Stretchable Kirigami Polyvinylidene Difluoride Thin Films for Energy Harvesting: Design, Analysis, and Performance

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Stretchable Kirigami polyvinylidene difluoride Thin Films for Energy Harvesting: Design, Analysis, and Performance

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Abstract: Kirigami**,** a modified form of origami which includes paper cutting, has been used to improve material stretchability and compliance. However, this technique is so far underexplored in patterning piezoelectric materials towards developing efficient and mechanically flexible thin-film energy generators. Motivated by existing kirigami-based applications, we introduce interdigitated cuts to polyvinylidene fluoride (PVDF) films to evaluate the effect on voltage generation and stretchability. Our results from theoretical analysis, numerical simulations, and experimental tests show that kirigami PVDF films exhibit an extended strain range while still maintaining significant voltage generation compared to films without cuts. Various cutting patterns were studied, and it was found that films with denser cuts have a larger voltage output. This kirigami design can enhance the properties of existing piezoelectric materials and help to integrate tunable PVDF generators into biomedical devices.

Keywords: PVDF film; kirigami; buckling; strain sensors; electric charge generation.

Kirigami, a variation of origami that introduces cutting, can create complex 3D geometries from flat 2D sheets through out-of-plane deformations. A wide range of technologies have been inspired by kirigami [1]. At the nanoscale, kirigami has enabled the shape formation and self-assembly of 3D nanostructures from 2D sheets. Examples include DNA nanotechnology [2], nanomembranes [3], and nanoelectromechanical systems [4]. Blees *et al.* [5] designed kirigami graphene sheets to achieve large ductility and resilience for stretchable electronics and photovoltaics. Based upon this work, the introduction of kirigami molybdenum disulfide has significantly increased yield and fracture strains [6]. Similarly, Shyu *et al.* [7] created kirigami nanocomposites that can extend ultimate strain up to 370%. At larger scales, kirigami has inspired novel designs in bio-sensing [8], steering mechanisms [9], cellular metamaterials [10], reconfigurable metamaterials [11], bio-probe devices [12], stretchable lithium-ion batteries [13], solar tracking systems [14], adaptive morphing wings [15], energy dissipation structures [16], and energy-efficient building skins [17]. While most studies focus on modifying geometry and morphology to achieve high stretchability [18], there has been a recent emphasis on mechanical instability related to origami and kirigami. Mechanical instabilities can be a favorable phenomenon for smart materials [19], and stimuli responsive systems [20,21]. For example, 3D micro/nanostructures were fabricated via the compressive buckling of filamentary ribbons, whose tunable geometric features enabled the rapid assembly of stimuli responsive structures [22].

In this letter, we use kirigami to improve the ability of piezoelectric materials to act as a power source for portable and implantable devices. In recent years, several flexible, stretchable devices have been developed for energy harvesting [23], self-power generation [24], spatiotemporal cardiac measurements [25], motion detection of fingers [26], wearable electronic devices [27], and high-strain sensors [28]. Among the many types of piezoelectric materials, PVDF is the most promising for biomedical applications due to its low cost, light weight, mechanical performance, and excellent biocompatibility. Current PVDF-based devices are mostly 2D structures, limited to in-plane deformation. Our previous studies on PVDF films have demonstrated their potential for energy generation [29] with both symmetric and asymmetric pore distribution [30]. Porous PVDF films, for example, have enabled a new generation of minimally invasive glucose sensors [31]. We introduced patterned cuts on PVDF films to induce out-of-plane deformation. The hypothesis is that kirigami can increase the strain range of piezoelectric structures while still maintaining significant energy generation. We envision that the tunability of kirigami can be applied to multifunctional piezoelectric devices such as biomedical devices.

As a proof of concept, we began by fabricating baseline solid PVDF films (see the Supplemental Material [35]). Fig. 1(a) shows a thin film 30 mm long, 15 mm wide, and 50 μm thick. The 200nm thick electrodes were deposited on the PVDF layer (25 μm) by an E-beam evaporator. The bottom Kapton film, with a thickness of 25 μm, is used as a supporting substrate to increase the stiffness of the specimen. We used a scalpel to cut the baseline PVDF films with two different patterns, center-cutting and edge-cutting. It should be noted that non-cutting regions of 6 mm were reserved on each end of the PVDF film for an electrical connection to measurement circuitry. As a result, cuts were only applied to the middle portion of the film (18 mm). The center-cutting design has the cut length of 10 mm in the center and 5 mm on the edge while the edge-cutting design contains only 10 mm-long cuts along the edge. PVDF films with both cutting patterns were uniaxially stretched with a motorized test stage. The maximum load (0.75 N) was set constant, since the piezoelectric output is directly related to the stress applied. We put a force gauge at one end of the kirigami structure during testing. A load-limiting test was used, as the moving stage will automatically stop once it reaches the maximum load.

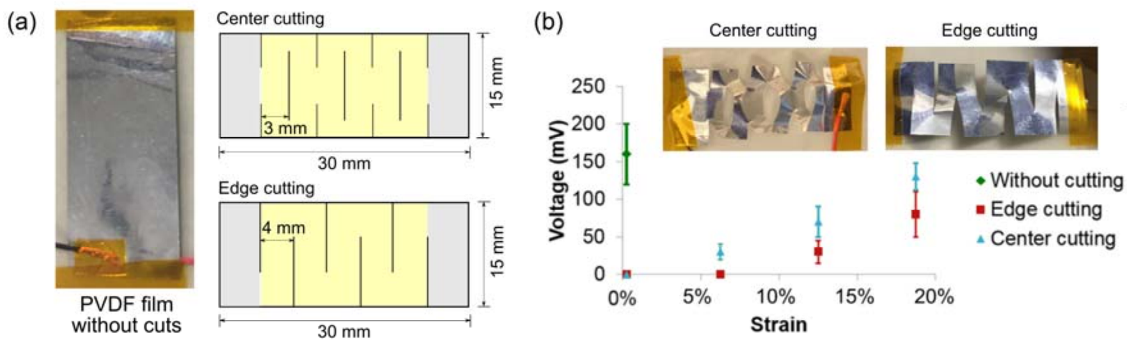
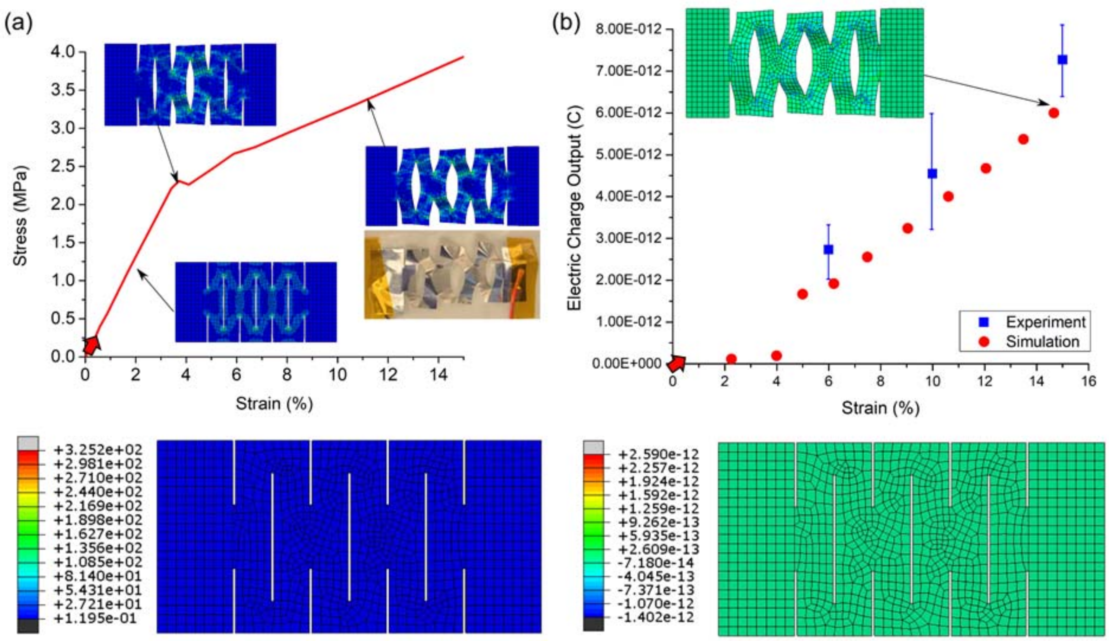


FIG. 1. The design and performance of kirigami PVDF films. (a) Baseline film without cuts and kirigami patterns. (b) Piezoelectric output between PVDF films with and without cuts.

After measuring the voltage output through the charge amplifier, we compared the performance of PVDF films with and without cuts. Fig. 1(b) shows the deformed shape of the two cutting patterns. The strain in our experiment is an effective strain, defined as the elongation divided by the original length. As expected, the PVDF film without cuts has a larger voltage output (160 mV) yet a smaller strain (1%). Kirigami-based PVDF films, in contrast, attain a slightly smaller voltage output but can attain strains of up to 18% without fracture. Note that the film with the center-cutting pattern has a larger voltage output (132 mV) than the one with the edge-cutting pattern (85 mV). The main contributor to the voltage output is the stress due to the in-plane surface stretching of the film. The center-cutting design has a larger portion of surface area under tensile stress during the stretching process, so it has a larger voltage output.

We characterised the response of the center-cut PVDF under axial stretching using finite element (FE) software (ABAQUS/Standard version 6.14), as shown in Video 1(a). The kirigami PVDF films were designed in SolidWorks and then imported to ABAQUS. The 3D solid geometry of the PVDF film was meshed with the C3D20RE element type and the Kapton film was meshed with the C3D20R element type. We did not include the aluminum layers due to the less significant thickness (200 nm) compared to the thicknesses of PVDF and Kapton layers. The Young's modulus of the PVDF film is 1.53 GPa and the Poisson's ratio is

0.37. The dielectric constant of the PVDF film is 1.06×10^{-10} and its piezoelectric properties d_{31} and d_{33} are -21×10^{-12} C/N and -29×10^{-12} C/N, respectively. The Young's modulus of the Kapton film is 2.5 GPa and the Poisson's ratio is 0.34. An axial load was applied at one end while a clamped condition was applied at the other. Simulations were performed using a dynamic implicit solver. a synchronized video featuring stress-strain curve and charge-strain curve is shown in Video 1. Video 1(a) shows two regimes in the force-displacement curve divided by a critical buckling load. Prior to the critical point, the film only undergoes in-plane deformation. A drop in force was observed after the critical point, indicating the onset of out-of-plane deformation. Numerically, the buckling of the film was triggered due to the asymmetric mesh of the computational model. The load maginitude then increases linearly as the stretching process continues. Excellent deformed shape agreement is found between experiments and FE simulations. The von Mises stress is defined as $\sigma_{VM} = \sqrt{[(\sigma_{11}-\sigma_{22})^2 + (\sigma_{22}-\sigma_{33})^2 + (\sigma_{33}-\sigma_{11})^2]/2 + 3(\tau_{12}^2 + \tau_{23}^2 + \tau_{13}^2)}$, where $\sigma_{11}, \sigma_{22}, \sigma_{33}$ are normal stresses and $\tau_{12}, \tau_{23}, \tau_{13}$ are shear stresses, which is widely used to predict the yielding of materials under complex loading. Here, the distributions of the von Mises stress from the simulation were plotted as insets in Video 1(a). It can be seen that a higher von Mises stress (lighter color) was observed at sharp corners of cuts, which does limit the stretchability of the film. In fact, a recent study [7] has found that the kirigami structures can be further stretched after introducing rounded edges at these sharp corners. Thus, the investigation on the stress redistribution and optimization of the kirigami PVDF is beyond the scope of this work.



VIDEO. 1. Simulation of kirigami PVDF films under axial stretching. (a) stress-strain curve for a PVDF film with center cuts. (b) Comparison of electric charges in PVDF film with center cutting between experiment and simulation.

We further validated the accuracy of our numerical model by comparing the charge output obtained from the experiment and the estimated charge output from the numerical model, see Video. 1(b). The experimental value of the electric charge is calculated by $Q=C\times V/A_{VD}$, where C is feedback capacitor used in charge amplifier (10×10^{-9} F); V is the voltage measured by charge amplifier; and A_{VD} is the amplifier voltage gain (110 V). For example, the electric charge when the measured voltage at 6% strain (22 mV) is 2.00×10^{-12} C while the simulated charge is 1.92×10^{-12} C. In the simulation, we requested a total of ten data point to show the changing of total charge within the film. It can be seen that after the film buckled at 4% strain, a significant jump was observed in the total electric charge output. The simulated electric charge is less than those experimental data but the error between experiment and simulation is acceptable.

We have demonstrated that kirigami PVDF films have an increased strain range without a significant loss in voltage output. We further explored center-cutting kirigami patterns to improve the voltage output and strain range of PVDF films. Shyu *et al.* [7] evaluated the effect of different cuts on film stretchability and found that longitudinal cuts have the most significant influence on maximum strain. Isobe and Okumura conducted an analysis to predict the stiffness and the critical stretching strain of a kirigami film [32]. Based on their work, we further develop theoretical analysis (see the Supplemental Material [35]) and run finite element simulations to study three kirigami designs with different cut spacing in the longitudinal direction as shown in Fig. 2(a). These three films have equal length (60 mm) and width (15 mm). The first sample has cuts spaced every 2mm, while a second has cuts spaced every 4 mm. The third film is a hybrid of both cuts, having 2 mm spaces in one segment and 4 mm in the other. All three films were stretched in their elastic regimes without considering material damage. We plot the stress vs. strain curve of the hybrid cut design and two single cut designs in Fig. 2(b). The response of a kirigami film transitions between two regimes: in-plane and out-of-plane deformation. In the hybrid design, the dense segment (2 mm) moves into the post-buckling, out-of-plane regime before the sparse segment (4 mm). At this point, the sparse-spacing segment is not fully stretched due to a large stress concentration at the interface between two segments. In Fig. 2(b) we plot the theoretical analysis as scatter points to compare with the numerical simulation results. Good agreement between simulation and theoretical analysis is observed.

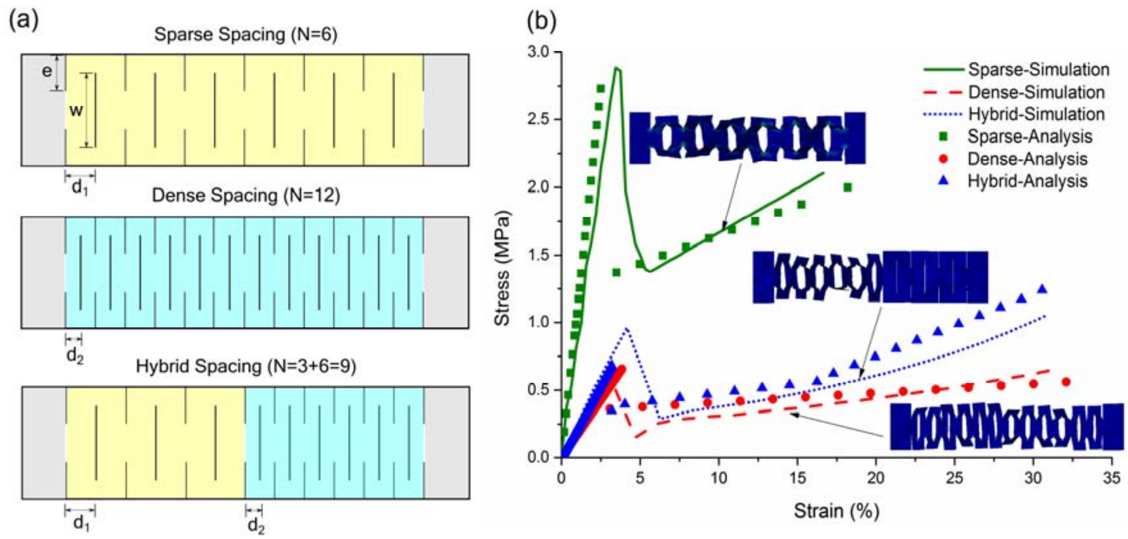


FIG. 2. The effect of kirigami pattern. (a) Pattern designs. (b) Comparsion between the stress-strain curves from simulations (lines) with theoritical predictions (scattered points).

We fabricated the above-mentioned films along with a baseline design without cuts and measured their voltage outputs through a charge amplifier (Fig. 3). These new films had a total length of 60 mm rather than the 30 mm of previous films. The voltage output of the PVDF film without cuts (325 mV) in the 60 mm long film is double that of the previous 30 mm long film (160 mV). The cut lengths stay the same as those in Fig. 1. As we stretched the films with cuts to about 20% strain, the dense design had a larger voltage output (283 mV) than both the hybrid design and the sparse design. At 20% strain the sparsely-cut film was fully stretched, and we observed larger strain limits for both the hybrid design (24%) and the dense design (33%). This stretchability is above the general upper limit for skin (20%). The voltage output (296 mV) associated with the hybrid design was approximately the same as the one without cuts, while the voltage output (333 mV) of the dense design even exceeds the cut-free film. This phenomenon is similar to the one we observed in Fig. 1, the underlying reason of which is that the main contributor to the voltage output is the stress due to the in-plane surface stretching of the film. In the sparse design, the film is limited by the stress distribution at those sharp corners, which in turn cause a lower stress on the other locations of the film surface. The denser design has higher stress at other locations of the film, which leads to higher voltage generation.

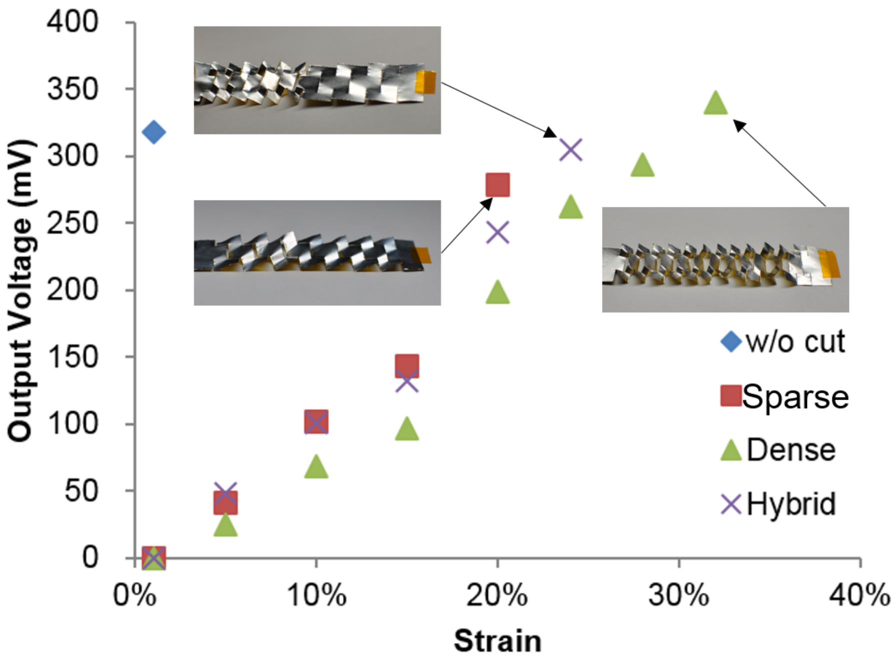


FIG. 3. Measured voltage output and strain for different cutting patterns. Inset: deformed configuration of kirigami PVDF film after stretching.

Among the patterns, the dense design has the largest number of cuts and sharp corners, and has the largest voltage output, which might indicate a correlation between these two parameters. The hybrid design was not fully stretched, as we observed cracks at the interface between the dense and the sparse portions of the film. Other designs also have the same damage at sharp corners. We also tested performance when the film was subjected to several stretching cycles. The dense design had a mean average of 340 mV for the voltage output but became damaged after five loading cycles. If we stretched the same film at a strain level 5% less than the limit of 33%, the voltage output remained at 299 mV without any damage.

In summary, we introduced interdigitated and other patterned cuts on PVDF thin films to enhance energy generation ability. Supported by theoretical analysis, FE simulations, and experiments, we proved that axially stretched kirigami PVDF films can attain a much higher strain limit (30%) while maintaining the same level of voltage output compared to regular PVDF films. The current designs can be extended beyond the component level, towards the exploration of biaxial stretching and 3D system assembly. As high strains will likely be observed in potential design of wearable and implantable devices (such as electronic clothes and finger posture detection), piezoelectric PVDF-TrFE films, in combination with careful design of supporting mechanical membranes, can be used to make flexible devices. We believe the concept of kirigami-patterned functional thin films can also be applied to other types of energy harvesters such as patch-based thin plates [33] and origami-based structures [34]. State-of-the-art piezoelectric polymer based devices rely on thin film geometries. These conventional devices have been intensively studied but have not proven capable of achieving sufficiently high voltage output. Our study shows that kirigami-based piezoelectric materials can enhance piezoelectric output with extended stress-strain responses for high-efficiency power generation devices. We envision a promising future in which kirigami-based piezoelectric materials are fully adapted into self-powered biomedical devices.

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Reference

[1] G. P. Collins, Science and Culture: Kirigami and technology cut a fine figure, together, Proceedings of the National Academy of Sciences **113**, 240 (2016).
[2] D. Han, S. Pal, Y. Liu, and H. Yan, Folding and cutting DNA into reconfigurable topological nanostructures, Nat Nano **5**, 712 (2010).
[3] F. Cavallo and M. G. Lagally, Nano-origami: Art and function, Nano Today **10**, 538 (2015).

[4] Z. Chen, G. Huang, I. Trase, X. Han, and Y. Mei, Mechanical Self-Assembly of a Strain-Engineered Flexible Layer: Wrinkling, Rolling, and Twisting, Physical Review Applied **5**, 017001 (2016).
[5] M. K. Blees, A. W. Barnard, P. A. Rose, S. P. Roberts, K. L. McGill, P. Y. Huang, A. R. Ruyack, J. W. Kevek, B. Kobrin, D. A. Muller, and P. L. McEuen, Graphene kirigami, Nature **524**, 204 (2015).
[6] P. Z. Hanakata, Z. Qi, D. K. Campbell, and H. S. Park, Highly stretchable MoS2 kirigami, Nanoscale **8**, 458 (2016).
[7] T. C. Shyu, P. F. Damasceno, P. M. Dodd, A. Lamoureux, L. Xu, M. Shlian, M. Shtein, S. C. Glotzer, and N. A. Kotov, A kirigami approach to engineering elasticity in nanocomposites through patterned defects, Nat Mater **14**, 785 (2015).
[8] L. Xu, X. Wang, Y. Kim, T. C. Shyu, J. Lyu, and N. A. Kotov, Kirigami Nanocomposites as Wide-Angle Diffraction Gratings, ACS Nano **10**, 6156 (2016).
[9] W. Wang, C. Li, H. Rodrigue, F. Yuan, M.-W. Han, M. Cho, and S.-H. Ahn, Kirigami/Origami-Based Soft Deployable Reflector for Optical Beam Steering, Advanced Functional Materials **27**, 1604214, 1604214 (2017).
[10] M. Eidini and G. H. Paulino, Unraveling metamaterial properties in zigzag-base folded sheets, Science Advances **1** (2015).
[11] A. Rafsanjani and K. Bertoldi, Buckling-Induced Kirigami, Physical Review Letters **118**, 084301 (2017).
[12] Y. Morikawa, S. Yamagiwa, H. Sawahata, M. Ishida, and T. Kawano, in *2016 IEEE 29th International Conference on Micro Electro Mechanical Systems (MEMS)*2016), pp. 149.
[13] Z. Song, X. Wang, C. Lv, Y. An, M. Liang, T. Ma, D. He, Y.-J. Zheng, S.-Q. Huang, H. Yu, and H. Jiang, Kirigami-based stretchable lithium-ion batteries, Scientific Reports **5**, 10988 (2015).
[14] A. Lamoureux, K. Lee, M. Shlian, S. R. Forrest, and M. Shtein, Dynamic kirigami structures for integrated solar tracking, Nat Commun **6** (2015).
[15] K. Saito, F. Agnese, and F. Scarpa, A Cellular Kirigami Morphing Wingbox Concept, Journal of Intelligent Material Systems and Structures **22**, 935 (2011).
[16] Y. Hou, R. Neville, F. Scarpa, C. Remillat, B. Gu, and M. Ruzzene, Graded conventional-auxetic Kirigami sandwich structures: Flatwise compression and edgewise loading, Composites Part B: Engineering **59**, 33 (2014).
[17] Y. Tang, G. Lin, S. Yang, Y. K. Yi, R. D. Kamien, and J. Yin, Programmable Kiri‐Kirigami Metamaterials, Advanced Materials (2016).
[18] D. M. Sussman, Y. Cho, T. Castle, X. Gong, E. Jung, S. Yang, and R. D. Kamien, Algorithmic lattice kirigami: A route to pluripotent materials, Proceedings of the National Academy of Sciences **112**, 7449 (2015).
[19] N. Hu and R. Burgueño, Buckling-induced smart applications: recent advances and trends, Smart Materials and Structures **24**, 063001 (2015).
[20] Z. Chen, Q. Guo, C. Majidi, W. Chen, D. J. Srolovitz, and M. P. Haataja, Nonlinear geometric effects in mechanical bistable morphing structures, Physical review letters **109**, 114302 (2012).
[21] Q. Guo, A. K. Mehta, M. A. Grover, W. Chen, D. G. Lynn, and Z. Chen, Shape selection and multi-stability in helical ribbons, Applied Physics Letters **104**, 211901 (2014).
[22] S. Xu, Z. Yan, K.-I. Jang, W. Huang, H. Fu, J. Kim, Z. Wei, M. Flavin, J. McCracken, R. Wang, A. Badea, Y. Liu, D. Xiao, G. Zhou, J. Lee, H. U. Chung, H. Cheng, W. Ren, A. Banks, X. Li, U. Paik, R. G. Nuzzo, Y. Huang, Y. Zhang, and J. A. Rogers, Assembly of micro/nanomaterials into complex, three-dimensional architectures by compressive buckling, Science **347**, 154 (2015).
[23] Y. Qi, J. Kim, T. D. Nguyen, B. Lisko, P. K. Purohit, and M. C. McAlpine, Enhanced Piezoelectricity and Stretchability in Energy Harvesting Devices Fabricated from Buckled PZT Ribbons, Nano Letters **11**, 1331 (2011).
[24] W. Wu, S. Bai, M. Yuan, Y. Qin, Z. L. Wang, and T. Jing, Lead Zirconate Titanate Nanowire Textile Nanogenerator for Wearable Energy-Harvesting and Self-Powered Devices, ACS Nano **6**, 6231 (2012).
[25] L. Xu, S. R. Gutbrod, A. P. Bonifas, Y. Su, M. S. Sulkin, N. Lu, H.-J. Chung, K.-I. Jang, Z. Liu, M. Ying, C. Lu, R. C. Webb, J.-S. Kim, J. I. Laughner, H. Cheng, Y. Liu, A. Ameen, J.-W. Jeong, G.-T. Kim, Y. Huang, I. R. Efimov, and J. A. Rogers, 3D multifunctional integumentary membranes for spatiotemporal cardiac measurements and stimulation across the entire epicardium, Nature

Communications **5**, 3329 (2014).
[26] M. Amjadi, A. Pichitpajongkit, S. Lee, S. Ryu, and I. Park, Highly Stretchable and Sensitive Strain Sensor Based on Silver Nanowire–Elastomer Nanocomposite, ACS Nano **8**, 5154 (2014).
[27] J. T. Muth, D. M. Vogt, R. L. Truby, Y. Mengüç, D. B. Kolesky, R. J. Wood, and J. A. Lewis, Embedded 3D Printing of Strain Sensors within Highly Stretchable Elastomers, Advanced Materials **26**, 6307 (2014).
[28] C. Yan, J. Wang, W. Kang, M. Cui, X. Wang, C. Y. Foo, K. J. Chee, and P. S. Lee, Highly Stretchable Piezoresistive Graphene–Nanocellulose Nanopaper for Strain Sensors, Advanced Materials **26**, 2022 (2014).
[29] D. Chen, T. Sharma, and J. X. J. Zhang, Mesoporous surface control of PVDF thin films for enhanced piezoelectric energy generation, Sensors and Actuators A: Physical **216**, 196 (2014).
[30] D. Chen and J. X. J. Zhang, Microporous polyvinylidene fluoride film with dense surface enables efficient piezoelectric conversion, Applied Physics Letters **106**, 193901 (2015).
[31] D. Chen, C. Wang, W. Chen, Y. Chen, and J. X. J. Zhang, PVDF-Nafion nanomembranes coated microneedles for in vivo transcutaneous implantable glucose sensing, Biosensors and Bioelectronics **74**, 1047 (2015).
[32] M. Isobe and K. Okumura, Initial rigid response and softening transition of highly stretchable kirigami sheet materials, Scientific Reports **6**, 24758 (2016).
[33] B. Bayik, A. Aghakhani, I. Basdogan, and A. Erturk, Equivalent circuit modeling of a piezo-patch energy harvester on a thin plate with AC–DC conversion, Smart Materials and Structures **25**, 055015 (2016).
[34] P.-K. Yang, Z.-H. Lin, K. C. Pradel, L. Lin, X. Li, X. Wen, J.-H. He, and Z. L. Wang, Paper-Based Origami Triboelectric Nanogenerators and Self-Powered Pressure Sensors, ACS Nano **9**, 901 (2015).
[35] See Supplemental Material at [URL will be inserted by publisher] for the key fabrication steps of PVDF films, theoretical derivation of films with hybrid pattern, and a movie of simulated stress-strain response and electric charge output for a PVDF film with center cutting.