibrating core. This also increases the effective area of the device within a small volume.33

For PENG, kirigami structure has more application than origami structure. It is usually used to control the stretching of the piezoelectric material. In Fang et al work, PVDF films were cut by laser with hierarchical kirigami structure, which can change the resonance frequency of a film for low-frequency wind energy harvesting.34 Our group has demonstrated the 3D printing of specially designed kirigami structure with BaTiO$_3$/P(VDF-TrFE) composite and silver-based 3D printed electrode, which overcomes the protruding problem of the common stretchable kirigami structure to make a stretchable PENG that can be used in pressing mode (Figure 3C).8 In addition, if the kirigami structure is applied to different materials, the function can be different. For example, if the piezoelectric material is in a kirigami structure, the stretchability or compliance of the device can be enabled. However, if the kirigami structure is created onto the nonpiezoelectric substrate, it can be used to control the strain in each direction on the piezoelectric material to improve the output. For example, Ferguson et al attached a piezoelectric plate onto the auxetic kirigami structure steel substrate. In this way, the piezoelectric plate will experience strain in both 1 and 2 direction when stretched in 1 direction, which increases the power output (Figure 3D).35 Although most kirigami and origami nanogenerators are not 3D printed, 3D printing is very suitable for fabricating the kirigami and origami structures in a bottom-up way. It eliminates the cutting process and saves material. With 3D printing, the materials or number of layers at the folding or junction areas can be varied, so that the local strain condition or function can be changed, which makes smart self-folding structures possible.
4D printing is defined as printing 3D objects with the ability to change the form or function under the influence of stimuli as time changes (Figure 4A). It is a development of 3D printing and it provides 3D printing more function and possibility. As discussed earlier, it is evident that both form and function factors of materials are important for the working mode and power output of nanogenerators. Therefore, the 4D printing technique should be very beneficial for the development of future nanogenerators.

Currently, most 4D printing focuses on the temperature-stimulated shape change, which is to print shape memory materials. Shape memory materials can be categorized by SMPs, shape memory hydrogels (SMHs), shape memory alloys (SMAs), shape memory composites (SMCs), and shape memory ceramics (SMCrS). All of these shape memory materials can be 3D printed with the above-mentioned 3D printing methods, in which SMP is the most popular candidate. SMPs have an original shape and one or two preset temporary shapes. It can retain the temporary shape and recover into the original shape when subjected to an environmental stimulus such as heat, temperature, pH, ion concentration, and electric field. Some SMP can repeatedly change between the original shape and the temporary shape. SMP can be printed with FDM, DIW, and SLA/DLP methods (Figure 4B). In addition, SMH materials are suitable for TENG as triboelectric material or ionic conductor. Hydrogels can also be 4D printed with SLA, DLP, and DIW techniques. In the 3D printing process, the shape memory effect and shape change properties can be adjusted by several printing parameters, including the printing speed, nozzle temperature, platform temperature, and infill pattern.

There are no 4D printed nanogenerators yet, but we found that it will be interesting if 4D printing is applied in the following aspects of nanogenerator fabrication. First, with the self-restoring property of 4D printed SMP, the TENG that was subjected to repetitive deformation may restore its surface morphology and retain the energy harvesting performance for a longer time. For example, Lee et al used shape memory polyurethane (SMPU) to make TENG with a micro-pyramid pattern. After cycling, the output voltage decreases significantly due to the damage of the pyramid pattern. By heating the SMP on a hot plate above the glass transition temperature, the pyramid structure, and the performance can be restored, which extends the lifetime of TENG. Further demonstrating the shape recovering property of SMP, our group developed an electro-spun TENG for a self-powered water temperature sensor, which is also based on an electrospin PU mat with microspheres-nanofibers architecture to enhance the charge density and the hydrophobicity. It can self-restore both macroscopic and microscopic structures to recover the triboelectric performance after damage (Figure 4C).

However, there are challenges to make the TENG 4D printable. As discussed above, self-restoring TENG depends on the restoration of microstructure, but 3D printing is not good at creating microstructures. To solve this problem, 3D printing porous material, for example, the solvent exchange method for 3D printing porous polymer in our group’s publication, may be adopted to create microstructure. Another challenge is that not all shape memory materials have good triboelectricity or piezoelectricity. Studies or modifications on the shape memory materials need to be done for 4D printing nanogenerators with good performance.

Since origami structure can replace the separator and enable more triboelectric contact-separation pairs, a 4D printed self-folding origami TENG will be interesting. Although self-folding TENG has not been reported yet, the self-folding or self-unfolding origami structure has been applied in many fields such as aerospace, electrical automation, robotics, drug delivery carriers, and biomedical devices. For electronic application, Zhao et al demonstrated a self-folding PEGDA based 4D printed LED device with both substrate and circuit printed (Figure 4D). Besides, self-unfolding origami devices are useful in the biomedical industry for scaffolds, stents, and implantable electronic devices. Miao et al developed an origami structure that can self-unfold at human body temperature by 4D printing with soybean oil epoxidized acrylate for biomedical scaffolds application. Besides, light- and water-responsive origami structures have also been developed. The 4D printing self-folding origami works provide inspirations and reference for developing self-folding origami TENGs, in which similar materials, printing methods, and structures can be considered.

5  |  CONCLUSION

In conclusion, the application of 3D printing in nanogenerator fabrication has been introduced in this paper. The ink formulation and the printing parameters that affect the property of the printed nanogenerator materials are discussed. 3D structures for nanogenerators are analyzed by different categories, and the kirigami and origami structures are suggested as a potential beneficial structure for 3D printing nanogenerators. Furthermore, the 4D printing principle, materials, and potential applications in nanogenerator fabrication are introduced. It is believed that 3D and 4D printing can bring more interesting forms, functions, and applications to the future nanogenerator design.
ACKNOWLEDGMENTS
This work was supported by the Competitive Research Program (Award No. NRF-CRP13-2014-02), and Campus for Research Excellence and Technological Enterprise (CREATE) that is supported by the National Research Foundation, Prime Minister’s Office, Singapore.

CONFLICT OF INTEREST
The authors declare no conflict of interest.

ORCID
Pooi See Lee https://orcid.org/0000-0003-1383-1623

REFERENCES
1. Wang ZL. On maxwell’s displacement current for energy and sensors: the origin of nanogenerators. Mater Today. 2017;20(2): 74-82. https://doi.org/10.1016/j.mattod.2016.12.001.
2. Qi Y, McAlpine MC. Nanotechnology-enabled flexible and bio-compatible energy harvesting. Energ Environ Sci. 2010;3(9): 1275. https://doi.org/10.1039/c0ee00137f.
3. Parida K, Xiong J, Zhou X, Lee PS. Progress on triboelectric nanogenerator with stretchability, self-healability and bio-compatibility. Nano Energy. 2019;59:237-257. https://doi.org/10. 1016/j.nanoen.2019.01.077.
4. Xu M, Zhao T, Wang C, et al. High power density tower-like triboelectric nanogenerator for harvesting arbitrary directional water wave energy. ACS Nano. 2019;13(2):1932-1939. https://doi.org/10.1021/acsnano.8b08274.
5. Qiao H, Zhang Y, Huang Z, Wang Y, Li D, Zhou H. 3D printing individualized triboelectric nanogenerator with macro-pattern. Nano Energy. 2018;50(April):126-132. https://doi.org/10.1016/j. nanoen.2018.04.071.
6. Bodaghi M, Noroozi R, Zolfagharian A, Fotouhi M, Noroozi S. 4D printing self-morphing structures. Materials (Basel). 2019;12 (8):1353. https://doi.org/10.3390/ma12081353.
7. Chen K, Zhang L, Kuang X, et al. Dynamic photomask-assisted direct ink writing multimaterial for multilevel triboelectric nanogenerator. Adv Funct Mater. 2019;29(33):1-9. https://doi. org/10.1002/adfm.201903568.
8. Zhou X, Parida K, Halevi O, et al. All 3d-printed stretchable piezoelectric nanogenerator with non-protruding kirigami structure. Nano Energy. 2020;72:104676. https://doi.org/10. 1016/j.nanoen.2020.104676.
9. Li H, Li R, Fang X, et al. 3D printed flexible triboelectric nanogenerator with viscoelastic inks for mechanical energy harvesting. Nano Energy. 2019;58(December 2018):447-454. https://doi.org/10.1016/j.nanoen.2019.01.066.
10. Haque RI, Chandran O, Lani S, Briand D. Self-powered triboelectric touch sensor made of 3d printed materials. Nano Energy. 2018; 52(May):54-62. https://doi.org/10.1016/j.nanoen.2018.07.038.
11. Parida K, Thangavel G, Cai G, et al. Extremely stretchable and self-healing conductor based on thermoplastic elastomer for all-three-dimensional printed triboelectric nanogenerator. Nat Commun. 2019;10(1):2158. https://doi.org/10.1038/s41467-019-10061-y.
12. Yoon HJ, Kim DH, Seung W, et al. 3D-printed biomimetic villus structure with maximized surface area for triboelectric nanogenerator and dust filter. Nano Energy. 2019;63(June): 103857. https://doi.org/10.1016/j.nanoen.2019.103857.
13. He C, Zhu W, Chen B, et al. Smart floor with integrated triboelectric nanogenerator as energy harvester and motion sensor. ACS Appl Mater Interfaces. 2017;9(31):26126-26133. https://doi. org/10.1021/acsami.7b08526.
14. Seol ML, Ivaskačiūtė R, Ciappesoni MA, et al. All 3d printed energy harvester for autonomous and sustainable resource utilization. Nano Energy. 2018;52(July):271-278. https://doi.org/10. 1016/j.nanoen.2018.07.061.
15. Yang UJ, Lee JW, Lee JP, Baik JM. Remarkable output power enhancement of sliding-mode triboelectric nanogenerator through direct metal-to-metal contact with the ground. Nano Energy. 2019;57(December 2018):293-299. https://doi.org/10. 1016/j.nanoen.2018.12.034.
16. Yu Z, Wang Y, Zheng J, et al. Rapidly fabricated triboelectric nanogenerator employing insoluble and insufible biomass materials by fused deposition modeling. Nano Energy. 2020;68(November 2019):104382. https://doi.org/10.1016/j.nanoen.2019.104382.
17. Chen S, Huang T, Zuo H, et al. A single integrated 3d-printing process customizes elastic and sustainable triboelectric nanogenerators for wearable electronics. Adv Funct Mater. 2018;28 (46):1-8. https://doi.org/10.1002/adfm.201805108.
18. Utela B, Storti D, Anderson R, Ganter M. A review of process development steps for new material systems in three dimensional printing (3dp). J Manuf Process. 2008;10(2):96-104. https://doi.org/10.1016/j.jmapro.2009.03.002.
19. Cao R, Zhou T, Wang B, et al. Rotating-sleeve triboelectric-electromagnetic hybrid nanogenerator for high efficiency of harvesting mechanical energy. ACS Nano. 2017;11(8):8370- 8378. https://doi.org/10.1021/acsnano.7b03683.
20. Du X, Li N, Liu Y, et al. Ultra-robust triboelectric nanogenerator for harvesting rotary mechanical energy. Nano Res. 2018;11(5): 2862-2871. https://doi.org/10.1007/s12274-017-1916-5.
21. Yang W, Wang Y, Li Y, Wang J, Cheng T, Wang ZL. Integrated flywheel and spiral spring triboelectric nanogenerator for improving energy harvesting of intermittent excitations/triggering. Nano Energy. 2019;66(104104):1-8. https://doi.org/10.1016/j.nanoen.2019.104104.
22. Yan C, Gao Y, Zhao S, et al. A linear-to-rotary hybrid nanogenerator for high-performance wearable biomechanical energy harvesting. Nano Energy. 2020;67:104235. https://doi.org/10. 1016/j.nanoen.2019.104235.
23. Lee JP, Ye BU, Kim KN, Lee JW, Choi WJ, Baik JM. 3D printed noise-cancelling triboelectric nanogenerator. Nano Energy. 2017; 38(May):377-384. https://doi.org/10.1016/j.nanoen.2017.05.054.
24. Xiao X, Zhang X, Wang S, et al. Honeycomb structure inspired triboelectric nanogenerator for highly effective vibration energy harvesting and self-powered engine condition monitoring. Adv Energy Mater. 2019;9(40):1-11. https://doi.org/10.1002/aenm.201902460.
25. Chandrasekharan N, Thompson LL. Increased power to weight ratio of piezoelectric energy harvesters through integration of cellular honeycomb structures. Smart Mater Struct. 2016;25(4): 045019. https://doi.org/10.1088/0964-1726/25/4/045019.
26. Cui H, Hensleigh R, Yao D, et al. Three-dimensional printing of piezoelectric materials with designed anisotropy and directional response. Nat Mater. 2019;18(3):234-241. https://doi.org/10. 1038/s41563-018-0268-1.
27. Kanik M, Say MG, Daglar B, et al. A motion- and sound-activated, 3d-printed, chalcogenide-based triboelectric
39. Lee JH, Hinchet R, Kim SK, Kim S, Kim SW. Shape memory nanogenerator. Adv Mater. 2015;27(14):2367-2376. https://doi.org/10.1002/adma.201405944.

28. Gao S, Zhu Y, Chen Y, et al. Self-power electroreduction of n2 into nh3 by 3d printed triboelectric nanogenerators. Mater Today. 2019;28(September):17-24. https://doi.org/10.1016/j.mattod.2019.05.004.

29. Chen B, Tang W, Jiang T, et al. Three-dimensional ultraflexible triboelectric nanogenerator made by 3d printing. Nano Energy. 2018;45(December 2017):380-389. https://doi.org/10.1016/j.nanoen.2017.12.049.

30. An J, Wang ZM, Jiang T, Liang X, Wang ZL. Whirling-folded triboelectric nanogenerator with high average power for power generation at low wave energy harvesting. Adv Funct Mater. 2019;29(39):1-10. https://doi.org/10.1002/adfm.201904867.

31. Yang PK, Lin ZH, Pradel KC, et al. Paper-based origami trubo-electric nanogenerators and self-powered pressure sensors. ACS Nano. 2015;9(1):901-907. https://doi.org/10.1021/nn506631t.

32. Xia K, Zhu Z, Zhang H, du C, Xu Z, Wang R. Painting a high-output triboelectric nanogenerator on paper for harvesting energy from human body motion. Nano Energy. 2018;50(April):571-580. https://doi.org/10.1016/j.nanoen.2018.06.019.

33. Yi H, Wang Y, Chang H, Tao K. Spherical wave power generator with origami-structured double-helix multifold electrets. 19th International Conference on Micro and Nanotechnology for Power Generation and Energy Conversion Applications (PowerMEMS). 2019;1-5.

34. Fang L, Li J, Zhu Z, Orrego S, Kang SH. Piezoelectric polymer thin films with architected cuts. J Mater Res. 2018;33(3):330-342. https://doi.org/10.1557/jmr.2018.6.

35. Ferguson WJG, Kuang Y, Evans KE, Smith CW, Zhu M. Auxetic structure for increased power output of strain vibration energy harvester. Sensors Actuators, A Phys. 2018;282:90-96. https://doi.org/10.1016/j.sna.2018.09.019.

36. Zarek M, Layani M, Cooperstein I, et al. 3D printing of shape memory polymers for flexible electronic devices. Adv Mater. 2016;28(22):4449-4454. https://doi.org/10.1002/adma.201503132.

37. Lv P, Shi L, Fan C, et al. Hydrophobic ionic liquid gel-based triboelectric nanogenerator: next generation of ultrastable, flexible, and transparent power sources for sustainable electronics. ACS Appl Mater Interfaces. 2020;12:15012-15022. https://doi.org/10.1021/acsami.9b19767.

38. Parida K, Kumar V, Jiangxin W, Bhavanasi V, Bendi R, Lee PS. Highly transparent, stretchable, and self-healing ionic-skin triboelectric nanogenerators for energy harvesting and touch applications. Adv Mater. 2017;29(37):1-8. https://doi.org/10.1002/adma.201702181.

39. Lee JH, Hinchet R, Kim SK, Kim S, Kim SW. Shape memory polymer-based self-healing triboelectric nanogenerator. Energy Environ Sci. 2015;8(12):3605-3613. https://doi.org/10.1039/c5ee02711j.

40. Xiong J, Luo H, Gao D, et al. Self-restoring, waterproof, tunable microstructural shape memory triboelectric nanogenerator for self-powered water temperature sensor. Nano Energy. 2019;61 (April):584-593. https://doi.org/10.1016/j.nanoen.2019.04.089.

41. Halevi O, Chen T, Lee PS, Magdassi S, Hriljac JA. Nuclear wastewater decontamination by 3d-printed hierarchical zeolite monoliths. RSC Adv. 2020;10:5766-5776. https://doi.org/10.1039/c9ra09967k.

42. Ge Q, Dunn CK, Qi HJ, Dunn ML. Active origami by 4d printing. Smart Mater Struct. 2014;23(9):094007. https://doi.org/10.1088/0964-1726/23/9/094007.

43. Zhao Z, Wu J, Mu X, Chen H, Qi HJ. Desolvation induced origami of photocurable polymers by digit light processing. Macromol Rapid Commun. 2017;38(1600625):1-6. https://doi.org/10.1002/marc.201600625.

44. Miao S, Zhu W, Castro NJ, et al. 4D printing smart biomedical scaffolds with novel soybean oil epoxidized acrylate. Sci Rep. 2016;6(May):1-10. https://doi.org/10.1038/srep27226.

45. Liu Y, Shaw B, Dickey MD, Genzer J. Sequential self-folding of polymer sheets. Sci Adv. 2017;3(e1602417):1-7.

46. Tibbits S, Linor S, Dikovsky D, Hirsch S. 4D printing: multi-material shape change. Arch Desi. 2014;86(1):116-121.

47. Mallineni SSK, Dong Y, Behlow H, Rao AM, Podila R. A wireless trubo-electric nanogenerator. Adv Energy Mater. 2018;8(10):1-7. https://doi.org/10.1002/aenm.201702736.

AUTHOR BIOGRAPHIES

Xinran Zhou received her bachelor’s degree from School of Materials Science and Engineering in Nanyang Technological University, Singapore in 2017. She is currently pursuing her doctoral degree under the supervision of Prof. Pooi See Lee at the School of Materials Science and Engineering in Nanyang Technological University, Singapore. Her research focuses on 3D printing of piezoelectric materials for application in energy harvesting and soft electronics.

Prof. Pooi See Lee received her PhD from National University of Singapore in 2002. She received the Norman Hackerman Young Author award presented by the Electrochemical Society in 2002. She joined the School of Materials Science and Engineering, Nanyang Technological University as an Assistant Professor in 2004. She was promoted to tenured Associate Professor in 2009 and full Professor in 2015. Her research focuses on energy and electronics, flexible and stretchable devices, electrochemical devices, and human-machine interface. She received the National Research Foundation Investigatorship and the Nanyang Research Excellence Award in 2016.

How to cite this article: Zhou X, Lee PS. Three dimensional printed nanogenerators. EcoMat. 2021;3:e12098. https://doi.org/10.1002/eom2.12098