

Simulation study on piezoelectric characteristics of two-dimensional ZnO nanodiscs

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Two-dimensional (2D) zinc oxide (ZnO) nanostructures have emerged as an attractive approach for constructing high-performance piezoelectric nanogenerators (NGs) because of their high rate of surface area to volume and good mechanical durability for applications in energy conversion devices. However, there has been to date no comprehensive study on piezoelectric characteristics of 2D ZnO nanostructures. In this paper, 2D nanodiscs have been prepared by aqueous solution method on flexible indium tin oxide coated polyethylene terephthalate substrates. Also, the piezoelectric characteristics are statistically demonstrated and analysed on the as-grown 2D ZnO nanodiscs by applying different external force with the finite element method (COMSOL Multiphysics). Besides, the size-dependent simulation analysis of piezopotentials is also conducted for further optimising output performance of NGs based on 2D ZnO nanostructures. Also, the simulation will provide a guideline for designing high-performance piezo-nanodevices.

1. Introduction: With the rapid development of electronic technology, a large variety of electronic products and portable electronic devices have drawn a great influence in our daily lives [1–4]. Harvesting energy from the environment is highly important for the sustainable operation of these electronic devices [5, 6]. Mechanical energy is the most ubiquitous and abundant energy source in our living environment regardless of weather or temperature conditions that can be readily collected and converted into electricity in contrast with solar and thermoelectric energies [7]. Compared with traditional technologies of harvesting mechanical energy, energy harvesting technologies based on the piezoelectric effect, called as nanogenerators (NGs), have been developed to convert random mechanical energy (such as human movement, light wind, and heart beating) to electricity, which is highly expected to realise self-powered micro/nanosystems [8–13].

Over the past few years, researchers have made valid progress in NGs by using various kinds of piezoelectric materials, such as zinc oxide (ZnO), gallium nitride, cadmium sulphide, lead zirconate titanate and barium titanate [8, 14–18]. Among these materials, ZnO has been recognised as the potential material for piezoelectric NGs due to the desirable semiconducting, piezoelectric and environmental-friendly properties. Recently, there have been many reports on the fabrication of ZnO NGs based on one-dimensional (1D) ZnO, such as nanorods and nanowires [19–21]. Also, 2D ZnO nanostructures, such as nanosheets or nanodiscs (NDs), are emerging as important nanostructures for constructing high-performance NGs because of their high rate of surface area to volume and good mechanical durability for applications in energy conversion devices [22–24]. Although 2D ZnO nanostructures have been synthesised for constructing piezoelectric NGs, there has been to date no comprehensive study on piezoelectric characteristics of 2D nanostructures.

In this Letter, we use the finite element method (FEM, COMSOL) simulations for estimating the piezoelectric characteristics of 2D disc-shaped ZnO nanostructures. The piezoelectric characteristics are statistically demonstrated and analysed on the ZnO NDs by applying external force along with three different directions. Besides, the size-dependent simulation analysis of piezopotentials is also conducted for further optimising output

performance of NGs based on 2D ZnO nanostructures. Also, the simulation will provide a guideline for designing high-performance piezo-nanodevices.

2. Experimental procedure

2.1. Growth of ZnO seed layer on indium tin oxide coated polyethylene terephthalate (ITO-PET) substrate: ITO-PET substrates (with the desired sized of $1 \times 1 \text{ cm}^2$) were first deposited with thin ZnO seed layer by room temperature radio frequency (RF) magnetron sputtering after being cleaned ultrasonically in acetone, ethanol, and then deionised water in order. The background pressure of the vacuum chamber was $1 \times 10^{-4} \text{ Pa}$, argon was utilised as a sputtering gas with a pressure of 3.5 Pa at room temperature, and the RF power is set as 180 W.

2.2. Synthesis of 2D ZnO NDs: Then the aqueous solution method was utilised to realise the growth of 2D ZnO NDs. $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (98%) and $\text{C}_6\text{H}_{12}\text{N}_4$ (99%) were chosen as solutes for their adequate chemical properties. The precursor solution was prepared by mixing 329.25 mg of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ powder and 210.279 mg of $\text{C}_6\text{H}_{12}\text{N}_4$ powder, with a mole ratio of 1:1, and diluted the mixture with deionised water until its volume reached 50 ml. The concentration was set as 30 mM. Then the as-prepared ZnO seed coated substrates were vertically immersed in a precursor solution in a sealed kettle for the growing process. The growth temperature was maintained at 95°C for 3 h in a baking oven. After the reaction, the substrates were removed from the solution, rinsed with deionised water, and dried.

3. Results and discussion: Fig. 1a is the typical scanning electron microscopy (SEM) image of as-grown ZnO NDs on ITO-PET substrates, which can be synthesised using a low-temperature hydrothermal method. It reveals that the ZnO NDs are hexagonal shaped dispersed onto the substrate. The typical diameter of the as-grown products is in the range of 300–800 nm and 100–200 nm in thickness. In our experiments, it is found that the size of NDs could be adjusted by controlling the reaction conditions (solution concentration, growth time as well as growth temperature). Besides this, from these SEM images, we can also find that the NDs have two growing modes. One part of NDs lies flat on

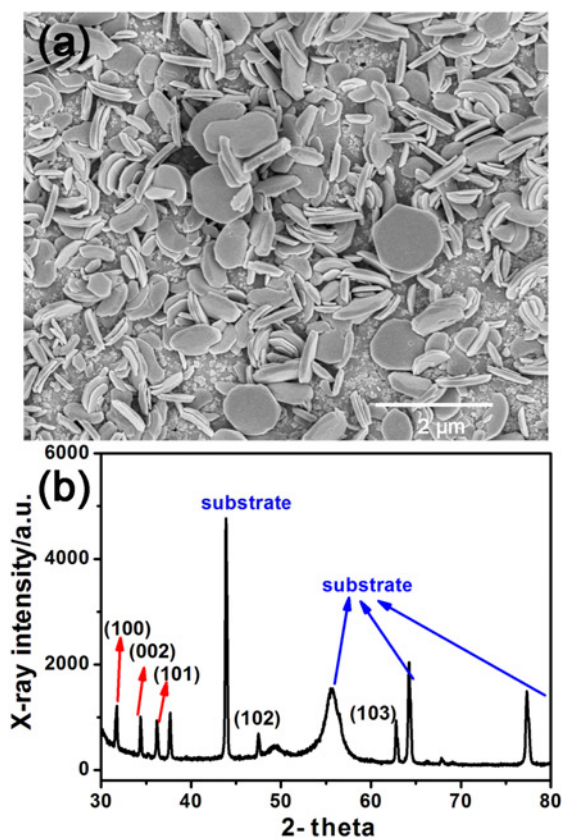


Fig. 1 SEM and XRD characterisation of ZnO NDs on ITO-PET substrate
a Typical SEM image of ZnO NDs grown on ITO-PET substrates by low-temperature hydrothermal method
b XRD pattern of as-grown ZnO NDs on ITO-PET substrate

the substrate, in which case the axis of NDs is vertically on the ITO-PET substrate. Also, the other part of NDs is vertically staggered with the axis parallel to the substrate. From the X-ray diffraction (XRD) pattern shown in Fig. 1*b*, we can see that most diffraction peaks, such as (100), (002), (101), (102) and (103) are in good agreement with the peaks of the ZnO crystal recorded in the XRD standard card, which indicates that our products have the basic features of ZnO crystals. Besides, the intensity of the ZnO diffraction peak (002) is not strong, showing that not all the as-synthesised ZnO NDs are grown along the *c*-axis direction.

According to the previous report, the direction of force would exert great influence on the magnitude and distribution of the potential and, therefore, it is necessary to classify different force modes applied to ZnO NDs. In order to make the subsequent explanation much clearer, we defined the three different force modes applied to ZnO NDs as shown in Fig. 2. Herein, we only consider three possible force modes: **F1**, **F2**, and **F3** as follows:

F1 is the vertical force along the axial direction of a ND, which is fixed at one end (bottom side) and the force is perpendicular to the upper surface along the $-z$ -axis; **F2** is the radial force along the $-x$ -axis, in which simulation, the left of 1/4 circumference boundary is fixed and radial force is on the right of 1/4 circumferential boundary along the $-x$ -axis). **F3** is a lateral bending force in which simulation the left of 1/4 circumference boundary is fixed and the corresponding bending force is exerting on the right of 1/4 circumference boundary along the $-z$ -axis. It needs to be noted that we take the magnitude of the piezopotential for ($V_{\max} - V_{\min}$). Then, on the one hand, we discuss under the Cartesian coordinate system, and part of the disc was fixed and electrically grounded. For simplicity of the calculation, ZnO NDs

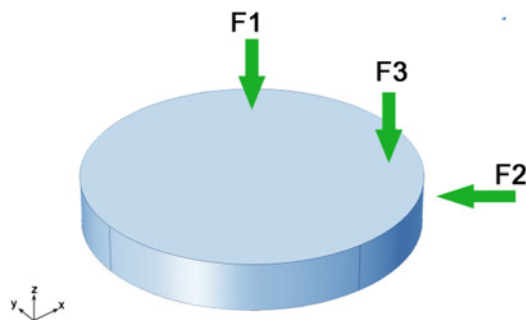


Fig. 2 Three different force modes applied to ZnO NDs

are assumed to be intrinsic and the hexagonal prisms of NDs can be considered as a cylinder. Furthermore, the Lippman theory is utilised to calculate the piezopotential distribution in a bent ZnO ND [25].

The material's constants used in the calculation including: anisotropic elastic constants of ZnO: $c_{11}=207$ GPa, $c_{12}=117.7$ GPa, $c_{13}=106.1$ GPa, $c_{33}=209.5$ GPa, $c_{44}=44.8$ GPa, $c_{55}=44.6$ GPa; and piezoelectric constants: $e_{15}=0.45$ C/m², $e_{31}=0.51$ C/m², $e_{33}=1.22$ C/m². Relative dielectric constants: $k_{\perp}=7.77$, $k_{\parallel}=8.91$, respectively. Also, the dimensions of the NDs used in our calculation are as follows: the radius, *r*, and length, *l*, for ZnO NDs, equal to 200 and 150 nm, respectively. Also, the external force is set to be $f=442$ nN.

Displacement and calculated piezoelectric potential distribution in the ZnO ND under three different force modes are revealed and viewed from the side (Figs. 3*a*, *c*, and *e*) and the oblique view of the ND. Fig. 3*b* presents the calculated piezopotential distributions when in the compressed ZnO ND when an external force is along the $-z$ -axial direction. According to the previous reports, the negative potential and positive potential are created along the top and bottom sides of NDs, respectively [26, 27]. Also, in this case, the calculated potential difference is -7.99 mV. When the ND suffers from a radial force along the

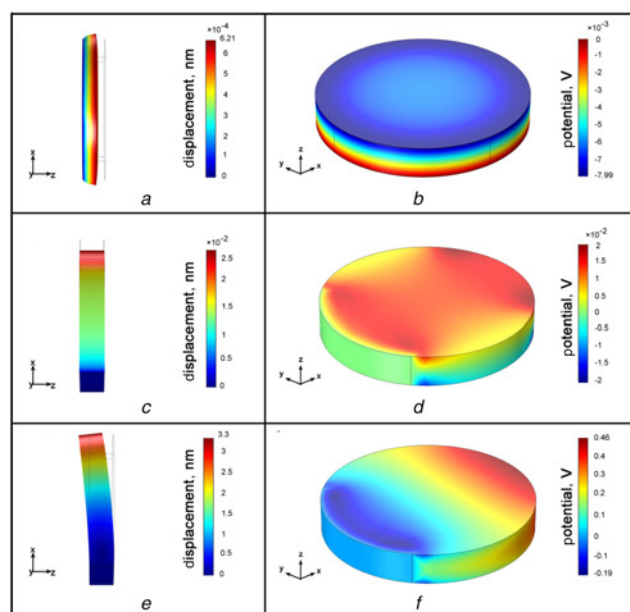


Fig. 3 Displacement and calculated piezoelectric potential distribution for a ZnO ND under three different force modes
a, *b* Vertical force
c, *d* Radial force
e, *f* Lateral bending force

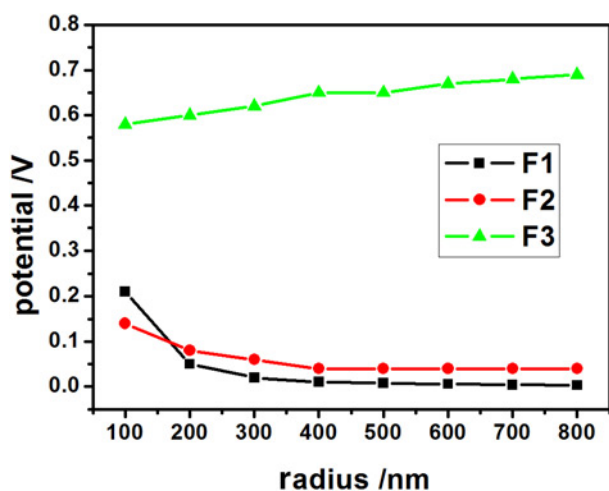


Fig. 4 Relationship between disc radius and piezoelectric potential (black curve shows the relationship between the radius of the disc and the piezoelectric potential under the vertical pressure (F1), red curve shows the relationship between the disc radius and the piezoelectric potential under radial force (F2), green curve shows the relationship between the disc radius and the piezoelectric potential under lateral bending force (F3))

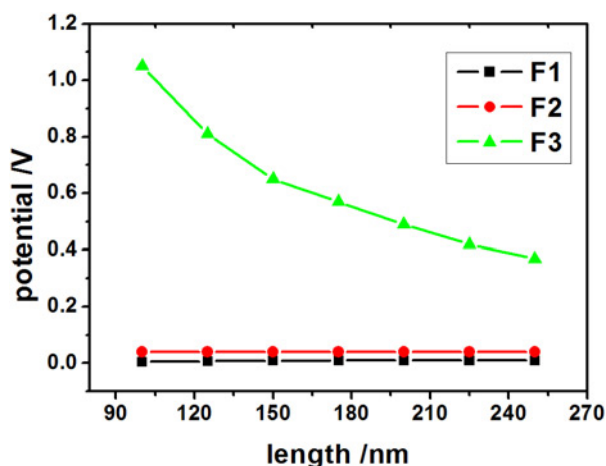


Fig. 5 Relationship between length and piezoelectric potential (black curve shows the relationship between the length of the disc and the piezoelectric potential under the vertical pressure (F1), red curve shows the relationship between the length and the piezoelectric potential under radial force (F2), green curve shows the relationship between the length and the piezoelectric potential under lateral bending force (F3))

– x -axis or lateral bending force along the – z -axis direction, the force will also cause the deformation of ZnO ND, which also contributes to piezopotential along the z -direction as shown in Figs. 3d and f. Also, the potential difference is about 40 and 650 mV, respectively. It can be seen that the maximum piezoelectric potential is generated when the ZnO NDs are subjected to the lateral bending force along the – z -axis.

In order to study the influence of the disc radius on the piezopotential, the ZnO NDs with different disc radii have been calculated. According to repeated experiments and lots of reports, we found that the typical disc radius is ~300–800 nm. The thickness we chose is 150 nm, and the piezoelectric potential versus the radius of the disc is plotted in Fig. 4. It can be seen that the piezoelectric potential increases linearly with the increase of disc radius under lateral bending force (F3). While under the radial force (F2) and vertical pressure (F1), the piezoelectric potential decreases with an increase in the radius of the disc. In addition, the potential obtained under lateral bending force (F3) is approximately ten

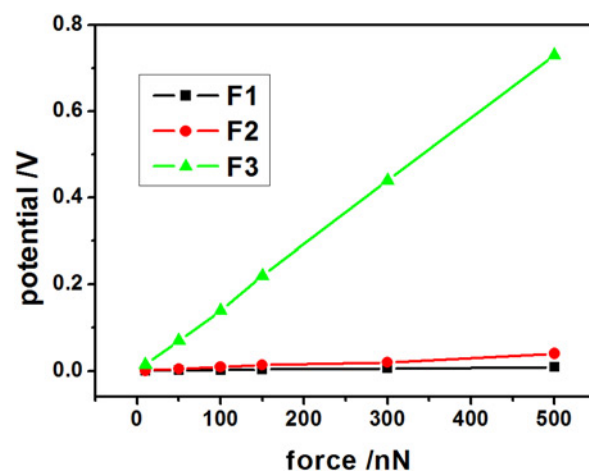


Fig. 6 Relationship between force modes and piezoelectric potential (black curve shows the relationship between the piezoelectric potential and vertical pressure (F1), red curve shows the relationship between the piezoelectric potential and radial force (F2), green curve shows the relationship between the piezoelectric potential and lateral bending force (F3))

times as large as that of lateral bending force (F2) and vertical pressure (F1).

Fig. 5 shows the piezoelectric potential of ZnO NDs at the function of the thickness of disc under the same external force of 442 nN, but with different force directions (F1, F2, and F3). Here, we took the 500 nm radius of the disc for further simulation. Also, the typical disc thickness ranges from 100 to 200 nm. For the same radius (500 nm) of ZnO NDs, the piezoelectric potential is almost invariant with the enhancing of thickness under vertical pressure (F1) and radial force (F2); however, for the case of lateral bending force (F3) the piezoelectric potential decreases with increasing thickness. It is therefore concluded that a larger radius and thinner thickness of ZnO ND might be more favourable for larger piezoelectric potentials.

Previous reports have shown that the piezoelectric potential is related to the external force directions. Here, further research is done to study the piezoelectric potential as a function of various forces of 0–500 nN. For the same radius (500 nm) and thickness (150 nm), the piezoelectric potential is positively related to the magnitude of the external force as shown in Fig. 6. Also, in the case of lateral bending force, the change is more severe and the resulting piezoelectric potential is greater.

4. Conclusion: In summary, 2D NDs were prepared by an aqueous solution method on flexible ITO-PET substrates. Also, we studied the piezoelectric characteristics of 2D ZnO NDs with the FEM (COMSOL Multiphysics). Comparing different force modes, we found that higher potentials can be generated when the NDs are suffering from lateral bending force (along the – z -axis). In addition, we studied the relationship between the geometric shape and the piezoelectric potential for the lateral pressure, finding the larger the radius and the smaller the thickness are, the greater the potential will be. Our results can provide guidelines for fabricating high-performance piezo-devices based on 2D ZnO nanodiscs for NGs, piezotronics, and piezo-phototronics.

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6 References

- [1] Mannsfeld S.C., Tee B.C., Stoltenberg R.M., *ET AL.*: 'Highly sensitive flexible pressure sensors with microstructured rubber dielectric layers', *Nature Mater.*, 2010, **9**, (10), pp. 859–864
- [2] Kang D., Pikhitsa P.V., Choi Y.W., *ET AL.*: 'Ultrasensitive mechanical crack-based sensor inspired by the spider sensory system', *Nature*, 2015, **516**, (7530), pp. 222–226
- [3] Jeong J.W., Yeo W.H., Akhtar A., *ET AL.*: 'Materials and optimized designs for human-machine interfaces via epidermal electronics', *Adv. Mater.*, 2013, **25**, (47), pp. 6776–6776
- [4] Pang C., Lee G.Y., Kim T., *ET AL.*: 'A flexible and highly sensitive strain-gauge sensor using reversible interlocking of nanofibres', *Nature Mater.*, 2012, **11**, (9), pp. 795–801
- [5] Lee M., Bae J., Lee J., *ET AL.*: 'Self-powered environmental sensor system driven by nanogenerators', *Energy Environ. Sci.*, 2011, **4**, (9), pp. 3359–3363
- [6] Wang X., Gao Y., Wei Y., *ET AL.*: 'Output of an ultrasonic wave-driven nanogenerator in a confined tube', *Nano Res.*, 2009, **2**, (3), pp. 177–182
- [7] Dresselhaus M.S., Thomas I.L.: 'Overview alternative energy technologies', *Nature*, 2001, **414**, (6861), pp. 332–337
- [8] Wang Z.L., Song J.: 'Piezoelectric nanogenerators based on zinc oxide nanowire arrays', *Science*, 2006, **312**, (5771), pp. 242–246
- [9] Wang X., Song J., Liu J., *ET AL.*: 'Direct-current nanogenerator driven by ultrasonic waves', *Science*, 2007, **316**, (5821), pp. 102–105
- [10] Hu Y., Wang Z.L.: 'Recent progress in piezoelectric nanogenerators as a sustainable power source in self-powered systems and active sensors', *Nano Energy*, 2015, **14**, pp. 3–14
- [11] Wang Z.L.: 'Towards self-powered nanosystems: from nanogenerators to nanopiezotronics', *Adv. Funct. Mater.*, 2010, **18**, (22), pp. 3553–3567
- [12] Fan F.R., Lin L., Zhu G., *ET AL.*: 'Transparent triboelectric nanogenerators and self-powered pressure sensors based on micro-patterned plastic films', *Nano Lett.*, 2012, **12**, (6), p. 3109
- [13] Yang Y., Guo W., Pradel K.C., *ET AL.*: 'Pyroelectric nanogenerators for harvesting thermoelectric energy', *Nano Lett.*, 2012, **12**, (6), p. 2833
- [14] Choi M., Murillo G., Hwang S., *ET AL.*: 'Mechanical and electrical characterization of PVDF-ZnO hybrid structure for application to nanogenerator', *Nano Energy*, 2017, **33**, pp. 462–468
- [15] Lin L., Lai C. H., Hu Y., *ET AL.*: 'High output nanogenerator based on assembly of GaN nanowires', *Nanotechnology*, 2011, **22**, (47), p. 475401
- [16] Ni X., Wang F., Lin A., *ET AL.*: 'Flexible nanogenerator based on single BaTiO₃ nanowire', *Sci. Adv. Mater.*, 2013, **5**, (11), pp. 1781–1787
- [17] Cha S., Kim S.M., Kim H., *ET AL.*: 'Porous PVDF as effective sonic wave driven nanogenerators', *Nano Lett.*, 2011, **11**, (12), pp. 5142–5147
- [18] Lin Y.F., Song J., Ding Y., *ET AL.*: 'Alternating the output of a CdS nanowire nanogenerator by a white-light-stimulated optoelectronic effect', *Adv. Mater.*, 2008, **20**, (16), pp. 3127–3130
- [19] Xue X., Nie Y., He B., *ET AL.*: 'Surface free-carrier screening effect on the output of a ZnO nanowire nanogenerator and its potential as a self-powered active gas sensor', *Nanotechnology*, 2013, **24**, (22), p. 225501
- [20] Zhu G., Yang R., Wang S., *ET AL.*: 'Flexible high-output nanogenerator based on lateral ZnO nanowire array', *Nano Lett.*, 2010, **10**, (8), p. 3151
- [21] Yang D., Qiu Y., Jiang Q., *ET AL.*: 'Patterned growth of ZnO nanowires on flexible substrates for enhanced performance of flexible piezoelectric nanogenerators', *Appl. Phys. Lett.*, 2017, **110**, (6), p. 063901
- [22] Shin S.H., Kwon Y.H., Lee M.H., *ET AL.*: 'A vanadium-doped ZnO nanosheets-polymer composite for flexible piezoelectric nanogenerators', *Nanoscale*, 2015, **8**, (3), pp. 1314–1321
- [23] Zhang R., Hummelgård M., Olsen M., *ET AL.*: 'Nanogenerator made of ZnO nanosheet networks', *Semicond. Sci. Technol.*, 2017, **32**, (5), p. 054002
- [24] Gupta M.K., Lee J.H., Lee K.Y., *ET AL.*: 'Two-dimensional vanadium-doped ZnO nanosheet-based flexible direct current nanogenerator', *ACS Nano*, 2013, **7**, (10), pp. 8932–8939
- [25] Gao Y., Wang Z.L.: 'Equilibrium potential of free charge carriers in a bent piezoelectric semiconductive nanowire', *Nano Lett.*, 2009, **9**, (3), p. 1103
- [26] Fang X.Q., Liu J.X., Gupta V.: 'Fundamental formulations and recent achievements in piezoelectric nano-structures: a review', *Nanoscale*, 2013, **5**, (5), pp. 1716–1726
- [27] Hinchet R., Lee S., Ardila G., *ET AL.*: 'Performance optimization of vertical nanowire-based piezoelectric nanogenerators', *Adv. Funct. Mater.*, 2014, **24**, (7), pp. 971–977