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Supporting Online Material for

Piezoelectric Nanogenerators Based on Zinc Oxide Nanowire Arrays

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Figs. S1 to S6

Table S1

Movies S1 and S2

SOM Text

Suplimentary materials for:

Piezo-Electric Nano-Generators Based on Zinc Oxide Nanowire Arrays

By Zhong Lin Wang * and Jinhui Song

Fig. S1: TEM images of ZnO nanowires showing no gold caps or with small gold caps at the growth fronts. Note the hespherical shape of the gold particles at the tips

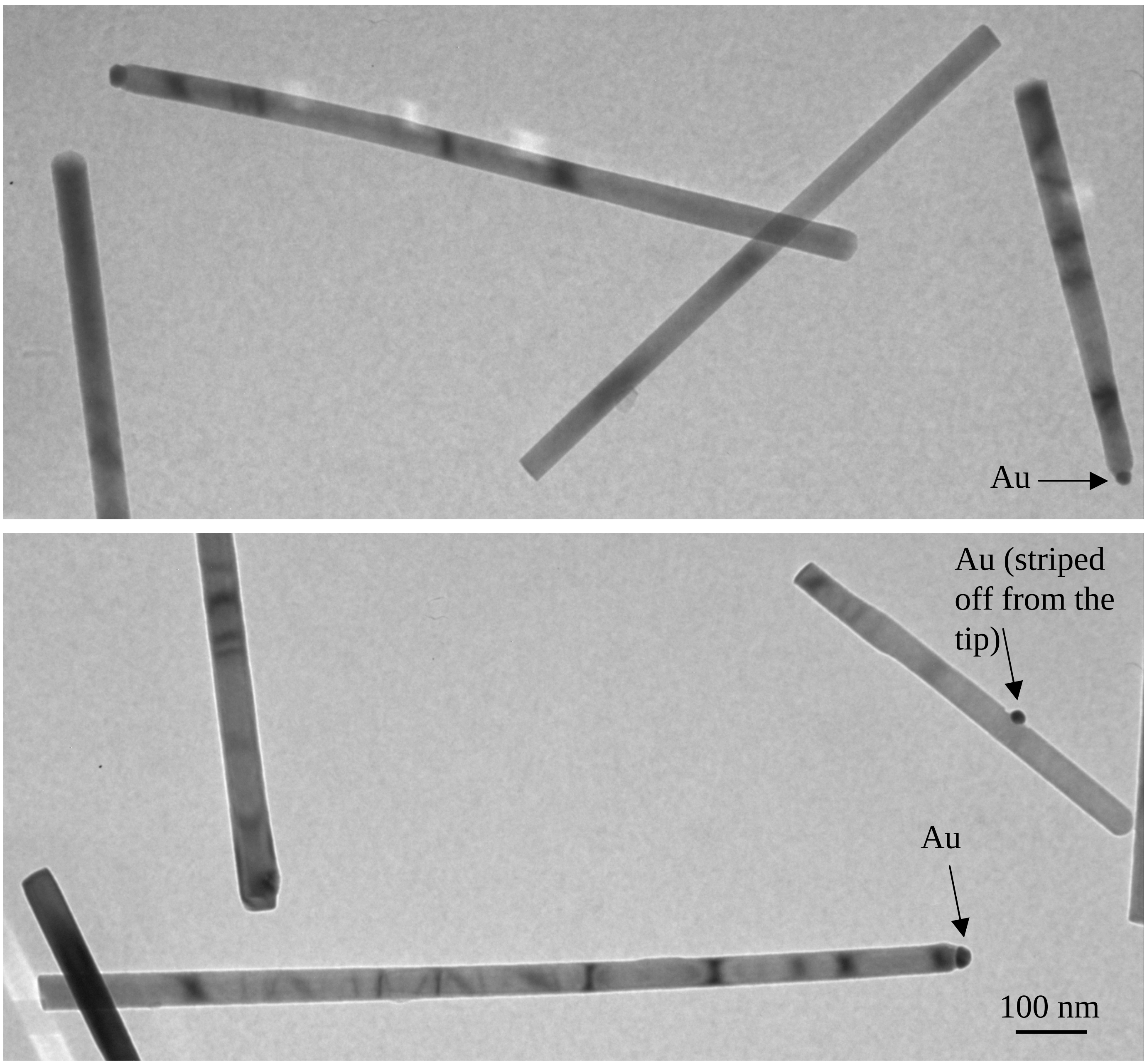


Fig. S2: Three different perspectives of outputting the data shown in Fig. 2B to clearly image the sharp piezoelectric voltage peaks.

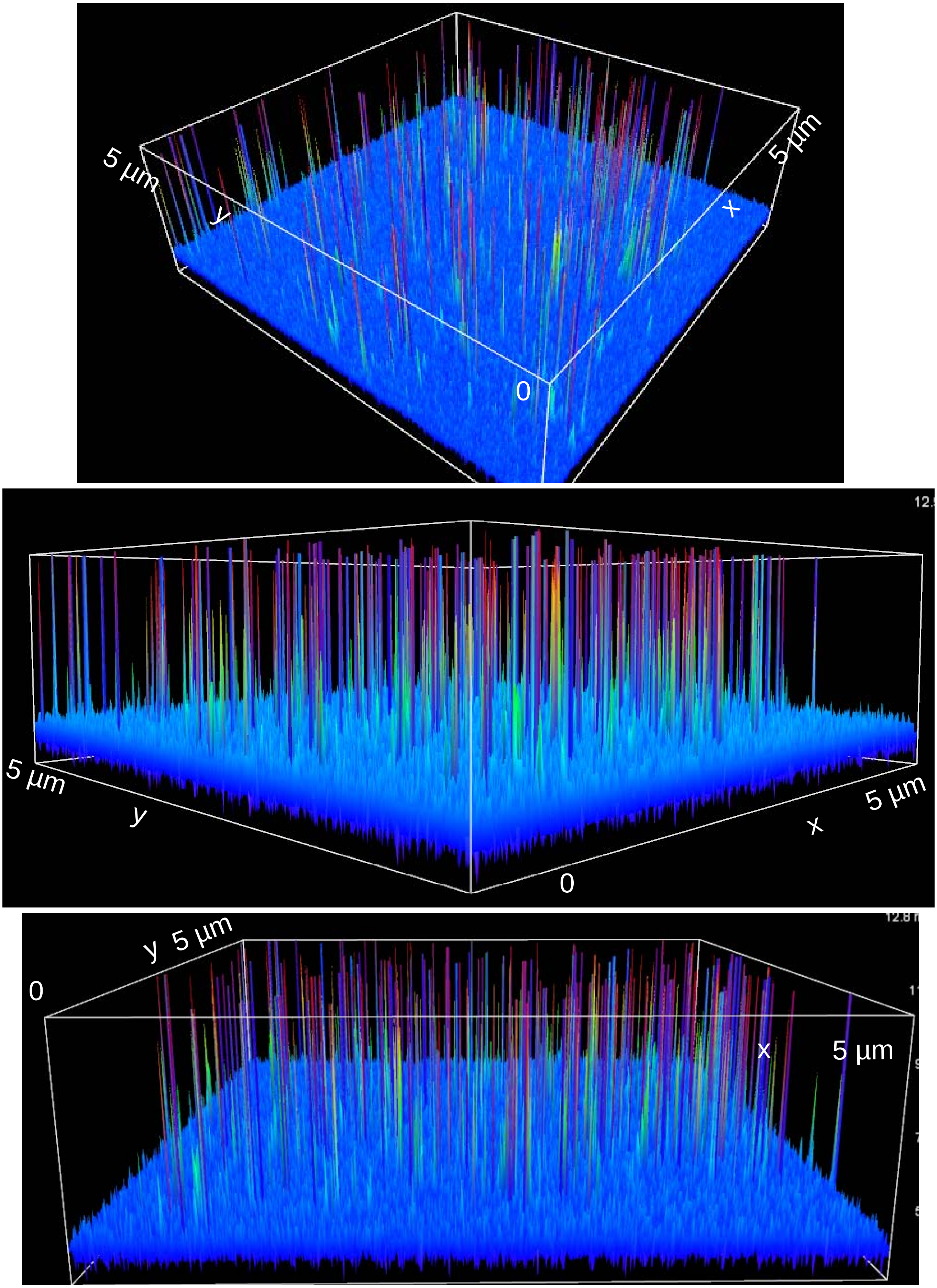


Fig. S3: Piezoelectic output voltage received at a higher scan frequency at a small scan region, showing the shape of the discharge peaks. The output voltage peak is as high as 20 mV.

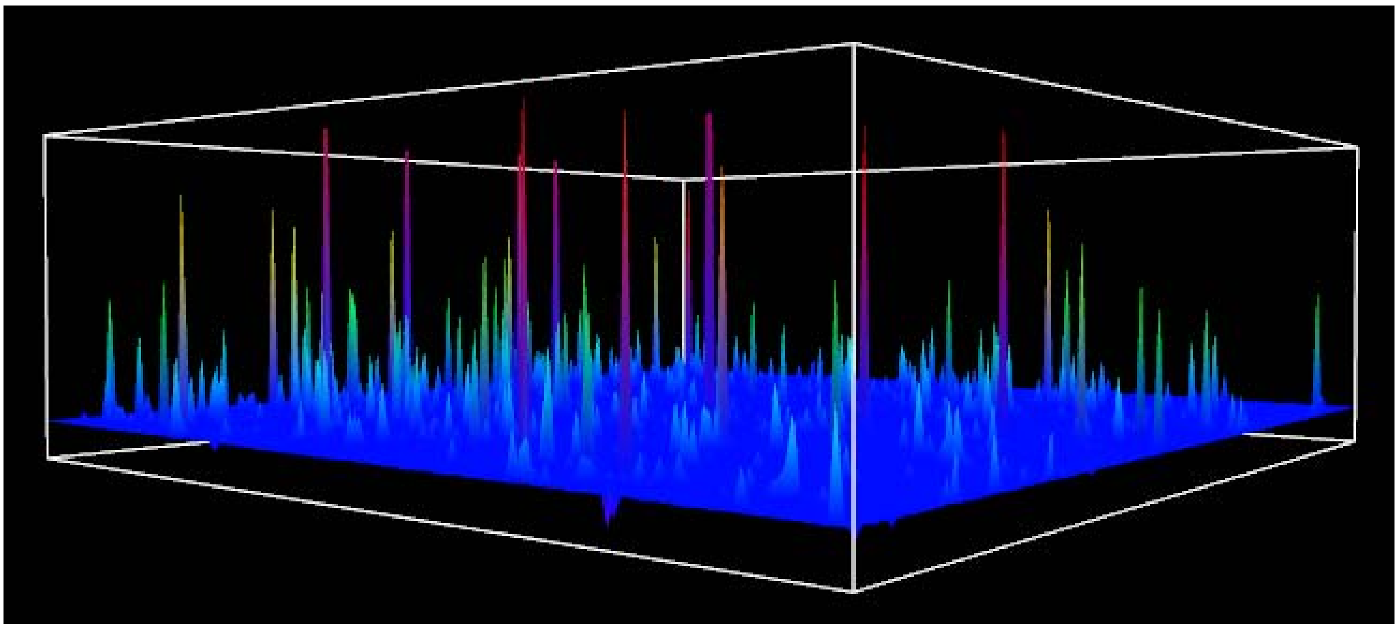


Fig. S4: To ensure the voltage output signal in Fig. 2B is due to piezoelectric induced charging effect rather than friction or contact potential, we immediately scanned the AFM tip at a side area covered by a metal film of the sample under exactly the same experimental conditions used for acquiring Fig. 2B. The output morphology image (A) and the voltage signals (B) of the metal film are displayed as the following. The output voltage shows no peaks but remains at the noise level, indicating that a metal film even with a different contact potential does not produce the observed discharge process. The data rule out the possibility of friction or contact potential being the cause of the observed charging event.

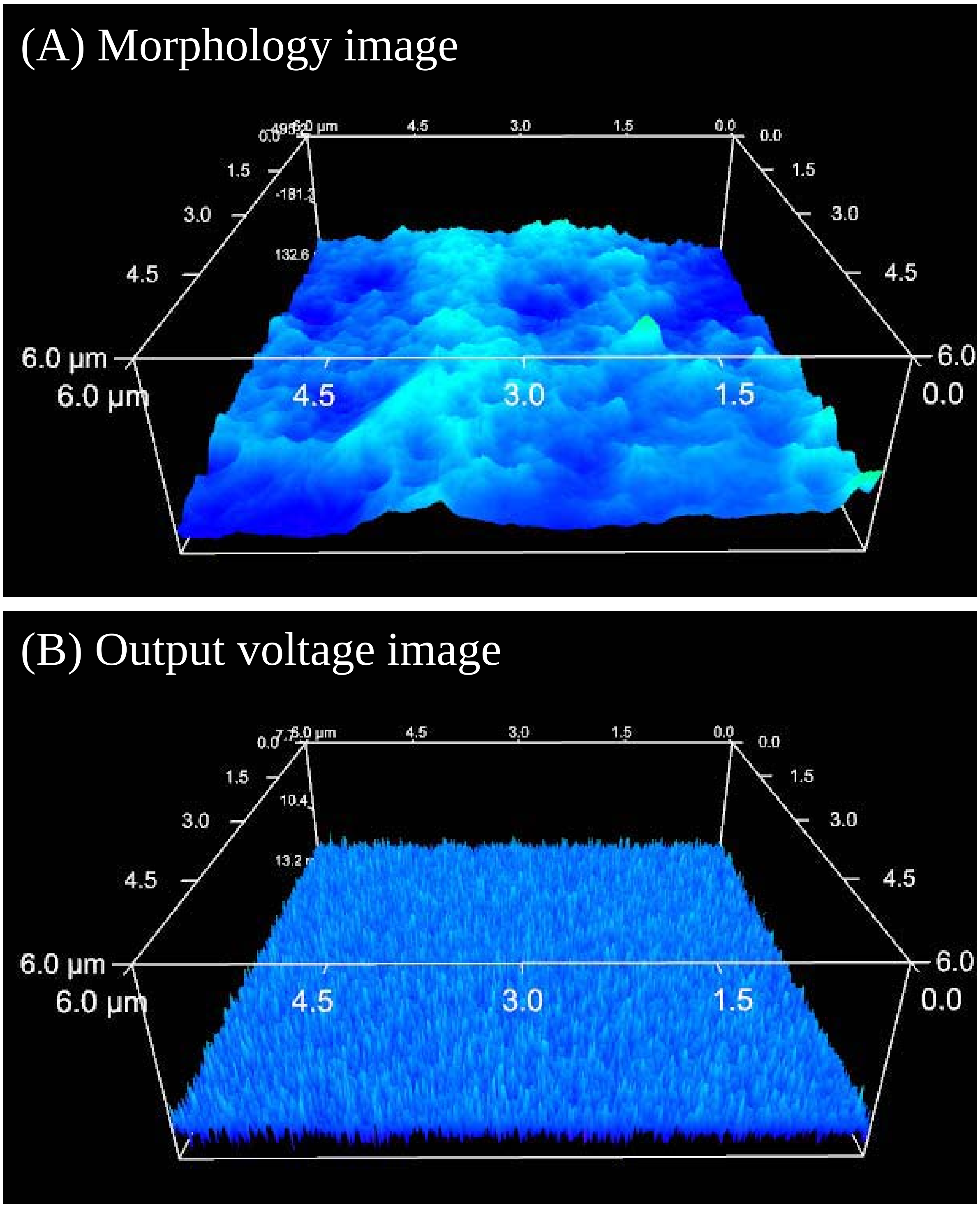


Fig. S5: To ensure the voltage output signal in Fig. 2B is due to piezoelectric induced charging effect rather than friction or contact potential, we carried out similar experiments using aligned carbon nanotubes. (A, B) Side and top views of aligned carbon nanotubes. (C) The output voltage image shows no peaks but noise, indicating that carbon nanotubes do not produce the discharge process presented in Fig. 2B for ZnO nanowires. The data rule out the possibility of friction or contact potential being the cause of the observed discharging event.

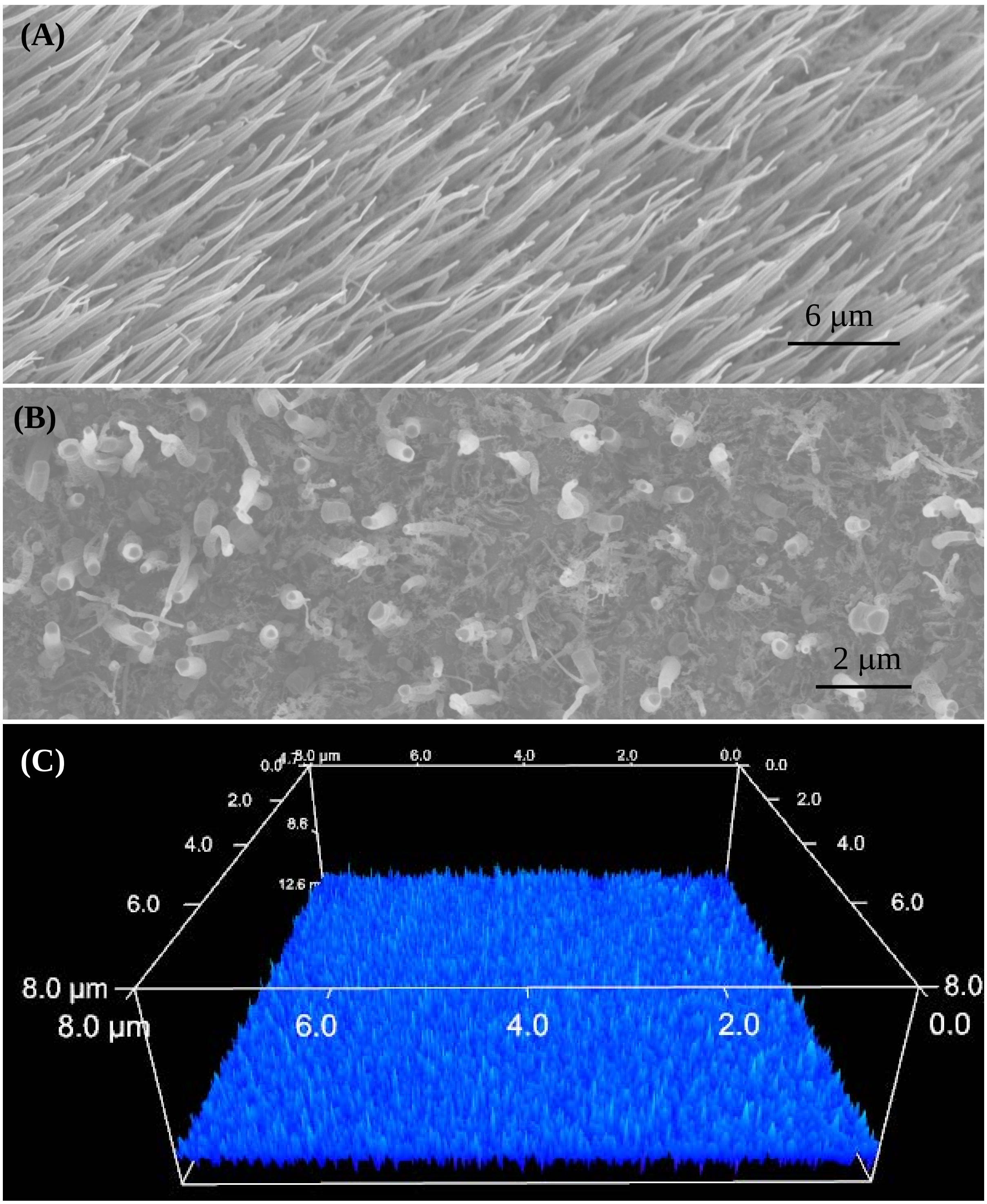


Fig. S6: To ensure the voltage output signal in Fig. 2B is due to piezoelectric induced charging effect rather than friction or contact potential, we carried out similar experiments using aligned WO_3 nanowires. The output voltage image shows no peaks but noise, indicating that WO_3 nanowires do not produce the discharge process presented in Fig. 2B. The data rule out the possibility of friction or contact potential being the cause of the observed discharging event for ZnO nanowires.

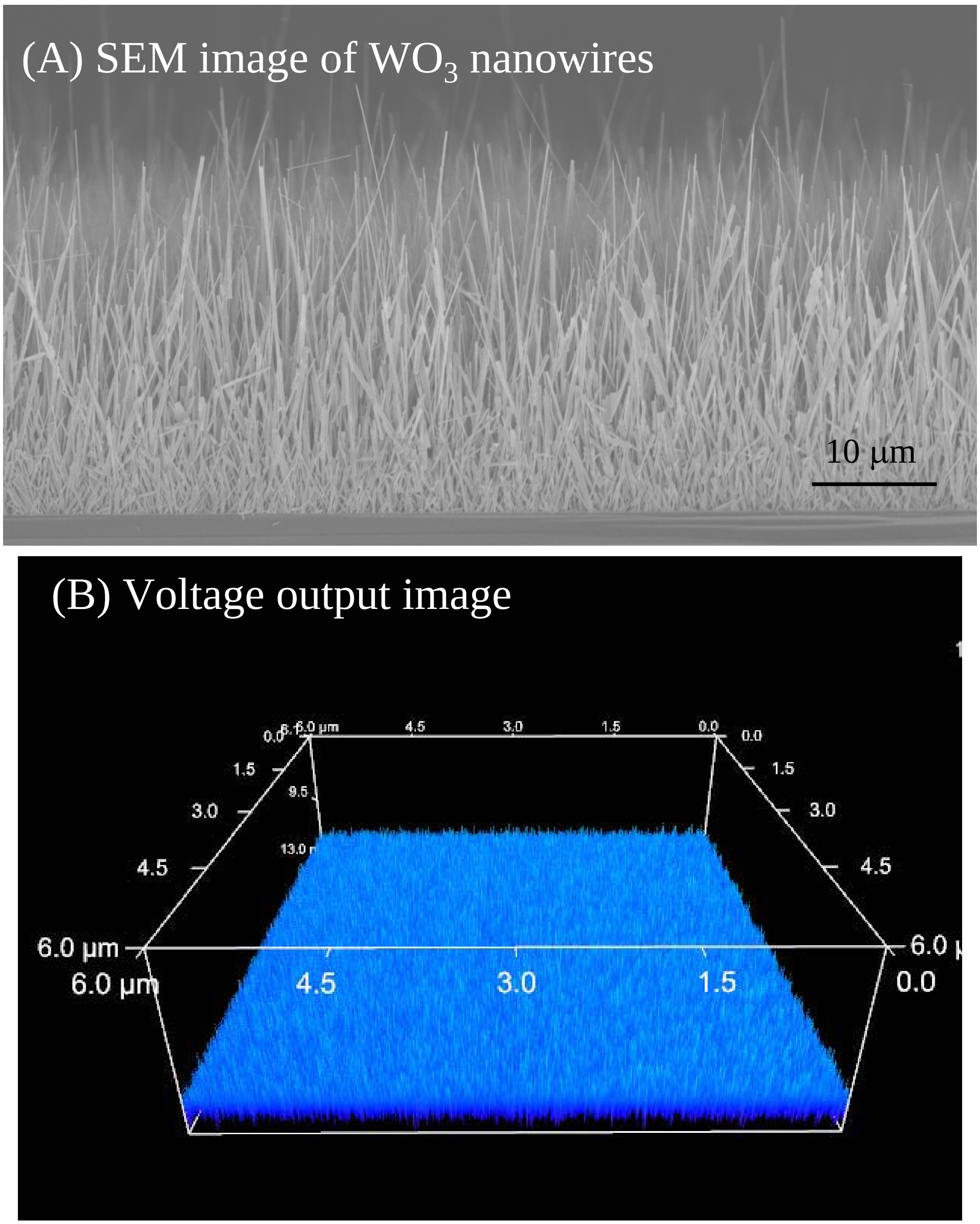


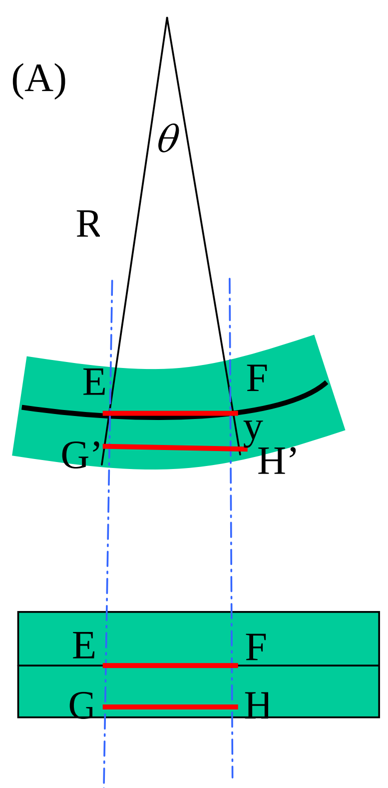
Table S1: The efficiency of converting elastic deformation energy into piezoelectric energy. The Young's modulus of ZnO NWs is 29 GPa (J.H. Song, X.D. Wang, E. Riedo and Z. L. Wang, *Nano Letters*, **5**, 1954 (2005).); piezoelectric coefficient 10 pm/V, NW size 60 nm.

NW	NW length (m)	Max. Bending ym (m)	Max. output voltage V0 (V)	Voltage peak width (s)	Elastic Def. Energy (J)	Piezoelectric energy (J)	Efficiencey of energy conversion (%)
1	**5.60E-08**	**6.66E-08**	**0.0085449**	**2.42E-03**	**1.53E-13**	**1.76437E-16**	**1.93E+01**
2	**1.15E-07**	**1.49E-07**	**0.0085449**	**1.21E-03**	**8.67E-14**	**8.82209E-17**	**1.70E+01**
3	**1.47E-07**	**8.80E-08**	**0.0018311**	**7.23E-03**	**1.46E-14**	**2.42357E-17**	**2.76E+01**
4	**1.08E-07**	**8.82E-08**	**0.0022888**	**7.23E-03**	**3.70E-14**	**3.78658E-17**	**1.70E+01**
5	**1.14E-07**	**1.39E-07**	**0.004425**	**7.23E-03**	**7.92E-14**	**1.41533E-16**	**2.98E+01**
6	**1.12E-07**	**8.54E-08**	**0.0030518**	**4.80E-03**	**3.12E-14**	**4.46956E-17**	**2.39E+01**

Analytical analysis of the bending induced piezoelectric voltage drop across a ZnO nanowire

For the following calculation, we consider the in-plane bending of a nanowire by an external point force F perpendicular to the nanowire. For a short segment of nanowire, the local bending can be approximated by a small arc characterized by a small angle θ and a local curvature of radius *R* (see Fig. S7), the local strain is

$$\varepsilon = \frac{H'G' - HG}{HG} = \frac{H'G' - HG}{EF} \approx \frac{(R+y)\theta - R\theta}{R\theta} = \frac{y}{R}$$



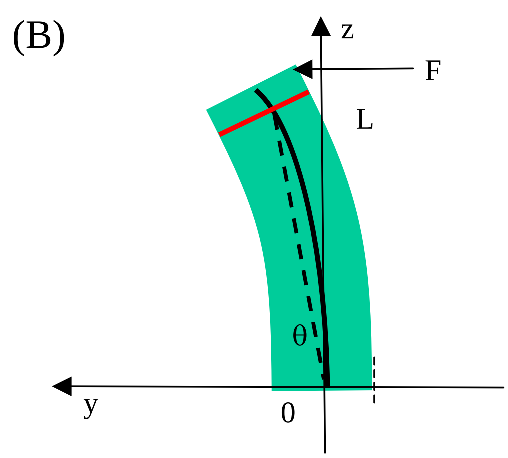


Fig. S7: (A) A segment of a nanowire for calculating the bending induced piezoelectric potential across the two side surfaces. (B) The definition of coordination system under an external displacement force F.

Using the stress and strain relationship, we have:

$$\sigma = Y\varepsilon = Y\frac{y}{R} \qquad \text{---------------------(1)}$$

where Y is the elastic modulus. In the static state of the system the moments are balanced. The total moment of the bent nanowire is

$$M = \int y \cdot \sigma \cdot dA$$

By using Eq. (1)

$$M = \int \frac{Y}{R} \cdot y^2 \cdot dA = \frac{Y}{R} \cdot \int y^2 \cdot dA = \frac{Y}{R} \cdot I$$

we have $$\frac{M}{I} = \frac{Y}{R} = \frac{\sigma}{y} \qquad \text{-----------------(2)}$$

From the geometry shown in Fig. S7(B), we have the following results under small angle approximation:

$$\frac{dy}{dz} = \tan\theta \approx \theta \qquad \text{thus} \qquad \frac{1}{R} = \frac{d\theta}{ds} \approx \frac{d\theta}{dz} = \frac{d}{dz}\left(\frac{dy}{dz}\right) = \frac{d^2 y}{dz^2}$$

In combining with Eq. (2),

$$\frac{1}{R} = \frac{M}{YI} = \frac{d^2 y}{dz^2} \qquad d\theta = \frac{1}{R} \cdot dz = \frac{M}{YI} \cdot dz \quad \text{-----------------(3)}$$

By the principle of balancing of moment: internal moment = external moment

$$M = YI \frac{d^2 y}{dz^2} = F \cdot (L - z) \quad \Rightarrow \quad \frac{d^2 y}{dz^2} = \frac{M}{YI} = \frac{F \cdot (L - z)}{YI} \quad \text{--------------(4)}$$

where the external force is assumed to act approximately perpendicular to the nanowire at the top and L is the nanowire length. Equation (4) determines the bending of the nanowire under the deflection of an external force at the front end.

Appendix 1: Piezoelectric induced potential

Now we calculate the potential produced by piezoelectric effect. From the definition of the piezoelectric coefficient (d): $d = \frac{\varepsilon}{E}$, the corresponding electric field along z-axis is

$$E_z = \frac{\varepsilon}{d} = \frac{y}{d \cdot R} \qquad \text{-------------- (5)}$$

Equation (5) is given by ignoring local polarization (or dielectric screening) for simplification of the analytical derivation.

For simplicity of analytical calculation and to illustrate the physical principle, we consider the potential at the side surface $y = a$ along the entire length of the nanowire:

$$E_z = \frac{a}{d \cdot R} \qquad \text{--------------(6)}$$

$$V = \int E \cdot ds = \int \frac{a}{d} \cdot \frac{1}{R} \cdot ds = \frac{a}{d} \cdot \int \frac{1}{R} \cdot ds = \frac{a}{d} \cdot \int d\theta \quad \text{--------------} \ (7)$$

Using Eqs. (3) and (4), Eq. (7) gives

$$V = \frac{a}{d} \int \frac{M}{YI} \cdot dz = \frac{a}{d} \int \frac{F \cdot (L - z)}{YI} \cdot dz = \frac{aF}{dYI} \int_0^L (L - z) \cdot dz = \frac{aFL^2}{2dYI} \quad \text{--------------} \ (8)$$

Together with the relationship between the maximum deflection y_m and the applied force: $F = \frac{3YIy_m}{L^3}$ (see next section), we have the potential induced by piezoelectric effect:

$$V = \frac{3ay_m}{2Ld} \quad \text{--------------}(9)$$

It must be pointed out that this is a qualitative estimation of the potential induced by PZ effect for understanding the physical process. Numerical calculation with considering the boundary conditions and dielectric screening is required to get quantitative results.

Appendix 2: Deflection of the nanowire under external force

We now consider the deflection of the nanowire under an externally applied force F perpendicular to the nanowire. From Equation (4) and boundary conditions:

$$y(z=0) = 0\,; \ \frac{dy(z=0)}{dz} = 0\,. \quad \text{--------------} \ (10)$$

Under small deflection and assuming that F is constant, integrating Eq. (4) gives

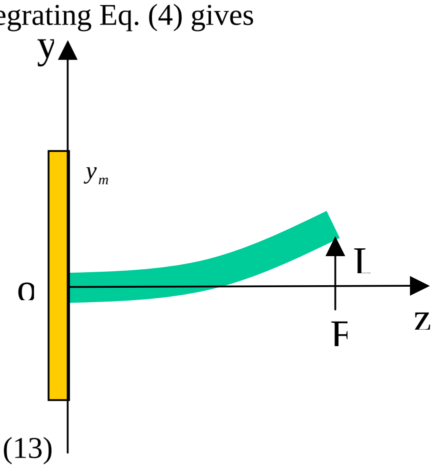
$$\frac{dy}{dz} = \frac{F}{YI}(Lz - \frac{1}{2}z^2) \quad \text{--------------} \ (11)$$

and

$$y = \frac{F}{YI}(\frac{1}{2}Lz^2 - \frac{1}{6}z^3)\,\mathrm{z} \quad \text{--------------} \ (12)$$

For $z = L$, $y = y_m$

$$y_m = \frac{FL^3}{3YI} \quad \Rightarrow \quad F = \frac{3YIy_m}{L^3} \quad \text{--------------} \ (13)$$

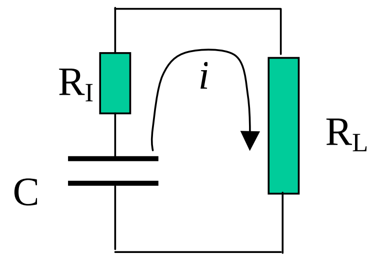


The mechanical work done by the external force for bending of the nanowire:

$$W = \int \vec{F} \cdot d\vec{l} = \int_0^{y_m} F(y)dy = \int_0^{y_m} \frac{3YI}{L^3} \cdot y \cdot dy = \frac{3YI}{2L^3} y_m^2 \quad \text{-------------- (14)}$$

Appendix 3: Discharge of an RC circuit

As shown in the diagram on the right-hand side:



$$\frac{1}{C}\int i \cdot dt + (R_L + R_I) \cdot i = 0 \quad \text{-------------- (15)}$$

$$\frac{i}{C} + (R_L + R_I)\frac{di}{dt} = 0 \quad \text{-------------- (16)}$$

$$i = I_0 \cdot e^{-\frac{t}{(R_L + R_I)C}} \quad \text{-------------- (17)}$$

For initial condition: $t = 0$, $i = \dfrac{V_0}{R_L + R_I}$, we have

$$i = \frac{V_0}{R + r} \cdot e^{-\frac{t}{(R_L + R_I)C}} \quad \text{-------------- (18)}$$

The decay time constant $\tau = (R_L + R_I)C$

The electric power consumed by the resistor R (the output work):

$$\begin{aligned}\Delta W_{PZD} &= \int i^2 R \cdot dt \\ &= \frac{V_0^{\,2} R_L}{(R_L + R_I)^2} \int_0^{\infty} e^{-\frac{2t}{(R_L + R_I)C}} \cdot dt \\ &= \frac{V_0^{\,2} R_L C}{2(R_L + R_I)}\end{aligned}$$

For $R_I << R_L$

$$\Delta W_{PZD} \approx \frac{V^2{}_0 C}{2} \quad \text{-------------- (19)}$$

Appendix 4: The elastic deformation energy of the nanowire dissipated in the first cycle of the resonance

To calculate the energy loss after a single cycle of vibration, we assume that the amplitude of the nanowire resonance decays with time as described by:

$$y_m = y_{mo} e^{-t/t_0} \quad \text{-------------- (20)}$$

where y_{mo} is the maximum deflection pushed by the AFM tip, and t_o is the decay constant of the vibration amplitude. Therefore, the elastic energy at a subsequent vibration from Eq. (14) is

$$W_{ELD} = \frac{3YI}{2L^3} y_m^2 = \frac{3YI}{2L^3} y_{m0}^2 \cdot e^{-2t/t_o} \quad \text{-------------- (21)}$$

The energy dissipated after one cycle of vibration is

$$\Delta W_{ELD} = \frac{3YI}{t_0 L^3} y_{m0}^2 \cdot e^{-2t/t_o} \cdot \Delta t \quad \text{-------------- (22)}$$

First the cycle: $t = 0$ and $\Delta t = \dfrac{1}{f}$:

$$\Delta W_{ELD} = \frac{3YI}{t_0 L^3} y_{m0}^2 \cdot \frac{1}{f} \quad \text{-------------- (23)}$$

Under the first order approximation (R.P. Gao, Z.L. Wang*, Z.G. Bai, W. de Heer, L. Dai and M. Gao, Phys. Rev. Letts., 85 (2000) 622-655), the life time of the resonance t_o is related to the quality factor Q and resonance frequency f by

$$t_0 \approx \frac{\sqrt{3}Q}{\pi f} \quad \text{-------------- (24)}$$

Therefore

$$\Delta W_{ELD} = \frac{3YI}{2L^3} y_{m0}^2 \cdot \frac{2\pi}{Q\sqrt{3}} = W_{\max} \cdot \frac{2\pi}{Q\sqrt{3}} \quad \text{-------------- (25)}$$

For ZnO nanobelts in a vacuum of 10^{-7} torr, $Q = 600$ (X.D. Bai, P.X. Gao, Z.L. Wang and E.G. Wang, *Appl. Phys. Letts*., **82**, 4806 (2003)), the efficiency of energy transform by the NW is $\Delta W_{PZD} / \Delta W_{ELD}$.