Electronic Supplementary Material (ESI) for Energy & Environmental Science

Control of naturally coupled piezoelectric and photovoltaic properties for multi-type energy scavengers

Dukhyun Choi,[a,c] Keun Young Lee,[b] Mi-Jin Jin,[b] Soo-Ghang Ihn,[a] Sungyoung Yun,[a] Xavier Bulliard,[a] Woong Choi,[a] Sang Yoon Lee,[a] Sang-Woo Kim,*[b] Jae-Young Choi,*[a] Jong Min Kim[a] and Zhong Lin Wang*[d]

Email: kimsw@skku.edu (Sang-Woo Kim), jaeyoung88.choi@samsung.com (Jae-Young Choi), zhong.wang@mse.gatech.edu (Zhong Lin Wang)

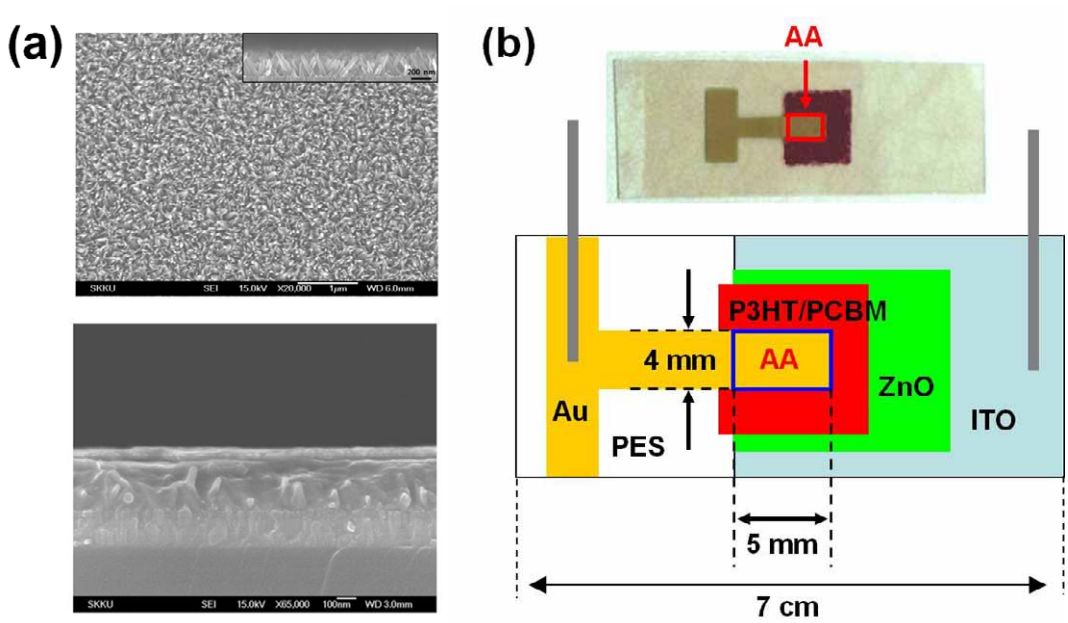

Fig. S1 (a) FE-SEM images (top) for top and cross-sectional views of ZnO nanorods and (bottom) for a cross-sectional view of Au/MoO_x/P3HT:PCBM blend/ZnO nanorods/ZnO thin film/ITO/PES. (b) Dimensions for a hybrid device, where *AA* means "active area". To minimize the variation of photo-induced voltage and current by bending of a device, the hybrid device was designed that the *AA* is placed at the center in the size of 4×5 mm^2 on the substrate with about 7 cm in the length. Furthermore, the wires to connect with measurement instruments are positioned at the both side far from the *AA* on the substrate not to generate high noise signals by bending.

Mechanical analysis of the hybrid device under bending

In a hybrid device, the neutral axis (*NA*) under bending is positioned around the middle of the polymer substrate, based on the geometry and the material properties of each element (see Table S1 and Fig. S2). When the device experiences a bending force, the hybrid layer including ITO/ZnO/Polymers/MoO_x/Au undergoes a tensile force along the length direction (the *3*-axis in Figs. S2c and S3a), whereas the hybrid layer undergoes a compressive force in the direction of the thickness (see Fig. S3b). Since the sputtered ZnO is polarized in the direction of the thickness (i.e. the *c*-axis of ZnO is aligned in the thickness direction: see Fig. S4), the piezoelectric field from ZnO is generated mainly by the strain in the thickness direction. In the thickness direction, the polymer blend layer experiences much less stress than the ZnO film layer, so the piezoelectric field is generated mainly from the ZnO film layer rather than from the ZnO nanorods. We could also obtain piezoelectric power from the hybrid device without ZnO nanorods (see Fig. S5).

Table S1 Mechanical properties for each element in our hybrid devices.

	Thickness	Young's modulus	Poisson ratio
Gold [a]	70 nm	69.8 GPa	0.44
P3HT/PCBM [b]	250 nm	6.02 GPa	0.35
ZnO [c]	50 nm	135 GPa	0.25
ITO [d]	80 nm	116 GPa	0.35
PES [e]	200 μm	2.6 GPa	0.42

[a] C. A. Neugebauer, *J. Appl. Phys.*, 1960, **31**, 1096.
[b] D. Tahk, H. H. Lee, D.-Y. Khang, *Marcromolecules*, 2009, **42**, 7079.
[c] P.-F. Yang, H.-C. Wen, S.-R. Jian, Y.-S. Lai, S. Wu, R.-S. Chen, *Microelectron. Reliab.*, 2008, **48**, 389.
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[e] J. T. Seitz, *J. Appl. Poly. Sci.*, 1993, **49**, 1331.

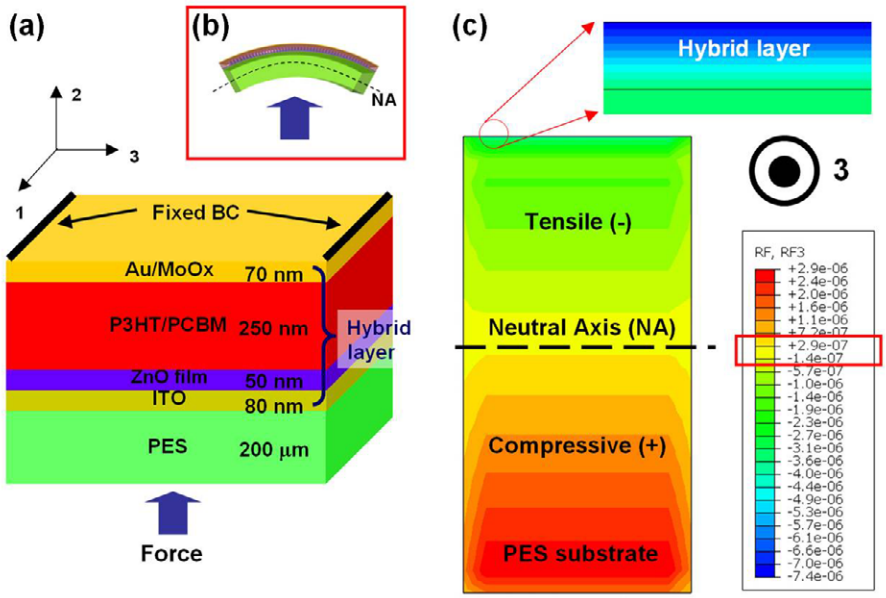

Fig. S2 (a) Simulation geometry, where *BC* refers to boundary condition. (b) Position of the neutral axis (*NA*) in the bent device. Because of the relatively thick PES substrate, the *NA* is positioned approximately in the middle of the PES. (c) Stress distributions in the hybrid device when the device is subjected to bending as shown in (b). The hybrid layer experiences tensile stress along the length direction (*3*-axis).

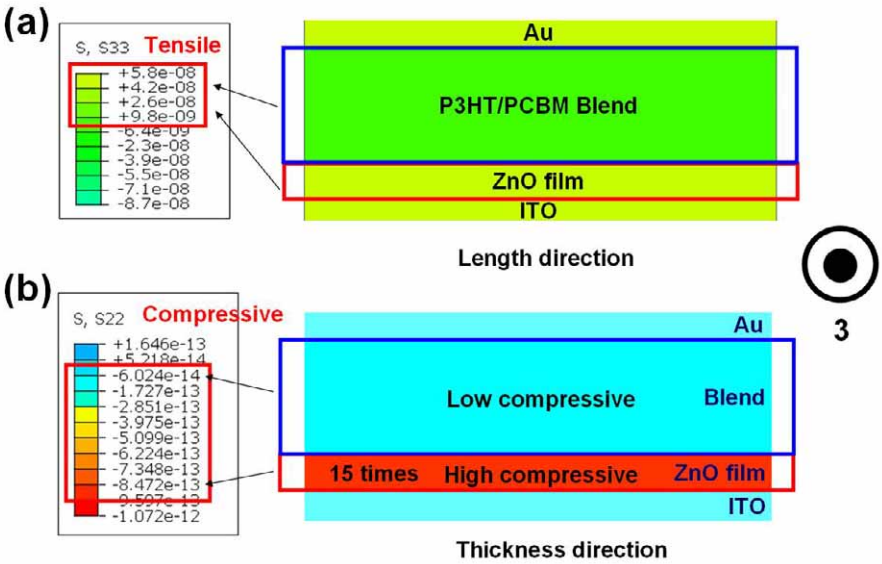

Fig. S3 Stress distribution in (a) the length direction (S33) and (b) the thickness direction (S22). Since the *c*-axis (002) of ZnO is aligned to the thickness direction (see Fig. S4), the piezoelectric field is generated mainly in the thickness direction. In the thickness direction, the polymer blend layer undergoes much less stress than the ZnO film layer, so that the piezoelectric field is generated mainly from the ZnO film layer.

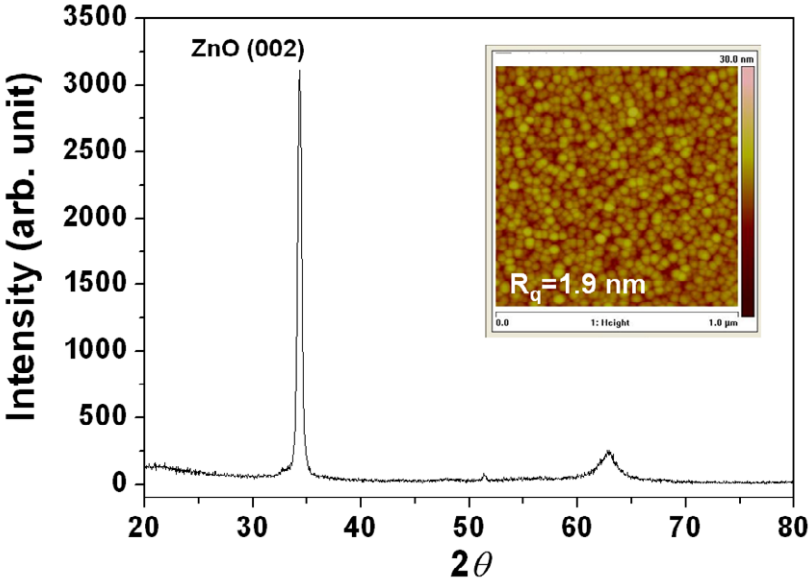

Fig. S4 The ZnO (002) diffraction peak in the X-ray diffraction profile for a ZnO thin film is predominant. The inset shows an atomic force microscopy image of the ZnO thin film. These XRD and AFM results indicate that the ZnO thin film was grown along the preferred *c*-axis.

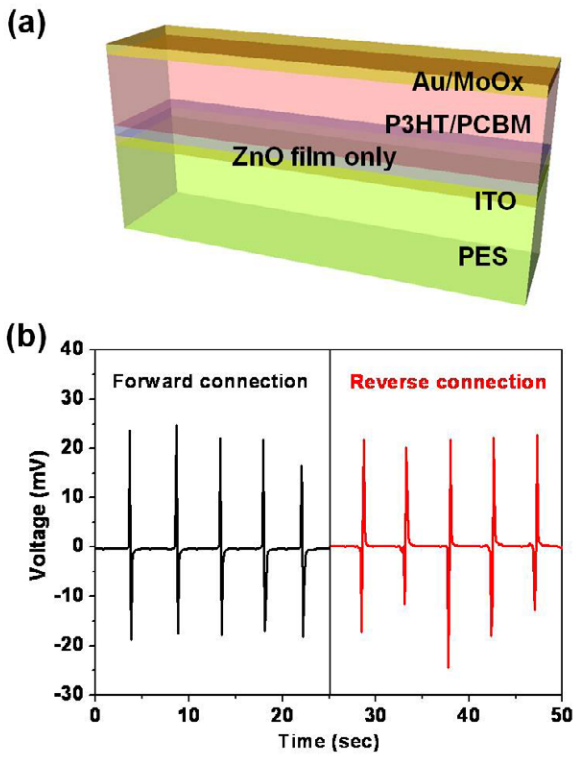

Fig. S5 (a) ITO/ZnO film only/P3HT:PCBM/MoO_x/Au structure. (b) Piezoelectric voltages with a switching polarity test. We see clearly the piezoelectric output voltage from the hybrid device without ZnO nanorods.

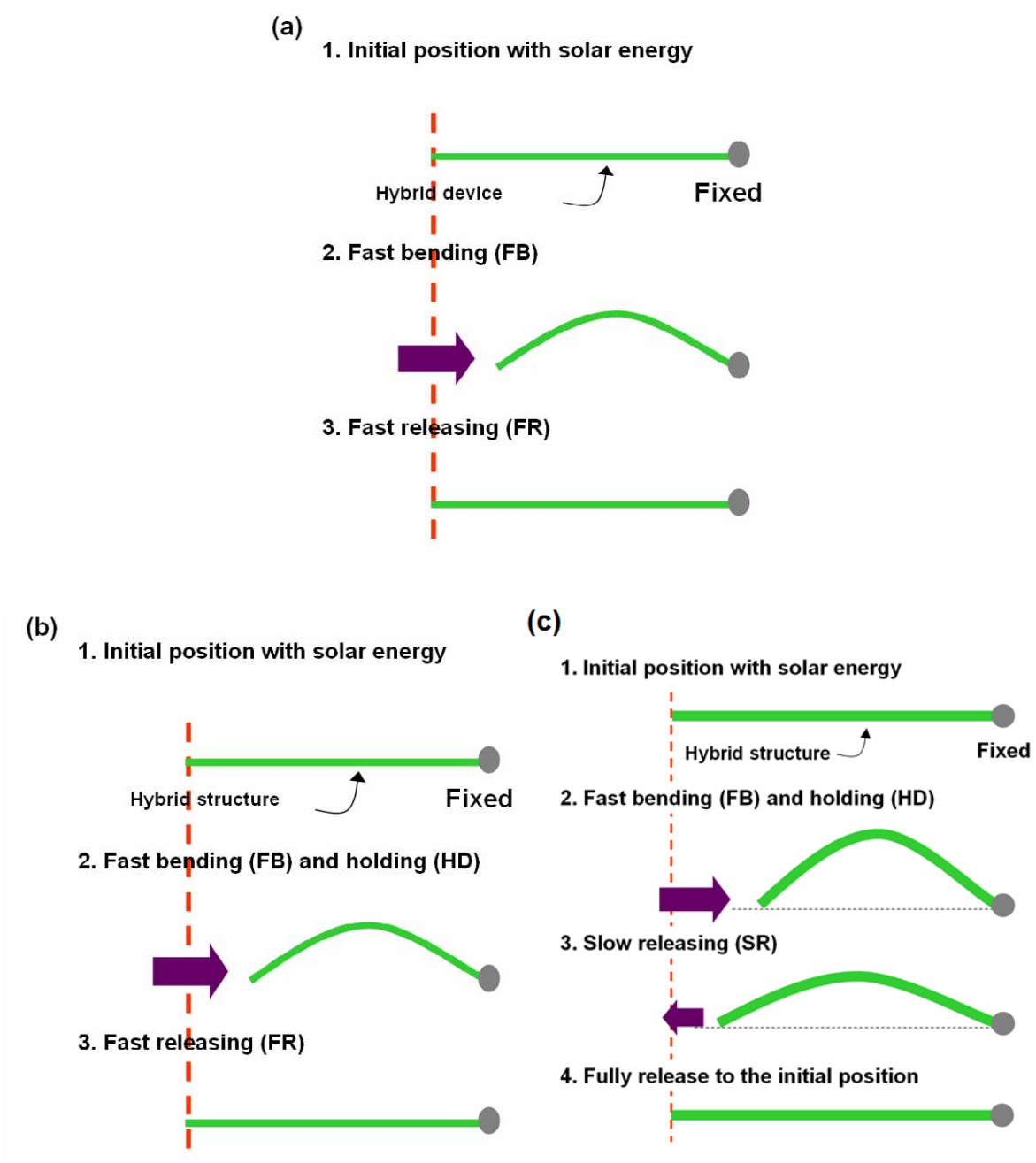

Fig. S6 Detail mechanical straining processes for output voltage under both mechanical energy and solar energy. The corresponding detail straining process for (a) Fig. 3a, (b) Fig. 3b, and (c) Fig. 3c. Green part is our hybrid device and the red dot line is the initial position of the hybrid device before mechanical bending. The purple arrow means the bending force and the size indicates the speed of straining rate.

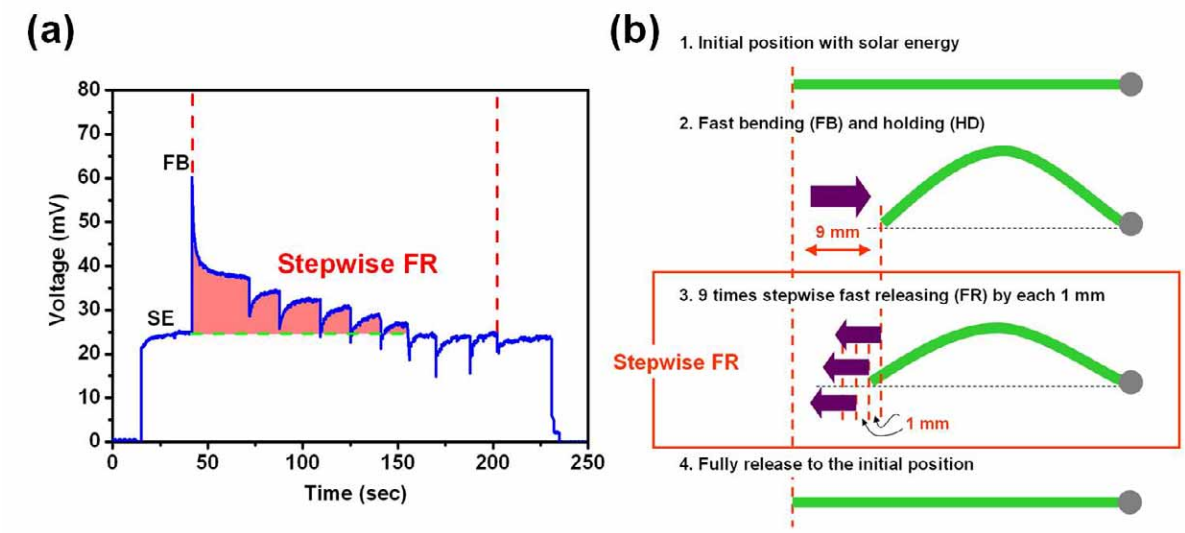

Fig. S7 Controlled hybrid operations by solar energy (*SE*) and mechanical energy (a) with fast bending (*FB*) and stepwise fast releasing (*FR*). (b) The detailed process.

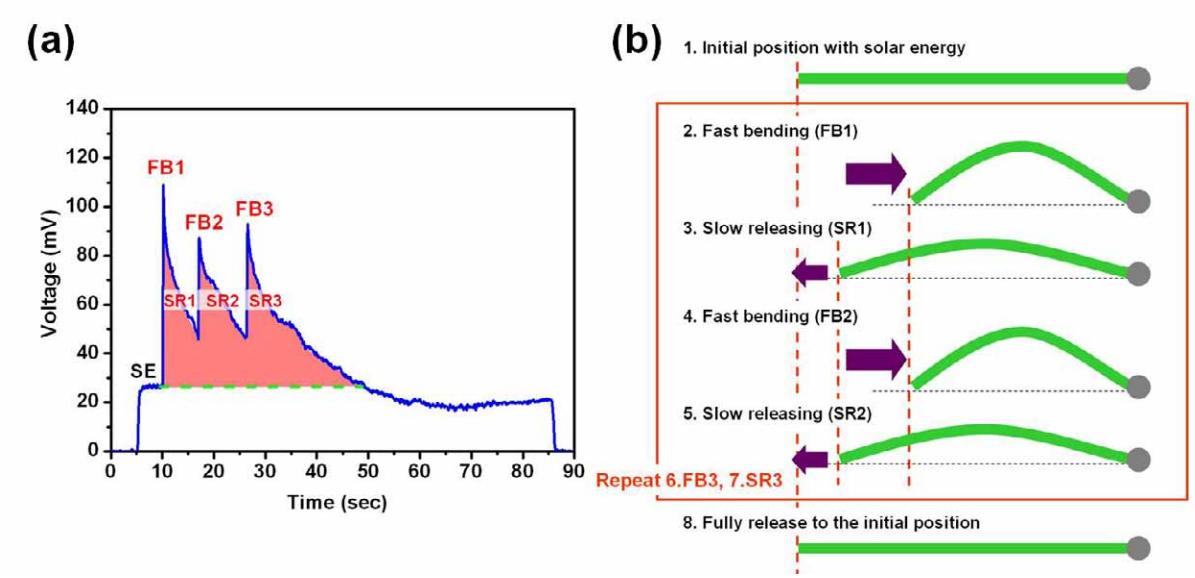

Fig. S8 Controlled hybrid operations by solar energy (*SE*) and mechanical energy (a) with repeating fast bending (*FB*) and slow releasing (*SR*). (b) The detailed process.