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A Novel Flexible Nanogenerator Made of ZnO Nanoparticles and Multiwall Carbon Nanotube

—Supporting Information

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Figs. S1-S9

Supplementary Discussions

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SUPPLEMENTARY FIGURES AND LEGENDS

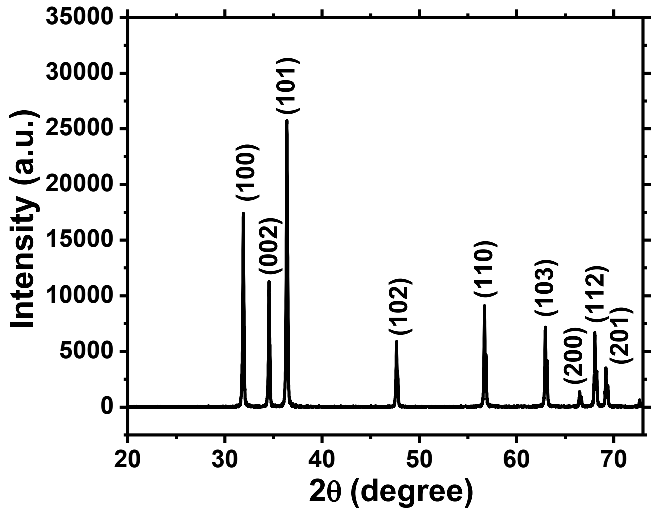

Figure S1 | XRD pattern of ZnO NPs.

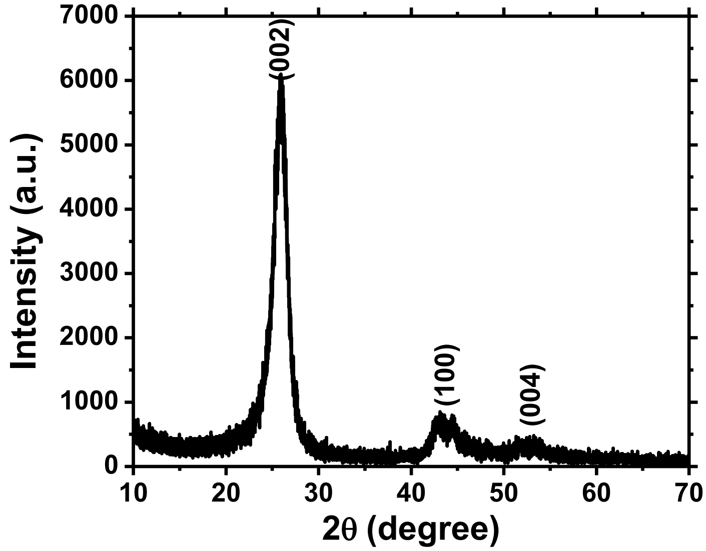

Figure S2 | XRD pattern of MW-CNTs.

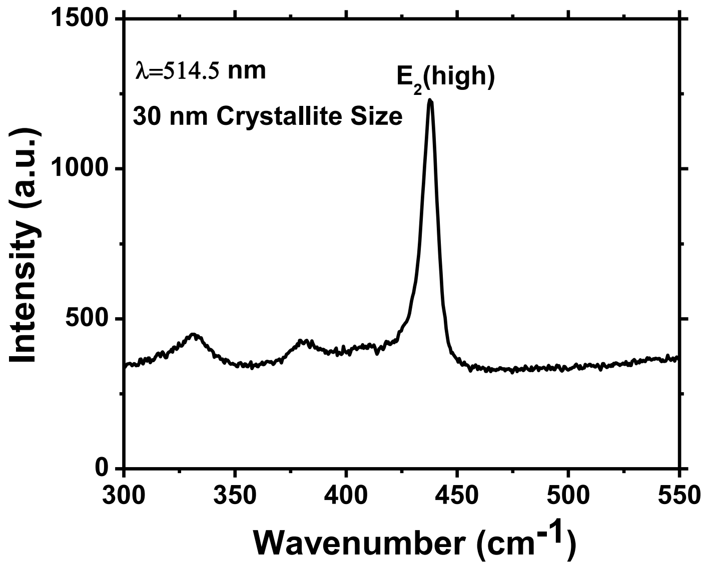

Figure S3 | Raman spectra of ZnO NPs.

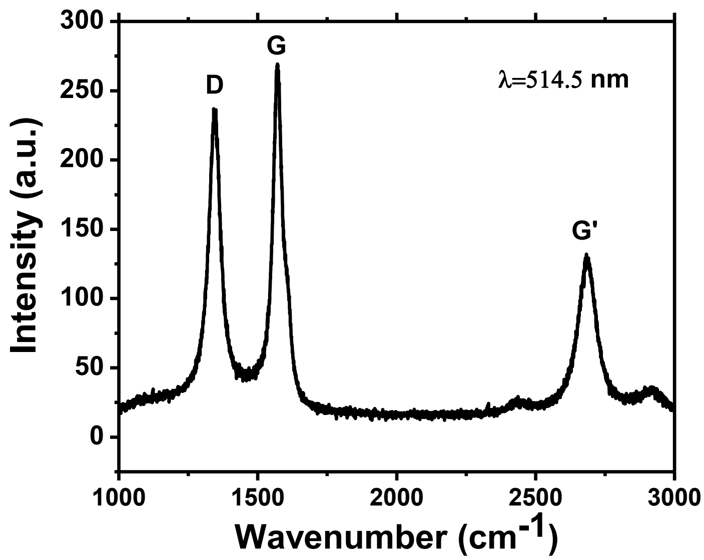

Figure S4 | Raman spectra of MW-CNTs.

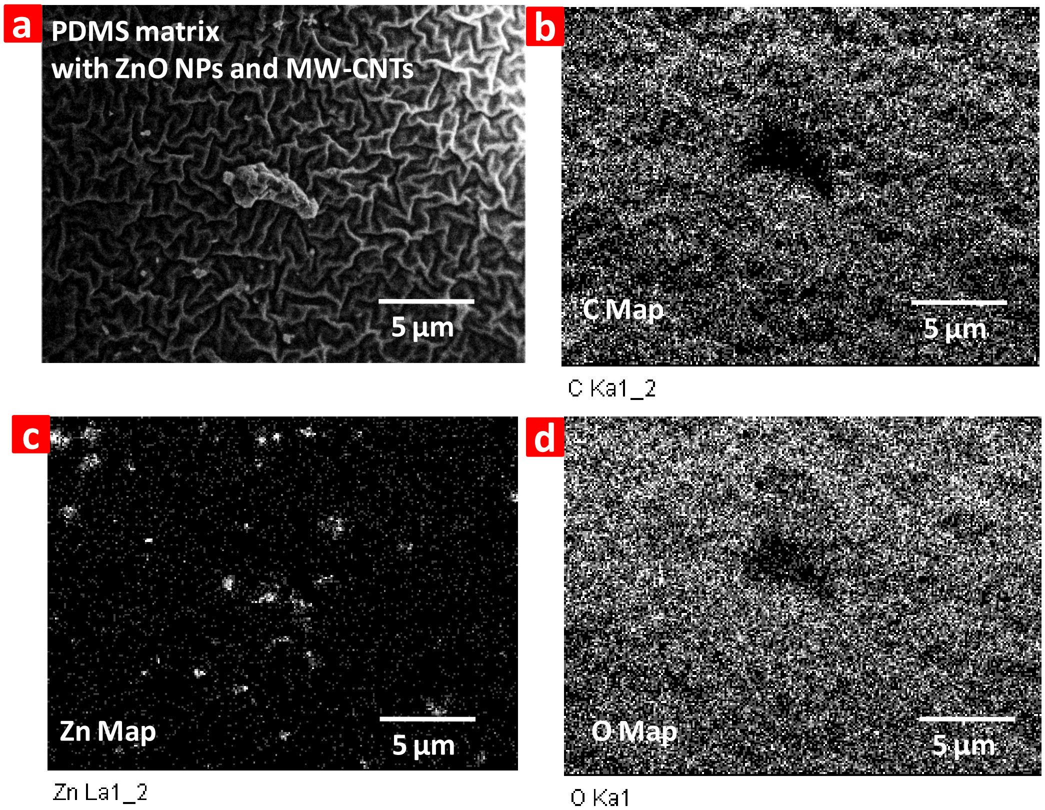

Figure S5 | SEM image (a) and the corresponding elemental mapping for carbon (b), zinc (c) and oxygen reveal a homogeneous ZnO NPs and MW-CNT mixing in the PDMS.

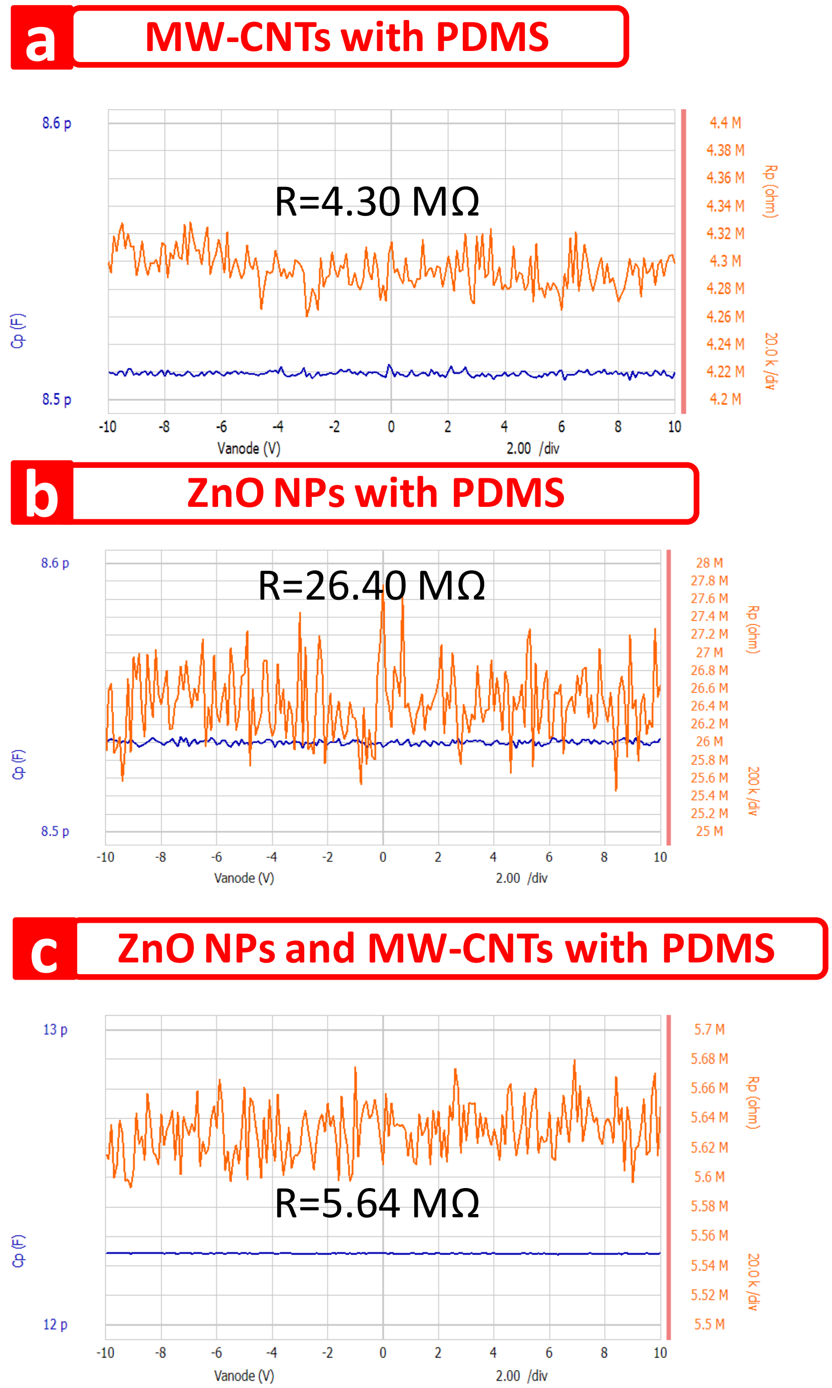

Figure S6 | The comparison results of the resistance among MW-CNT with PDMS structure, ZnO NPs with PDMS structure and ZnO NPs and MW-CNT with PDMS structure under 100 k frequency using C-V Model.

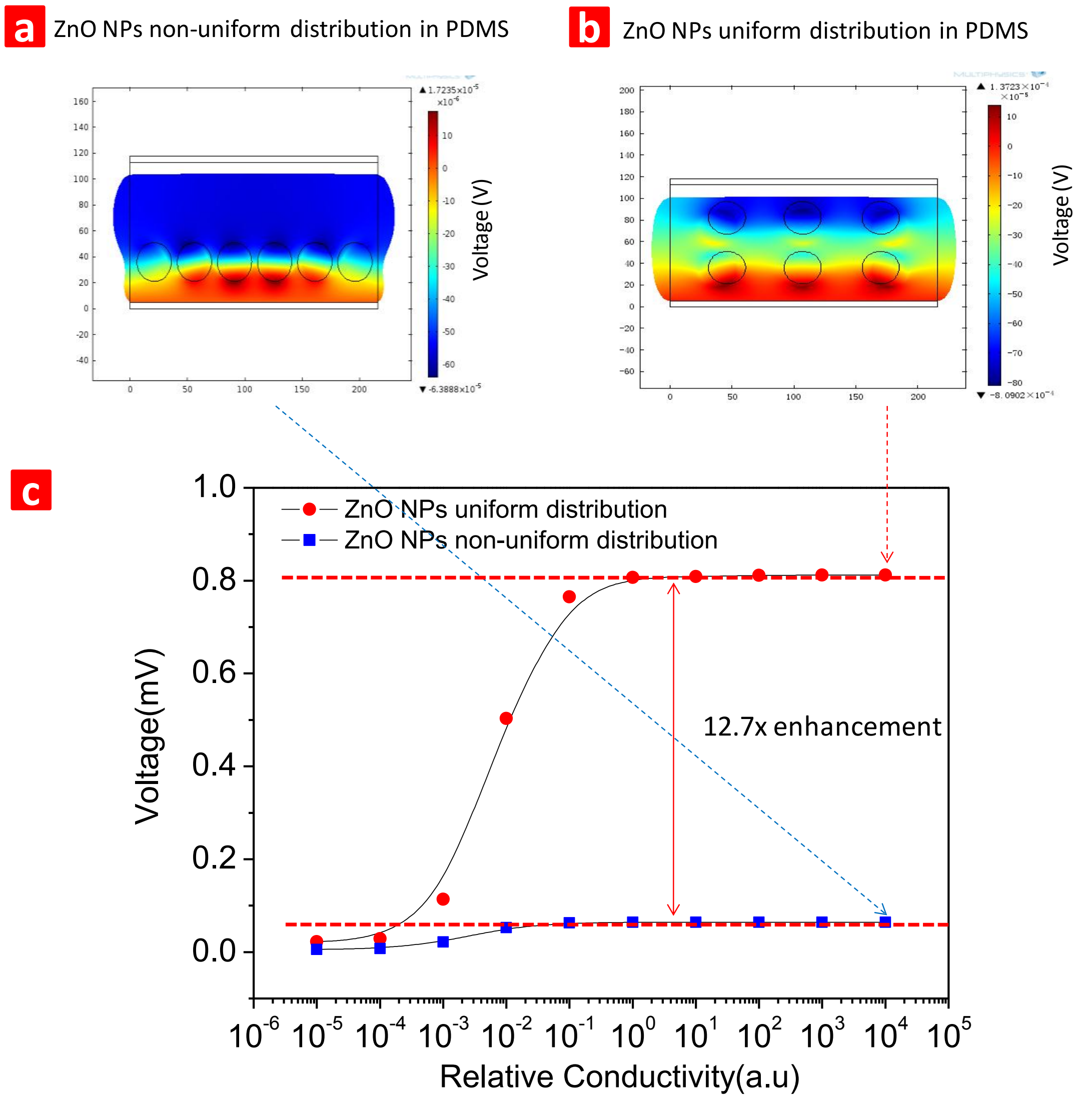

Figure S7. (a) Finite element model (FEM) results showing the voltage distribution under condition of ZnO NPs non-uniform distribution in PDMS. (b) FEM results showing the voltage distribution under condition of ZnO NPs uniform distribution in PDMS. (c) Compared with non-uniform ZnO Nps, relative conductivity vs. output voltage showing the uniform conductive film could produce higher voltage.

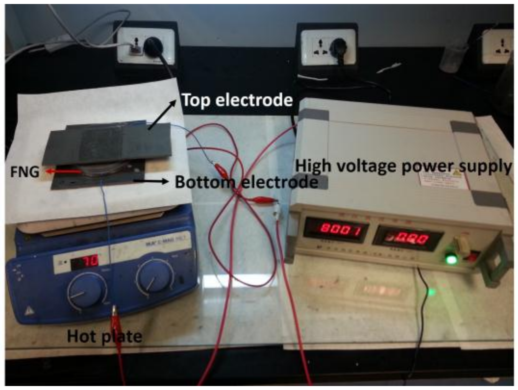

Figure S8. Experimental setup for poling process. 8001 V high voltage is applied on the FNG with 1.5 mm thickness for 12 hours on hot plate with the temperature of 70℃.

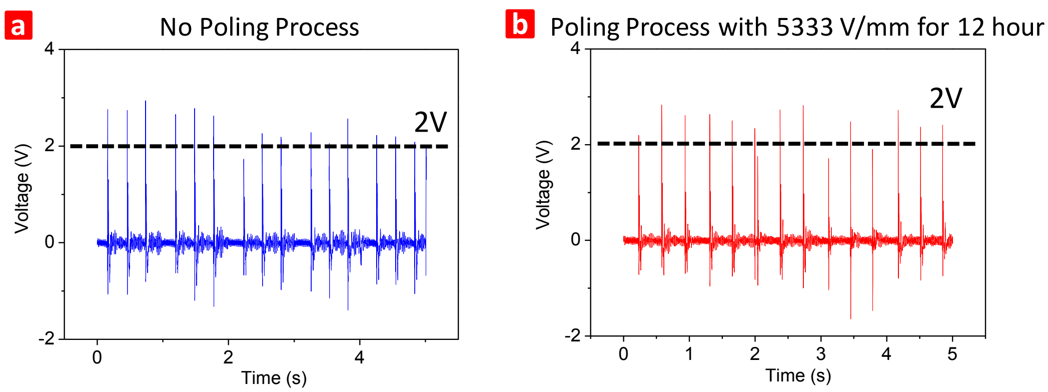

Figure S9. The comparison results of the hammer pressing between the samples with and without electric field process. (a) The output voltages generated from the device without poling process. (b) The output voltages generated from the device with poling process.

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SUPPLEMENTARY DISCUSSIONS

Figure S1 and S2 exhibit the X-ray diffraction (XRD) patterns of ZnO NPs and MW-CNTs, respectively, to characterize their crystalline structures. ZnO NPs show strong peaks at <100>, <002> and <101> and MW-CNTs show peaks at <002>, <100> and <004>. Unlike the images from SEM, X-ray diffraction (XRD) patterns shown in Figure S1 and S2 reveals the crystal structure of ZnO NPs and MW-CNTs. ZnO and MW-CNT utilized here both have polycrystalline structure. With the help of professional analysis software Jade and Scherrer formula, we have obtained the grain diameter for every crystal orientation of ZnO which is illustrated in Table S1. It is found that the grain diameter is far less than the diameter of particles shown in SEM image, thus we can infer that every particle is consist of multiple grains with various crystal orientations and may possibly leads to the output voltage and current under the non-specific direction of top and bottom electrodes. For MW-CNT, only the diameter of (002) crystal orientation is obtained as 3.53nm, since the other peaks are not strong enough for the analysis software to recognize them.

Figure S3 and S4 demonstrate the Raman spectrum obtained from ZnO NPs and MW-CNTs, respectively. The Raman spectrum of the ZnO NPs displays a E2-band at 437.7 cm^{-1}. Through fitting this peak, the crystallite size of ZnO NPs is estimated 30 nm, which is consistent with the Table S1 information provided from DK404, Beijing DK nano technology Co., LTD. The Raman spectrum of the MW-CNTs displays a D-band at 1346 cm^{-1}, a G-band at 1570 cm^{-1} and a G'-band at 2683 cm^{-1}. The prominent D peak is brought about by the structural defect in the carbon nanotube structure. The G-band is corresponding to the first-order scattering of the E2g mode and G'-band shows that the carbon nanotube has multi-wall structure.

Figure S5 shows the corresponding elemental mapping for carbon, zinc and oxygen, revealing a homogeneous mixing of ZnO NPs and MW-CNT in the PDMS.

Figure S6 displays the resistances of MW-CNT with PDMS structure, ZnO NPs with PDMS structure and ZnO NPs and MW-CNT with PDMS structure successively under 100kHz frequency according to the C-V model. As shown in Figure S6, the resistance of MW-CNTs with PDMS structure is just 4.3 MΩ and the resistance of ZnO NPs with PDMS structure hits to 26.40 MΩ. For ZnO NPs and MW-CNT with PDMS structure, the resistance is 5.64 MΩ, which is just in between of previous two situations. These results prove the function of MW-CNT which efficiently enhances the conductivity of the whole device.

As MW-CNT could form a mesh structure in the matrix and hold the NPs on its surface, this could make the ZnO NPs more uniform in PDMS. To verify this effect on the performance of FNG, theoretical analysis is performed. Figure S7 (a) shows the FEM results of the voltage distribution under condition of ZnO NPs non-uniform distribution in PDMS. While Figure S7 (b) shows the FEM results of the voltage distribution under condition of ZnO NPs uniform distribution in PDMS. Compared with non-uniform ZnO NPs, relative conductivity vs. output voltage (Figure S7 (c)) shows the uniform conductive film could produce higher voltage output.

Since Zinc Oxide is a piezoelectric material without ferroelectricity, external electric field is hardly to influence the spontaneous polarization of ZnO. But we still added some experiments to testify the possibility that external electric field will make ZnO nanoparticles “aligned”. In this test, 8001 V high voltage is applied on the FNG 1 with 1.5 mm thickness for 12 hour at hot plate with 70 degree heat and FNG 2 with the same parameters of FNG 1 is just heated on the hot plate with 70 degree heat, acting as a controlled group. The equipment being used is shown in Figure S8. The comparison result exhibited that, there was nearly no difference between these two samples, shown in Figure S9. One possible reason leading to this phenomenon is that heating curing process may make the ZnO NPs aligned.

The ZnO NPs is provided by DK404, Beijing DK nano technology Co., LTD. The detail information about this ZnO NPs is described in Table S2.What's more, the MWCNT is also provided by CNT103, Beijing DK nano technology Co., LTD. The detail information about this MW-CNT is described in Table S3.

SUPPLEMENTARY TABLES

Table S1 | The material information of ZnO NPs

Purity	99.9 %
Diameter	30 nm
Specific Surface Area	50 m^2/g
Color	milky white
Morphology	nearly spherical
Bulk density	0.3 - 0.45 g/cm^3
True density	5.606 g/cm^3

Table S2 | The material information of MW-CNTs

Purity	>95 %
External Diameter	8-15 nm
Inner Diameter	3-5 nm
Length	10-20 μm
Specific Surface Area	> 450 m^2/g
Grey Degree	<0.5 wt%
Amorphous Carbon	<2 %
Colour	Black
Density	~2.1 g/cm^3
Conductivity	120-170 s/cm

Table S3 | Grain diameter for every crystal orientation of ZnO

Crystal orientation	Grain diameter (nm)
（100）	2.8045
（002）	2.5949
（101）	2.4687
（102）	1.9070
（110）	1.6222
（103）	1.4751
（200）	1.4053
（112）	1.3766
（201）	1.3567