ZnO Nanorod From Structure, Properties to Applications

Zhiyuan Ji

WLSA Shanghai Academy, Shanghai, 200243, China

Abstract. This paper aims to review current understandings of ZnO Nanorods (NRs) and summarizes them into a clear pathway from structure to properties and to applications. The crystal structure of ZnO NRs is a hexagonal wurtzite structure with asymmetry giving rise to its prominent piezoelectric property. Using methods such as AFM, researchers have confirmed and modeled the piezoelectric potential generated by ZnO NRs in deformation, and the intensity of the potential is strongly correlated with resistivity and dimensions of NRs. Several techniques, such as doping, are invented to enhance the piezoelectric intensity of ZnO NRs, suppressing the screening effect of ZnO NRs. Recent research has shown potential applications based on the piezoelectric property of ZnO NRs or nanowires (NWs) as nanogenerators (NGs) or nanosensors for self-powered devices in a range of areas.

Keywords: ZnO Nanorods, piezoelectricity, nanogenerator.

1. Introduction

There is an increasing number of reviews on ZnO nanomaterials (ZnO NMs) because of their wide range of properties based on doping, possessing high transparency, a range of conductivity, wide band gap, and notably piezoelectricity [8]. Various ways are suitable for growing ZnO NMs, although they might differ in cost and quality. Many papers may have demonstrated a precise understanding of a particular property of ZnO NMs but seldom emphasizes the connection within the pathway. Also, many edging applications on the properties of ZnO NRs might be neglected. This paper aims to clearly state how the structure of ZnO NRs leads to the piezoelectric property which paves the way for many applications.

2. The Structure of ZnO Crystal

There are two main types of zinc oxide crystal structures: cubic zinc-blende and hexagonal wurtzite structures. The hexagonal wurtzite structure exists in ambient temperature and pressure and is widely studied [1]. The hexagonal wurtzite structure could be seen as tetrahedral shapes inlaid with each other. Each zinc ion forms the tetrahedral geometry with four oxide ions and vice versa (Fig. 1). This structure possesses a net charge of zero, due to the coincidence of the center of mass of anions and cations in the absence of stress. When stress is exerted upon the structure, polarization of charges on the surface of the ZnO structure occurs; it is known as the piezoelectric property.

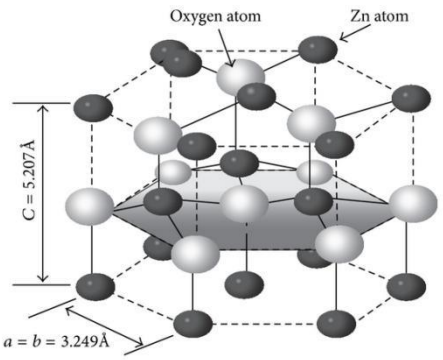


Fig. 1. Crystal structure of zinc oxide NPs [12].

3. The Pieozoelectric Property of ZnO Nanorods

The piezoelectric property of ZnO materials is due to the polarization at the atomic scale. When mechanical stress is exerted on ZnO crystal, the elongation or contraction causes a separation of the center of mass of cations and anions.

3.1. The Growth Method of ZnO Nanorods

The piezoelectric property of ZnO NRs is heavily related to the method of synthesis. There are three main methods: chemical vapor deposition (CVD), hydrothermal, and electrochemical deposition, each presents its strength and weakness [2]. The CVD method with a relatively high synthesis temperature can readily synthesize vertically grown ZnO NR along the [0001] direction with high crystal quality [4]. However, the drawbacks are high costs and high synthesis temperature deforming polymeric substrates. Alternatively, the hydrothermal and electrochemical deposition approaches are both two step-process with relatively low synthesis temperatures allowing flexible substrates. Consequently, the low synthesis temperature had a hard time assuring good crystal quality ZnO NRs [2].

3.2. Basic Understandings of the Piezoelectric Effect

In the first study on piezoelectric ZnO NGs, Wang and Song investigated the piezoelectric properties of ZnO nanowires grown on the c-plane [5]. Using the AFM contact mode with a constant normal force of 5 nN between the tip and sample surface, they measured both the topography and voltage output of the nanowire arrays. When the tip of AFM is scanned over an individual nanowire and caused it to deform, a strain field is created (Fig. 2). The outer surface being stretched, havings a positive strain, and the inner surface being compressed, havings a negative strain. Thus, an electric field is created. Again, the electric potential created is based on the relative displacement of Zn2+ to O2- ions. Unless the strain is released, the ionic charges cannot freely move.

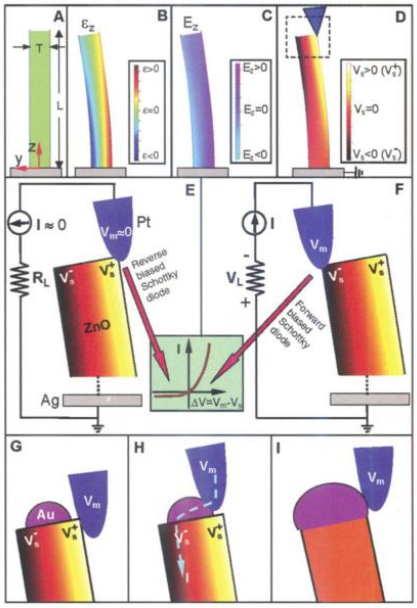


Fig. 2. Methodology to measure piezoelectric intensity by AFM. (A) Schematic definition of a NW and the coordination system. (B) Longitudinal strain distribution in the NW. (C) The corresponding longitudinal piezoelectrically induced electric field distribution in the NW. (D) Effects of the piezoelectricity on the potential field. (E and F) Contacts between the AFM tip and the sample at two reversed local contact potentials [5].

Furthermore, researchers found a strong correlation between individual NRs' resistivity and piezoelectric response [6]. Using AFM to measure the out-of-plane vibrations induced by single NR, they found variances in piezoelectric intensity among the ZnO rods grown at the same time on the

same sample. Calculating the resistivity of each NRs through their height and cross-sectional area, Scrymgeour and Julia graphed the relationship between the piezoelectric response and the resistivity of ZnO NRs (Fig. 3a).

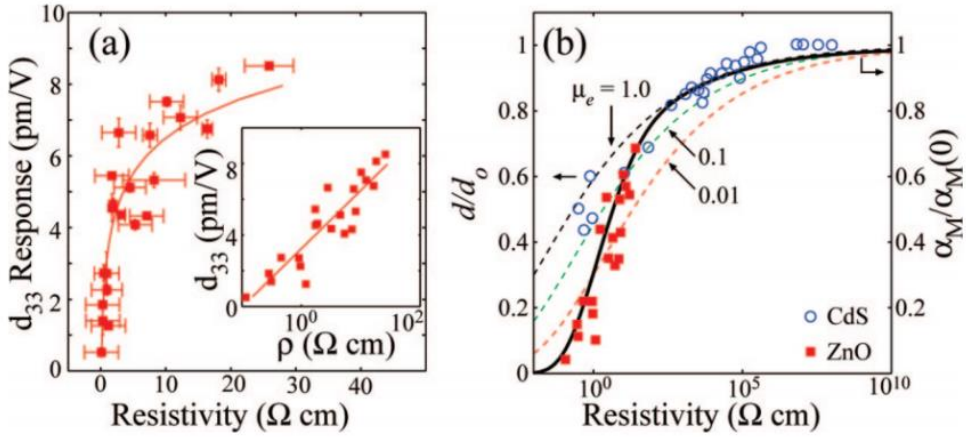


Fig. 3. (a) Correlation of resistivity to piezoelectric response in ZnO NRs. (b) Comparison between normalized data in (a) and CdS data (open blue circles) reported by Ogawa [13]. The dashed lines represent Madelung constant calculation corresponding to constant mobility on the right axis. The constant mobility of μ_e equals to 1.0 (black), 0.1 (green), and 0.01 cm^2/Vs (red). The solid line represents the calculated resistivity dependent mobility [6].

3.3. The Challenge and Solution of ZnO Pieozoelectric Performance.

Although evidence has shown the excellent performance of ZnO piezoelectric property, there remains a main problem: the screening effect. There are two types of screening effects that reduce the performance of ZnO NRs: internal and external screening effects. First, the internal screening effects have resulted from excess free charge carriers or crystal defects acting as donors [2]. Free electrons tend to balance the piezoelectric potential when they move to the positive potential area of the NRs. Thus, the stored electrons in this area would prevent the subsequent flow of electrons generated by the piezoelectric effect [2]. Second, the external screening effect has resulted from charge leakage through the metal-semiconductor interface to an external load [10].

There are multiple targets to overcome screening effects and enhance the performance of ZnO NRs: doping, areal density, surface treatment, interfacial modification, and a combination of the above techniques [2]. One recent research has argued doping can essentially improve piezoelectricity while approaches fail to reach the maximum piezoelectric performance [11]. This research team deduced that rear earth metal ions (RE3+) doped ZnO NMs could effectively reduce the screening effects, by regulating the free carriers, and substantially increase the piezoelectric performance 53.8% higher. Exogenous ions would switch with endogenous ions (Fig. 4a), potentially improving the electromechanical properties of ZnO NRs by either acting as holes (Fig. 4c) which can decrease the concentration of free carriers or forming more lattice defects (Fig. 4d) which limit the migration of free carriers [11]. The team investigated ZnO NRs doped by a series of RE ions, La3+, Ce3+, Pr3+, Sm3+, Eu3+, Gd3+, and Y3+, all having the same valence state but varied extranuclear electrons. Ultimately, the team characterizes its results through the feedback from the tip of piezoresponse force microscopy and the output of the ZnO-based piezoelectric NGs.

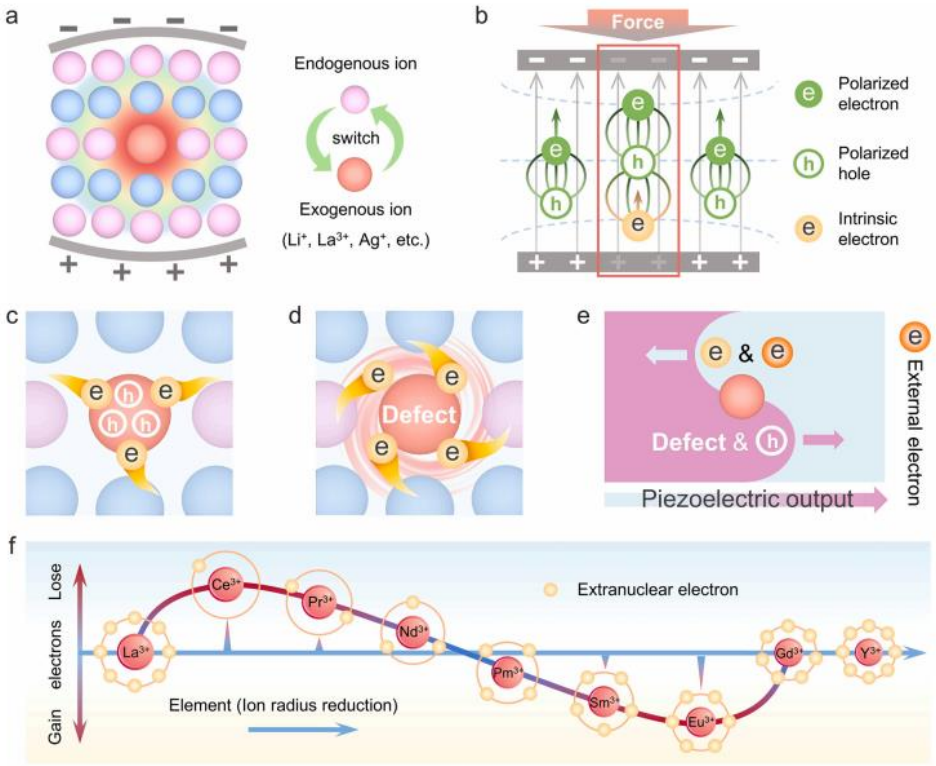


Fig. 4. (a) Illustrative diagram of ion-doped piezoelectric semiconductor. (b) Illustrative diagram of the internal screening effect model in ZnO NRs. (c) The suppression of screening effect by hole recombination. (d) The suppression of screening effect by defect binding. (e) Effect of doping on piezoelectric output. (f) Tendency of extranuclear electron gain-and-loss stability of RE ions [11].

4. Applications of ZnO Nanorods

4.1. Self-powered LCD Screen and Nano-sensors

Energy harvesting from the environment has been a crucial point for self-sustained energy resources. As electronic devices could be properly made in the size of nanoscales, they require much less power and energy than those of macroscopic size. By simply harvesting energy from mechanical vibrations in the environment, the small size electronic device could power itself without wires. By adopting the piezoelectric potential created by the deformation of ZnO NRs, Hu proved the feasibility of self-powered LCD screens or nano-sensors on bicycle tires [7]. They targeted the bending of bicycle tires as the trigger to induce the piezoelectric effect of ZnO nanomaterial: the position of touching or retouching the road quickly induces or withdraws the bending (Fig. 5a). The NG was designed to consist of five layers: a flexible polyester (PS) substrate, ZnO nanowire (NW) textured films on its top and bottom surfaces, and electrodes on the surfaces (Fig. 5c). The results of a single NG on a tire traveling a distance of 12 mm with an acceleration of 30 m s-2 were 1.5 V measured voltage and 25 nA, which was enough to power a commercial LCD screen. Furthermore, they showed the achievement of higher output voltage of two NGs connected in parallel than that of a single NG. Moreover, the device could also be a nano-sensor for pressure and speed which are positively correlated with the output voltage of the NGs.

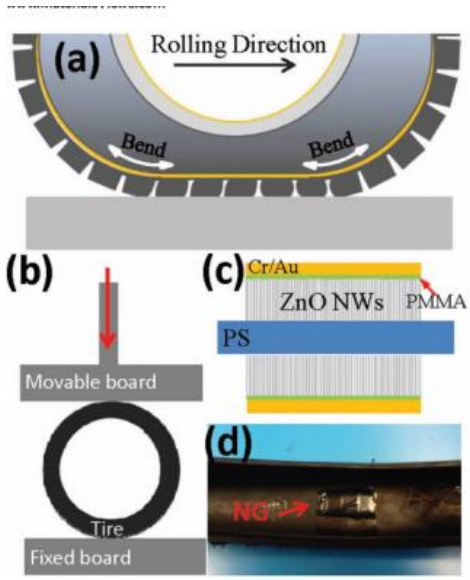


Fig. 5. (a) Deformation of the tire during the movement of the vehicle. (b) The experiment setup. The tire's deformation was simulated by catching the tire with two boards, one fixed and one movable. (c) The composition design of the NG. (d) The photograph that showed how NG is fixed on the inner surface of a tire [7].

4.2. Self-powered Photoelectrochemical Sensing Platform

Furthermore, Jiang et. al designed a new sensitive self-powered photoelectrochemical (PEC) sensing platform by integrating the piezoelectric effect with the localized surface plasmon resonance (LSPR) effect of ZnO-WO3-x [9]. It has two parts: a ZnO NRs-WO3-x/FTO photoanode and an aptamer for recognizing elements. The team first fabricated ZnO NRs array-modified FTO by hydrothermal method and then fabricated dWO3·H2O nanocomposite via a one-pot hydrothermal method. Using SEM, TEM, and XPS, the team was able to confirm the desired product ZnO-WO3-x. Then, the team confirmed the presence of oxygen vacancies in WO3-x nanosheets, which could extend the light absorption range and promote charge transfer. While the WO3-x portion excelled at absorbing a wide range of light, the ZnO NRs part shows piezoelectric properties for powering the system. Similarly in the previous application, the dipole moment is induced by the movement of Zn2+ and O2- positions. The difference is that the team chose the action of the fluid eddy, with adequate stirring in the experiment, to be the source of bending ZnO-WO3-x nanocomposite. Moreover, when the aptasensor reacted with ENR, the target for sensing, the output of electric power density significantly decreased, suggesting the success of the sensing system. The system was able to reach a consistent result in sensing Enrofloxacin in a sample of RuoYu Lake at Changzhou University [9].

5. Summary

This article reviewed the pathway from ZnO NRs structure to piezoelectric property to its application. Notably, ZnO NRs' piezoelectric properties are well-studied by many researchers. Although there remain some challenges to achieve the maximum pieozoelectric intensity of ZnO NRs, several methods such as doping could effectively enhance the performance, which proves ZnO NRs' feasibility in the field of piezo electronics. Further research may incorporate ZnO NRs, as the source of power, into nano-scale systems.

Acknowledgements

The authors gratefully acknowledge the academic teachings from Professor Jiang from National Center for Nanoscience and Technology, China.

References

[1] Barzinjy, A. A.; Hamad, S.; Azeez, H. Structure, Synthesis and Applications of ZnO Nanoparticles: A Review. ResearchGate. https://www.researchgate.net/publication/342347708_Structure_Synthesis_and_Applications_of_ZnO_Nanoparticles_A_Review.

[2] Le, A. D.; Mohsen Ahmadipour; Pung, S.-Y. A Review on ZnO-Based Piezoelectric Nanogenerators: Synthesis, Characterization Techniques, Performance Enhancement and Applications. 2020, 844, 156172–156172. https://doi.org/10.1016/j.jallcom.2020.156172.

[3] Lu, Y. J.; Shi, Z. F.; Shan, C. X.; Shen, D. Z. Chapter 4 - ZnO nanostructures and lasers. ScienceDirect. https://www.sciencedirect.com/science/article/abs/pii/B9780128141625000042?via%3Dihub (accessed 2023-07-13).

[4] Ghosh, M.; Rao, M. G. Growth Mechanism of ZnO Nanostructures for Ultra-High Piezoelectric D 33 Coefficient. Materials Express 2013, 3 (4), 319–327. https://doi.org/10.1166/mex.2013.1134.

[5] Wang, Z. L.; Song, J. Piezoelectric Nanogenerators Based on Zinc Oxide Nanowire Arrays. Science 2006, 312 (5771), 242–246.

[6] Scrymgeour, D.; Julia. Correlated Piezoelectric and Electrical Properties in Individual ZnO Nanorods. 2008, 8 (8), 2204–2209. https://doi.org/10.1021/nl080704n.

[7] Hu, Y.; Xu, C.; Zhang, Y.; Lin, L.; Snyder, R. L.; Wang, Z. L. A Nanogenerator for Energy Harvesting from a Rotating Tire and Its Application as a Self-Powered Pressure/Speed Sensor. Advanced Materials 2011, 23 (35), 4068–4071. https://doi.org/10.1002/adma.201102067.

[8] Schmidt-Mende, L.; MacManus-Driscoll, J. L. ZnO – Nanostructures, Defects, and Devices. Materials Today 2007, 10 (5), 40–48. https://doi.org/10.1016/s1369-7021(07)70078-0.

[9] Jiang, Jinghan. Ultrasensitive Self-Powered Photoelectrochemical Sensing for Enrofloxacin Detection by Coupling Piezoelectric Effect with Nonmetallic Surface Plasmon Resonance Based on ZnO Nanorod Arrays/WO3-x. Analytica Chimica Acta 2023, 1273, 341557. https://doi.org/10.1016/j.aca.2023.341557.

[10] Jung, D.-Y.; Baek, S.-H.; Hasan, M. R.; Park, I.-K. Performance-Enhanced ZnO Nanorod-Based Piezoelectric Nanogenerators on Double-Sided Stainless-Steel Foil. Journal of Alloys and Compounds 2015, 641, 163–169. https://doi.org/10.1016/j.jallcom.2015.03.066.

[11] Sun, Y.; Shen, S.; Deng, W.; Tian, G.; Xiong, D.; Zhang, H.; Yang, T.; Wang, S.; Chen, J.; Yang, W. Suppressing Piezoelectric Screening Effect at Atomic Scale for Enhanced Piezoelectricity. Nano Energy 2023, 105, 108024. https://doi.org/10.1016/j.nanoen.2022.108024.

[12] Sabir, S.; Arshad, M.; Chaudhari, S. K. Zinc Oxide Nanoparticles for Revolutionizing Agriculture: Synthesis and Applications. The Scientific World Journal. https://www.hindawi.com/journals/tswj/2014/925494/.

[13] Ogawa, T.; Hideo Oikawa; Kojima, A. Decrement of Piezoelectric Constants Caused by Screening Effect of Conduction Electrons on the Effective Charge of CdS Crystals. Japanese Journal of Applied Physics 1971, 10 (5), 593–593. https://doi.org/10.1143/jjap.10.593.