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# Ten years' venturing in ZnO nanostructures: from discovery to scientific understanding and to technology applications

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**Zinc oxide is a unique material that exhibits semiconducting, piezoelectric and pyroelectric multiple properties. Nanostructures of ZnO are equally important as carbon nanotubes and silicon nanowires (NWs) for nanotechnology, and have great potential applications in nano-electronics, optoelectronics, sensors, field emission, light emitting diodes, photocatalysis, nanogenerators, and nanopiezotronics. Ever since the discovery of nanobelts (NBs) in 2001 by my group, a world wide research in ZnO has been kicked off. This review introduces my group's experience in venturing the discovery, understanding and applications of ZnO NWs and NBs. The aim is to introduce the progress made in my research in the last 10 years in accompany to the huge social advances and economic development taking place in China in the last 10 years.**

ZnO, nanowire, nanobelt, nanosensor, nanogenerator, nanopiezotronics



Zinc oxide (ZnO) is a wide bandgap (3.37 eV) semiconductor having a high electron-hole binding energy (60 meV) and important applications in electronics, optics, optoelectronics, laser and light-emitting diode[1]. The piezoelectric and pyroelectric properties of ZnO make it a great candidate for sensors, transducers, energy generators and photocatalysis for hydrogen production. ZnO is also a green material that is bio-compatible, biodegradable and bio-safe for medical applications and environmental science[2,3]. Research in one-dimensional nanostructures of ZnO was first inspired by the discovery of oxide NB by my group[4] and the demonstration of UV lasers in aligned NW arrays[5] in 2001. Ever since then, the number of papers published in ZnO nanostructures increases exponentially (Figure 1). Take 2008 as an example, over 550 papers have been published in ZnO nanostructures. As for one-dimensional (1D) nanostructures, ZnO has equal importance as Si based 1D nanostructures according to the published articles in the literature, and it is playing an increasingly key role in developing nanoscience and nanotechnology. It is fair to state that carbon nanotubes, silicon NWs and ZnO NWs/NBs are probably the most important 1D nanomaterials in today's research. From a recent report on the map of physics by *Physics World*, research in ZnO NWs is as important as quantum computing, dark matters, string theory, semiconductor thin films, photonic crystals and carbon nanotubes (Figure 2)[6].

The growth, structure analysis, property measurements and novel applications of ZnO nanostructures have been systematically covered by a few review articles[6–14]. In this paper, I mainly focus on my group's studies related to ZnO, aiming at giving a story telling background about our step-by-step progress in the last 10 years.

## 1 Discovery of nanobelts (2001)

Research in one-dimensional nanomaterials has been dominated by carbon nanotubes, silicon NWs and ZnO

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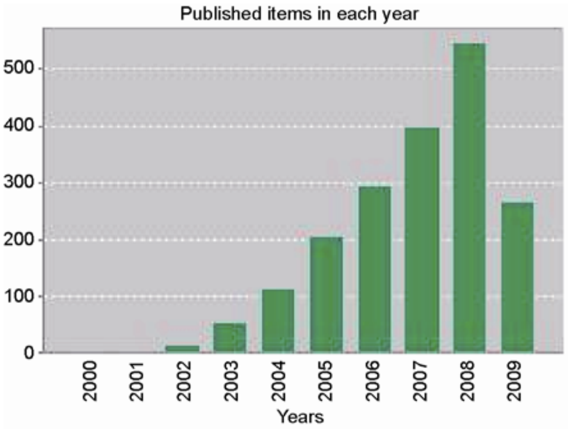


**Figure 1** Publication statistics on nanostructures for ZnO. The data were received on May 20, 2009 through the data base from Institute of Scientific Information using the following key words that appear in the title, abstracts and keywords: ZnO (or zinc oxide) together with nanowire, nanobelt, nanoribbon, nanorod, nanotip, nanoring, nanofiber, nanospring, nanohelix, nanoflower, or nano-brush.

NWs and NBs. The world wide effort in carbon nanotube research was inspired by Iijima's report about the structure of nanotubes in 1991[8]. The report of silicon nanowires (NWs) in 1998 by Lieber's group launched the study of silicon nanostructures[9]. My research from 1997 to 2000 was about *in-situ* measurement of the mechanical, electrical and field emission properties of single carbon nanotubes using transmission electron microscopy (TEM)[10,11]. This study later leads to a branch of research for characterizing the size-dependent physical properties of nanomaterials. Although this was the first demonstration of *in-situ* measurements in TEM, I soon realize that the difficulty of sorting semiconductor carbon nanotubes from metallic nanotubes may prohibit their applications in electronics. As inspired by my own research experience with functional oxides[12], I guided my postdoctoral fellow Zhengwei Pan to look into oxide nanostructures in early of 2000, which was an area of very few existing studies back to then. This initial drive started the field of growth of oxide nanostructures, and later led to the first publication of oxide nanobelts (NBs) in April 2001 (Figure 3), which is the top 10 most cited papers in materials science in the last decade, and it has been cited for over 2700 times. This work was a turning point of our research from structure analysis to materials synthesis. After discovering a few key nanostructures, our effort turned into understanding the formation process and growth of nanostructures.

## 2 Polar surface induced growth phenomena (2003—2005)

The wurtzite structured ZnO has two important characteristics: non-central symmetry and the polar surfaces.

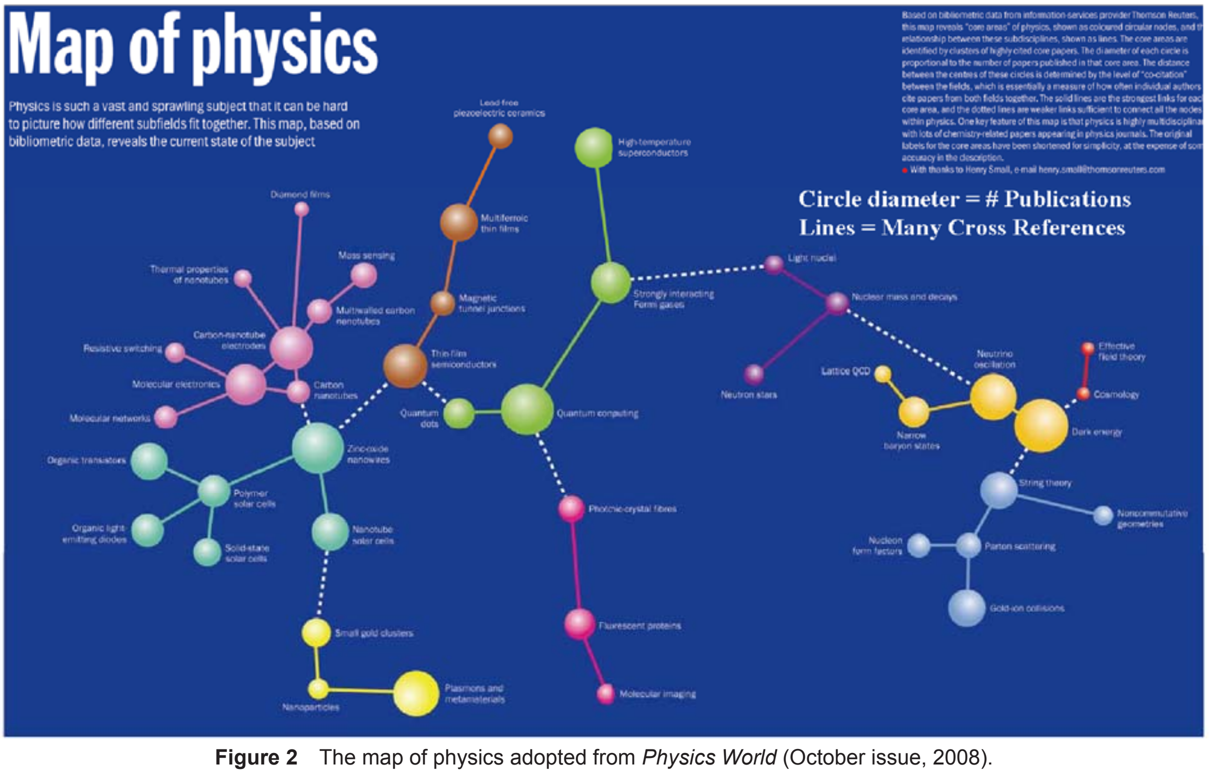


**Figure 2** The map of physics adopted from *Physics World* (October issue, 2008).

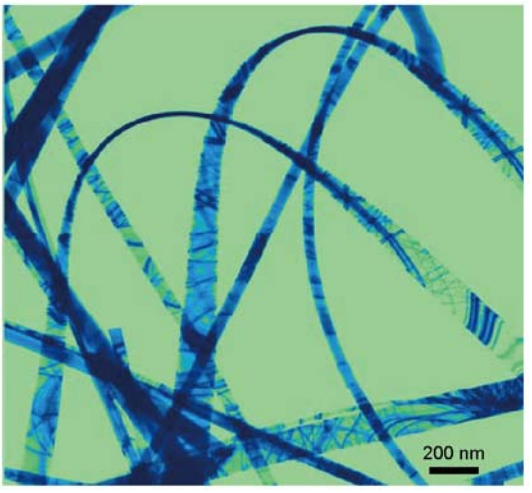


**Figure 3** TEM image of the as-synthesized ZnO nanobelts.

The structure of ZnO can be described as a number of alternating planes composed of tetrahedrally coordinated $O^{2-}$ and $Zn^{2+}$ ions, stacked alternatively along the *c*-axis. The oppositely charged ions produce positively charged (0001)-Zn and negatively charged (000-1)-O polar surfaces. The polar surface dominated ZnO NBs are likely to be an ideal system for understanding piezoelectricity and polarization induced ferroelectricity at nano-scale; and they could have applications as one-dimensional nano-scale sensors, transducers and resonators. In January of 2003, a visiting scholar Xiangyang Kong in my group synthesized a spring like ZnO nanostructure that was made of a single NB dominated by (0001) polar surfaces (Figure 4(a))[13]. The formation of such a structure by a crystalline NB was found after careful microscopy study by myself. By the end of February of 2003, I realized that it must be the polar charges on the surfaces of the NB that induced the shape and then I proposed a model to explain the formation of the nanospring. Owing to the positive and negative ionic charges on the zinc- and oxygen-terminated ±(0001) surfaces, respectively, a spontaneous polarization is induced across the NB thickness. As a result, helical nanostructures and nanorings are formed by rolling up single-crystal NBs; this phenomenon is attributed to a consequence of minimizing the total energy contributed by spontaneous polarization and elasticity, which was confirmed by the experiments of my PhD student Will Hughes[14]. This model is the foundation of explaining many polar surface dominated nanostructures in the wurtzite family.

As an immediate follow up to this work, my PhD student Rusen Yang discovered another nano-helix structure in November of 2003[15]. The structure was

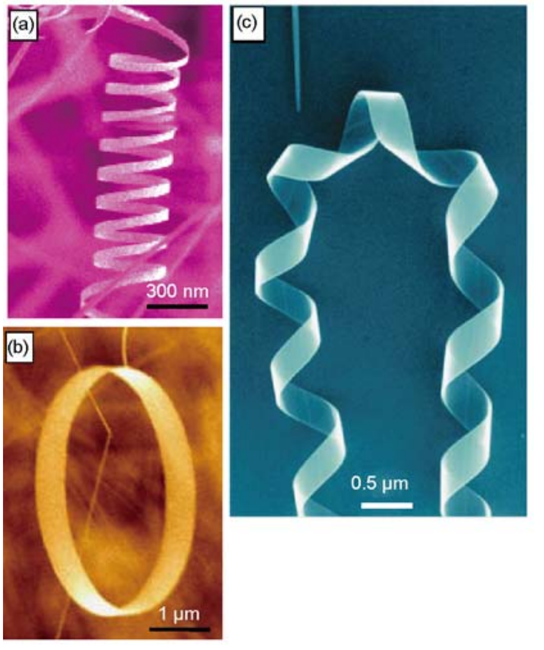


**Figure 4** SEM images of (a) single-crystal nanospring, (b) nanoring, and (c) superlattice structured nanohelix of ZnO.

deformation-free, single-crystalline nanohelixes/nanosprings. The nanohelixes are made of ~ 12 nm NWs and have a uniform mean diameter of ~ 30 nm. The growth follows a hexagonal screw-coiling model, in which the growth of the NW is led by the Zn-terminated (0001) front surface due to self-catalysis. A sequential and periodic 60° rotation in growth direction among the six equivalent directions of $\langle 0\bar{1}11 \rangle$ in an ordered and equally spaced distance results in the formation of the nanohelix. The sequential change in growth direction is to reduce the electrostatic interaction energy caused by the $\pm\{01\bar{1}1\}$ polar surfaces of the NW, in analogous to the charge model of a RNA molecule. This study was also the first study that proves the $\pm\{01\bar{1}1\}$ are polar surfaces.

In June of 2004, Xiangyang Kong has received another nanostructure of ZnO, freestanding, single-crystal, completely closed nanorings (Figure 4(b)). After a careful and detailed study of the nanoring structure by Yong Ding, a postdoctoral fellow in my group then, we finally understood the structure and formation process of the nanoring[16]. The nanoring appears to be initiated by circularly folding a NB caused by long-range electrostatic interaction. Co-axial and uni-radius loop-by-loop winding of the NB forms a complete ring. Short-range chemical bonding among the loops results in a single-crystal structure. The self-coiling is likely to be driven by minimizing the energy contributed by polar charges, surface area, and elastic deformation. This is the second example of polar surface dominated growth phenomenon.

In January of 2005, my PhD student Puxian Gao found another exciting and unexpected structural configuration of ZnO, a new rigid helical structure of zinc oxide that is made of a superlattice-structured NB formed spontaneously in a vapor-solid growth process (Figure 4(c))[17]. In conjunction to the structural information provided by Yong Ding, the formation process of the nanohelix was proposed. The nanohelix was initiated from a single-crystal stiff-nanoribbon that was dominated by the *c*-plane polar-surfaces. An abrupt structural transformation of the single-crystal nanoribbon into stripes of the superlattice-structured NB led to the formation of a uniform and perfect nanohelix due to rigid structural alteration. The superlattice NB was a periodic, coherent, epitaxial and parallel assembly of two alternating stripes of zinc oxide crystals oriented with their *c*-axes perpendicular to each other. The growth of the nanohelix was terminated by transforming the partial polar-surface-dominated NB into a nonpolar-surface-dominated single-crystal NB. Again, our data suggest that reducing the polar-surfaces could be the driving force for forming the superlattice structure, and the rigid structural rotation/twist caused by the superlattice results in the initiation and formation of the nanohelix. This type of homostructured superlattice formed in one step of synthesis was a surprise. The nanohelix is likely to be an ideal and unique structure for fabricating and studying electromechanically-coupled nano-scale sensors, transducers and resonators that have unusual elasticity and transport characteristics[18,19].

## 3 Growth of aligned NWs and its physical properties (2004—2005)

The NBs were usually grown on an alumina substrate so that they were distributed randomly on the substrate. One has to pull individual NB for fabricating nanodevices. For practical applications, growth of aligned NW arrays is more attractive, which has played a key role in our development of nanodevices and energy applications. The growth of NW arrays by vapor phase vapor approach was first carried out in my group by Xudong Wang et al. in 2004 (Figure 5)[20]. Using a sapphire crystal as a substrate and gold dots deposited on the surface using a soft lithography patterning technique, aligned NWs were received at a growth temperature of ~900℃. The growth of aligned NW arrays using chemical approach at temperatures 70—90℃ was demonstrated by Sheng Xu et al. in my group, who showed the location control, orientation control and dimensionality control of NWs[21,22].

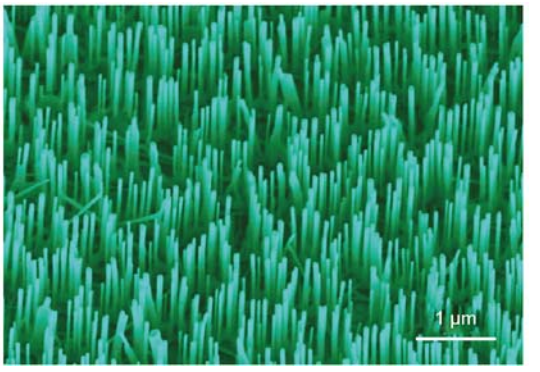

**Figure 5** Grown aligned ZnO nanowire arrays on a sapphire surface.

The characterization of the mechanical properties of the aligned NW array was carried out by my PhD student Jinhui Song in 2005[23], who developed an atomic force microscopy (AFM) based technique without constructing the sample. By scanning the NW array in contact mode by an AFM tip, the elastic modulus is received by correlating the observed lateral deflection distance and the applied lateral force. Although this is a small step progress in nanomechanics in comparison to the existing techniques[24], it sets the basic methodology for discovering the nanogenerator, as will be presented in the next section.

## 4 Nanogenerators: from science to engineering and to technology (2005—present)

Piezoelectricity is an important phenomenon that characterizes the electromechanically coupled response of a material, and it has been widely used in science and technology. At nano-scale, most of the studies had been carried out for exploring the semiconducting properties of quantum dots, NWs as well as nanotubes, but the nano-scale piezoelectric property remained an unexplored field until 2004. In collaboration with Minhua Zhao and Scott Mao, we found that the piezoelectric coefficient of a single ZnO NB is 2—3 times of the bulk value[25]. The measurement was based on AFM by applying a constant voltage across the tip and the substrate. Following this work, I started to look into the piezoelectric properties of ZnO nanostructures and look for new approaches for converting mechanical energy into electricity in early of 2005.

There have been abundant of nanodevices that have been developed by scientists in the past few decades, but few studies are available for discussing how to power such devices using the energy harvested from the environment except with the use of a battery or an external power source. A major advantage offered by nanodevice is its extremely small power consumption, in the range of nano-Watt to micro-Watt. If our aim is to build a nanosystem, which is composed of nanodevices, nano-interconnects, a nano-scale power source is required for powering such devices. With such a motivation in my mind, I started to explore the self-powered nanosystems, or self-powered nanotechnology in early of 2005[26]. This research is now a new and exciting field in nanotechnology and energy science.

It is known that photovoltaic, thermal electricity and electromagnetic induction are the well established technologies for energy harvesting, what is the motivation to harvest mechanical energy? We now consider the following sceneries. In a case of individual sensors are difficult to get to (e.g. in hostile territory), or if the sensor network consists of a large number of nodes distributed over a large geographic area, then it may not be possible to replace batteries when required. A self sufficient power source deriving its power from the environment and thus not requiring any maintenance would be very desirable. In order for any system to be self sufficient, it must harness its energy from its surrounding environment and store this harnessed energy for later use. A nanorobot, for example, is proposed to be a smart machine that may be able to sense and adapt to the environment, manipulate objects, taking actions and perform complex functions, but a key challenge is to find a power source that can drive the nanorobot without adding much weight. If a nanorobot is placed in the body for performing sensing, diagnostic and therapeutic action, one can easily introduces it in the body, but it will be rather difficult/impossible to fish it out to replace the battery. In the context of military sensing/surveillance node placement may be in difficult to reach locations, may need to be hidden, and may be in the environment of dusty, rainy, dark and/or deep forest. This precludes the use of solar cell technologies because light is typically not available.

What types of mechanical energies are we aiming at to harvest? There are abundant amount and types of mechanical energy exist in our living environment, such as light wind, body movement, muscle stretching, acoustic/ultrasonic waves, noises, mechanical vibrations, and blood flow. The sources of mechanical energy we are looking at have the following characteristics. First, the magnitude of such energy could be small and tiny, which may exclude the application of some conventional energy harvesting technologies because the available mechanical force may not be strong enough to drive the generator. Second, the frequency range of the available signal can be quite wide, and most of the energy is in low-frequency range. This requires a technique that operates from low (~Hz) to relatively high (~kHz) frequency range. Finally, the situation of the environment can vary. This requires a technique that has a high adoptability. The nanogenerator we developed in the last 5 years is a potential technology for solving these problems[27].

### 4.1 The science of nanogenerators (2005—2006)

With a clear objective in mind, the next challenge is how to harvest the mechanical energy? In order to demonstrate the principle of the nanogenerator, my student Jinhui Song and I started a research in the summer of 2005 for using AFM to manipulate aligned ZnO NW arrays (Figure 6). In the AFM contact mode, a constant normal force of 5 nN was maintained between the tip and sample surface. The tip scanned over the top of the ZnO NWs, which were thus bent and then released. In corresponding to the mechanical bending, about half of the NWs of diameters 30—50 nm and length 1—2 μm produced a negative output voltage of 3—12 mV[28]. Such electric output was received only for piezoelectric ZnO NWs, but not for Si NWs, carbon nanotubes and $WO_3$ NWs. This phenomenon is a direct result of piezoelectric effect. A key observation received then was that the output voltage peak is received when the scanning tip touches the compressive side of a vertical NW[29].

The next question is what is the mechanism for the electricity generation and output process? A breakthrough understanding was made in the afternoon of November 30, 2005. When I was reviewing the experimental data with Jinhui Song in the afternoon of November 30, 2005, a book about semiconductor devices

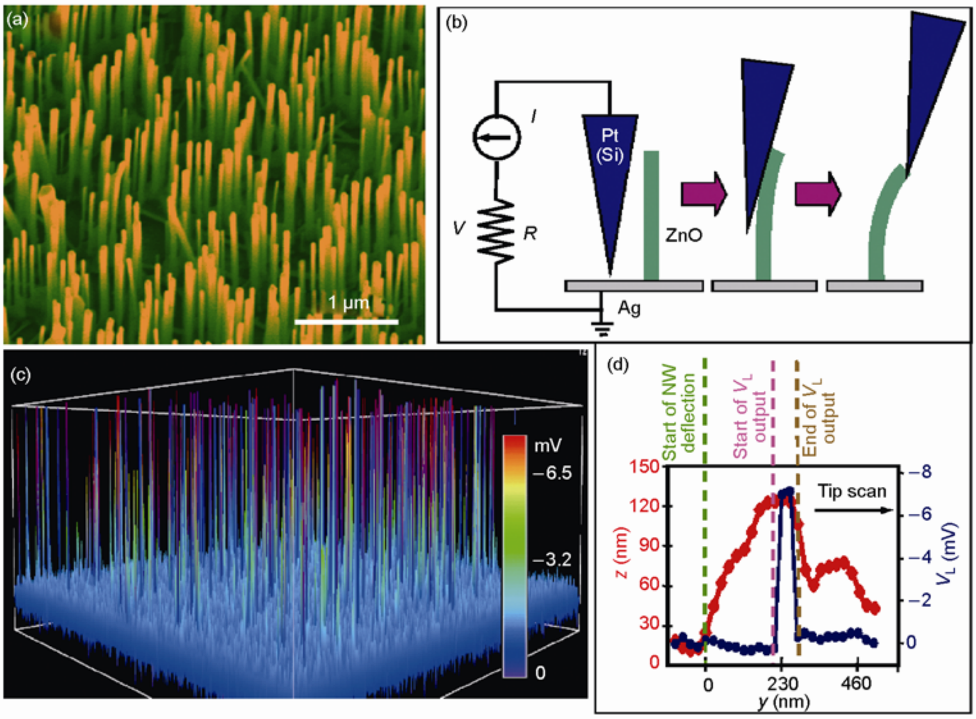


**Figure 6** (a) Scanning electron microscopy images of aligned ZnO NWs grown on GaN/sapphire substrate; (b) Experimental set up and procedures for generating electricity by deforming a piezoelectric NW using a conductive AFM tip. The AFM scans across the NW arrays in contact mode; (c) Output voltage image of the NW arrays when the AFM tip scans across the NW arrays; (d) An overlap plot of the AFM topological image (red line) and the corresponding generated voltage (blue line) for a single scan of the tip across a NW. A delay in the electricity generation is apparent.

was laying on my desk. I picked it up and flipped through the chapter about metal and semiconductor contact. I suddenly realized that there is a Schottky barrier between the Pt coated Si tip and the ZnO NW. Instantly, the working mechanism was proposed as follows. When a NW is bent by an AFM tip, the outer arc surface of the NW is under tensile strain, while the inner arc surface is under compressive strain. The tensile surface shows a positive piezoelectric potential, while the compressive surface shows a negative piezoelectric potential. The piezoelectric potential is the potential created by the polarized ions in the crystal once subjects to straining. As long as the strain is maintained, the piezoelectric potential remains. When the tip is in contact with the tensile surface of the NW, the local positive piezoelectric potential created sets the metal-semiconductor (n-type) contact as a reversely biased Schottky contact. In such a case, no current would flow through across the contact interface. This is a process for creating and preserving piezoelectric potential. Then, when the tip scans across the nanowire and reach the compressive side of the NW, the local negative piezoelectric potential sets the Schottky contact as forward bias, resulting in the flow of the electric current from the tip into the NW. Thus, a negative output potential is observed across an external load in reference to the grounded side. The flow of external electrons under the driving of the piezoelectric potential is the mechanism of energy generation. The role played by the Schottky barrier is essential to direct the one-directional flow of the electrons. A direct observation of this charge releasing process was received in the evening of December 24, 2005 by coupling optical imaging with AFM manipulation. This is the demonstration of science related to nanogenerator.

The above proposed mechanism for the nanogenerator has systematically explained each and every and all of our observations received in the last 4 years. Professor Stephen Hawking in his book on *Black Holes and Baby Universes* said "a theory is a good theory if it is an elegant model, if it describes a wide class of observations, and if it predicts the results of new observations".

### 4.2 The engineering of nanogenerators (2006—2008)

Although the above approach has explored the principle and potential of the nanogenerator, for technological applications, we must make an innovative design to drastically improve the performance of the nanogenerator in following aspects. Firstly, we must eliminate the use of AFM for making the mechanical deformation of the NWs so that the power generation can be achieved by an adaptable, mobile and cost-effective approach over a larger scale. Secondly, all of the NWs are required to generate electricity simultaneously and continuously, and all the electricity can be effectively collected and output. Finally, the energy to be converted into electricity has to be provided in a form of wave/ vibration from the environment, so the nanogenerator can operate "independently" and wirelessly. I came out a design to address these issues, and a team composed of Xudong Wang, Jinhui Song and Jin Liu was given the task in February 2006 for carrying out a systematic group of experiments as described below. The design was based on the mechanism proposed for the nanogenerator. Instead of using of AFM tips, a zigzag electrode was fabricated that was located above the array of ZnO NWs (Figure 7). The zigzag electrode acted as an array of aligned AFM tips. The DC nanogenerator was driven by ultrasonic wave. Once the device was subject to the excitation of an ultrasonic wave, the vertical and/or lateral movement of the zigzag electrode deflected the NWs underneath. The Schottky contact between the electrode and the NWs directed the current to flow from the electrode to the NWs. This is the DC nanogenerator

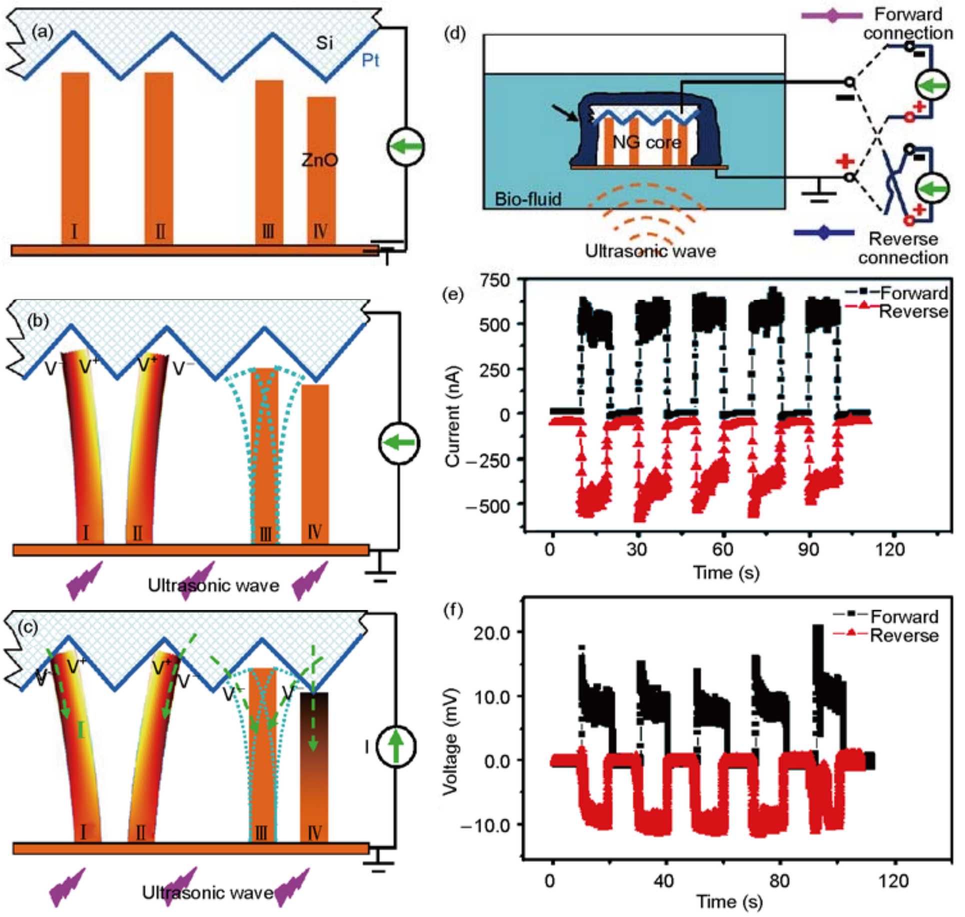


**Figure 7** The mechanism of the nanogenerator driven by ultrasonic wave. (a) Schematic illustration of the zigzag electrode and the four types of representing configurations of the NWs; (b) The piezoelectric potential created across the NW I and II under the push/deflection of the electrode as driven by the ultrasonic wave, but without flow of current due to the reversely biased Schottky barrier at the electrode-NW interface. The NW III is in vibration under the stimulation of the ultrasonic wave. The NW IV is in compressive strain without bending; (c) Once the NWs touches the surface of the adjacent teeth, the Schottky barrier at the electrode-NW interface is forward biased, piezoelectric discharge occurs, resulting in the observation of current flow in the external circuit; (d) Schematic of a NG that operates in bio-fluid and the two types of connections used to characterize the performance of the NG. The pink and blue curves represent signals from forward connected current/voltage (*I*/*V*) meter and reversely connected *I*/*V* meter, respectively; (e), (f) The short circuit current and open circuit voltage measured by the two types of connections when the ultrasonic wave was periodically turned on and off.

we reported in 2007[30], which was firstly demonstrated for ultrasonic wave at a frequency of 41 kHz. The approach is the basic platform for optimizing and improving the performance of the nanogenerators by integrating them into layered structures, which was later demonstrated by Sheng Xu and Yaguang Wei in 2008[31]. This is the engineering of the nanogenerator.

A nanogenerator that is capable of harvesting biomechanical energy has to operate at low-frequency (< 10 Hz). The substrate used for building the nanogenerator has to be flexible and foldable so that it can respond to the low frequency excitation. To meet the requirements of such a design, I initiated an idea of using fibers as substrate, on which ZnO NWs were grown. This research was carried out by Xudong Wang and Yong Qin starting in April 2007[32]. Using piezoelectric ZnO NWs grown radially around textile fibers, the design is based on two intertwisted fibers that form a pair of "teeth-to-teeth brushes", with one fiber covered with Au coated NWs and the other just by bare NWs (Figure 8). A relative brushing of the NWs rooted at the two fibers produces electricity owing to a coupled piezoelectric-semiconductor process. This was the first demonstration of fiber based nanogenerator. The research establishes the fundamental methodology of scavenging light-wind energy and body movement (heart beating, foot steps) energy using fabric based nanomaterials, making it possible for making flexible and foldable "power shirt/curtain/tent".

We have developed rich experience in measurement of small electrical signals in the last 5 years. For electrical measurement, it is challenging if the voltage is in the mV range and the current is in pA range. As for the nanogenerator, electrical measurement is even more challenging because we are looking for the electricity generated by the nanogenerator provided the applied bias from the measurement system is very small and it is unaffected by the feed back and coupling of the nanogenerator. The output of a nanogenerator may be affected by the measurement system, change in capacitance of the NW and electric circuit during mechanical deformation, and the coupling of the nanogenerator with the measurement system, it is thus easy to observe false signals. To differentiate the electric power that is generated by the nanogenerator from possible artifacts, we have developed three criteria consisting of 11 tests to rule out artifacts[33]. The generator must satisfy not only the Schottky behavior test (1) and switching polarity

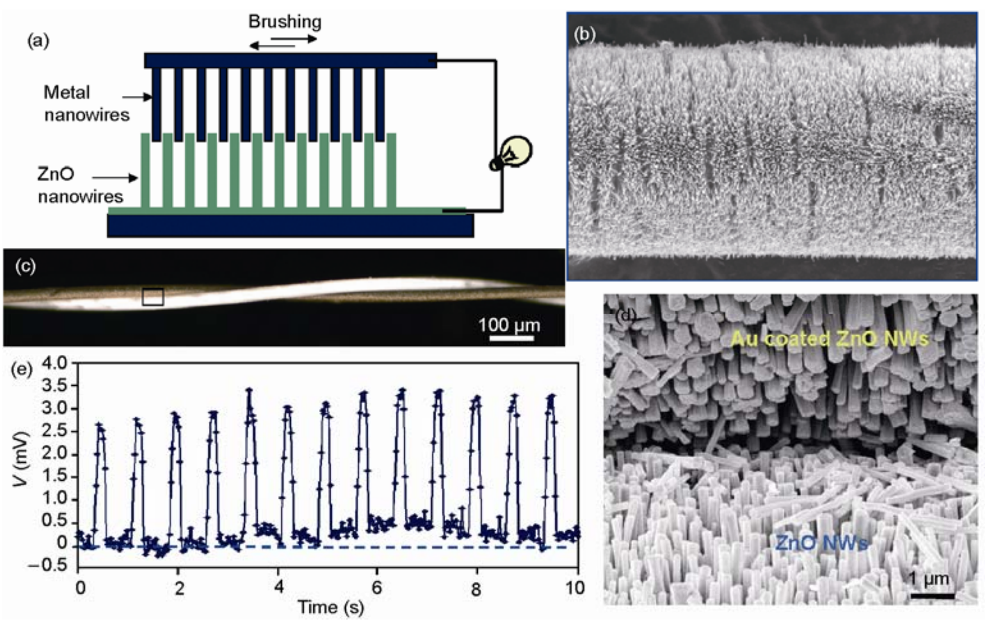


**Figure 8** The design and mechanism of the fiber based nanogenerator as driven by a low-frequency, external vibration/friction/pulling force. (a) Schematic idea of "two-brush" nanogenerator. One brush is made of ZnO nanowires, and the other brush is metal nanowires; (b) SEM image showing the distribution of NWs grown on a fiber surface; (c) An optical micrograph of a pair of entangled fibers, one of which is coated with Au (in darker contrast); (d) SEM image at the "teeth-to-teeth" interface of two fibers covered by NWs, with the top one coated with Au. The Au coated NWs at the top serve as the conductive "tips" that deflect/bend the NWs at the bottom, a piezoelectric-semiconducting couple process generates electric current; (e) The piezoelectric potential output by the two-fiber nanogenerator under the pulling and releasing of the top fiber by an external force.

tests (2), but also a linear superposition of current and voltage for 8 configurations as well. A true signal (current and voltage) generated from a generator must pass each and all of the tests. Those criteria and configurations are applicable to all types of nanogenerators and can serve as standard tests for general purposes.

### 4.3 The technology of nanogenerators (2008—present)

The nanogenerators presented above are based on vertically aligned ZnO NWs that are rooted at a substrate and are free at tips. The core of the direct-current nanogenerator is based on vertically aligned piezoelectric ZnO NWs that are rooted at a substrate and are free at the tips. Under the driving of an external force/disturbance, a zigzag electrode that is placed above the NW arrays moves up and down or laterally to bend/deflect the NWs. A piezoelectric-semiconducting coupling process converts mechanical energy into electricity and outputs it as a direct current due to a rectifying effect of the Schottky barrier between the electrode and the NWs. In this design, maintaining an appropriate gap (typically 50—100 nm) between the zigzag electrode and the NW arrays is rather challenging during packaging especially when the size of the nanogenerator is large, the substrate has some roughness or it is made of soft material. A large gap prevents the contact of the electrode with the NWs, but a small gap limits the lateral degree of bending of the NWs. Moreover, the contact between the electrode and the NWs is transiently on and off for each cycle of the driving action, and a relative scrubbing and sliding between the two is purposely designed, which may result in wearing, increased contact resistance/instability, and liquid/vapor infiltration. Therefore, the output stability, mechanical robustness, life time, environmental adaptability and washability of the nanogenerator remain to be addressed. To solve these problems, we designed an alternating-current (AC) generator that is based on cyclic stretching-releasing of a piezoelectric fine-wire (PFW) (microwire, NW), which is firmly contacted at two ends with metal electrodes, laterally bonded and packaged on a flexible substrate (Figure 9). When the PFW is stretched as driven by substrate bending, a piezoelectric-potential-drop is created along the PFW. A Schottky barrier formed at least at one end-contact of the PFW serves as a “gate” that prevents the flow of electrons in the external circuit through the PFW so that the piezoelectric potential is preserved. The PFW acts as a “capacitor” and “charge pump”, which drives the back and forth flow of the electrons in the external circuit to achieve a charging and discharging process when the PFW is



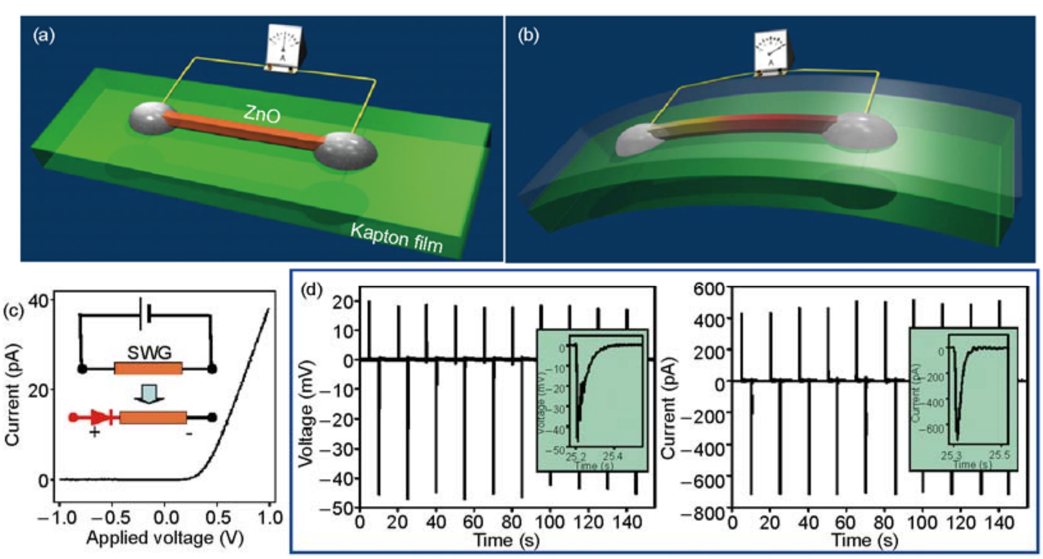


**Figure 9** Design of a piezoelectric fine-wire generator on a flexible substrate. (a) The PFW lays on a polymer Kapton film substrate, and its two ends are tightly bonded to the substrate and outlet interconnects; (b) Mechanical bending of the substrate creates tensile strain and corresponding piezoelectric potential in the PFW, which drives the flow of the electrons through the external load; (c) *I*-*V* characteristic of a SWG that is effective for producing output power, showing a typical Schottky diode characteristic with a forward-bias threshold voltage of ~0.3 V. In our study, the end-contact of the SWG that has the Schottky behavior is defined to be positive, where a diode symbol is introduced to represent its presence at the interface (lower diagram); (d) Generated alternating voltage and current of a SWG when repeatedly stretched and released. The insets are an enlarged output voltage and current peak.

stretched and released, respectively. The AC nanogenerator was firstly investigated by Rusen Yang and Yong Qin starting in February, 2007[34]. An energy conversion efficiency up to 6.8% was demonstrated if one exclusively considered the PFW. The reported work demonstrates a robust, no sliding-contact and packageable NW technology in polymer films for harvesting low-frequency energy from vibration, air flow/wind and mechanical deformation. The flexible AC generators are feasible and practical to be implanted in muscles, embedded in cloths, built in surface layers, and placed in shoe pads.

The muscle driven nanogenerator was demonstrated following the approach developed for AC nanogenerators for converting biomechanical energy, such as the movement of a human finger and the body motion of a live hamster (Campbell's dwarf), into electricity. A team led by Rusen Yang and composed of Yong Qin, Cheng Li and Guang Zhu was charged for this effort starting in May 2008[35]. A single wire generator (SWG) consists of a flexible substrate with a ZnO NW affixed laterally at its two ends on the substrate surface. Muscle stretching results in the back and forth stretching of the substrate and the NW. The piezoelectric potential created inside the wire leads to the flow of electrons in the external circuit. The output voltage has been increased by integrating multiple SWGs. A series connection of four SWGs produced an output voltage of up to ~0.1—0.15 V. The success of energy harvesting from a tapping finger and a running hamster reveals the potential of using the nanogenerators for scavenging low-frequency energy from regular and irregular biomotion.

### 4.4 Hybrid nanogenerator (2007—present)

Our living environment has an abundance of energies in the forms of light, thermal, mechanical (such as vibration, sonic wave, wind and hydraulic), magnetic, chemical and biological. Harvesting these types of energies is of critical importance for long-term energy needs and sustainable development of the world. Over the years, rationally designed materials and technologies have been developed for converting solar and mechanical energies into electricity. But these existing approaches are developed as independent technologies and entities that are designed based on drastically different physical principles and diverse engineering approaches to uniquely harvest a particularly type of energy. A solar cell works only under sufficient light illumination; a mechanical energy generator is applicable if there is significant mechanical movement/vibration. Starting in August 2007, we started to develop the first hybrid cell that is designed for simultaneously harvesting solar and mechanical energies using nanotechnology[36]. This research was carried out by Xudong Wang and Chen Xu, a PhD student in my group. Our approach relies on aligned ZnO NW arrays grown on surfaces of a flat substrate, a dye-sensitized solar cell is built on its top surface to convert solar energy, and a piezoelectric nanogenerator is built on its bottom surface for harvesting ultrasonic wave energy from the surroundings. The two energy harvesting approaches can work simultaneously or individually, and they can be integrated in parallel and serial for raising the output current and voltage, respectively. Our study demonstrates an innovative approach for developing integrated technologies for effectively scavenging available energies in our environment around the clock.

Our current research in the nanogenerators is focusing on raising the output voltage and output power through three-dimensional integration of multiple nanogenerators. Once the output voltage is raised to > 0.3 V, it will be possible to store the generated charges. Then, immediate applications are open.

## 5 The field of nano-piezotronics (2006—present)

Starting in 2004, a key change in my group was the establishment of electrical measurement systems and nanofabrication, as initiated by my PhD student Changshi Lao. This has dramatically changed our research style in the last few years toward property measurements and device applications. In 2006, two independent research experiments were carried out in my group. The first group of experiment was led by Xudong Wang who measured the electric transport of a long ZnO wire, the two ends of which were completely enclosed by electrodes, as its shape being bent inside an SEM[37]. A dramatic drop in electric conductance was received as the degree of bending increased. The interpretation was that a piezoelectric potential drop was created across the wire when it is bent, which acted as a gate voltage for controlling the transport of charge carriers through the wire. This is referred to piezoelectric field effect transistor (PE-FET).

The second experiment was carried out by Jr-Hau He, a visiting postdoctoral in my group, who used a two-probe to manipulate a single ZnO NW and measured its transport property[38]. One probe held one end of a NW that laid on an insulator substrate, the other probe pushed the NW from the other end by in-contact with the tensile surface of the NW. The tungsten tips had Ohmic contact with the NW. The I-V curve changed from a linear shape to a rectifying behavior with the increase of the degree of NW bending. This phenomenon was interpreted as a result of creating a positive piezopotential at the interface region, which served as potential barrier for blocking the flow of electrons to one direction. This is the piezoelectric-diode (PE-diode).

Both the PE-FET and PE-diode were based on the presence of a strain induced piezoelectric potential in the NW. The induced flow of electrons in the external circuit by the piezoelectric potential is the energy generation process. The presence of the piezopotential can drastically change the transport characteristic of a NW based FET. To systematically represent the piezoelectric-semiconductor coupled properties of such a system, I introduced the concept of nanopiezotronics on November 24, 2006 and publicly disclosed in the MRS fall conference in Boston a few days later[39]. Then, I published my definition about nanopiezotronics in 2007[40,41]. The basis of nanopiezotronics is to use the coupled piezoelectric and semiconducting properties of NWs and NBs for designing and fabricating electronic devices and components, such as field effect transistors and diodes.

The contents of nanopiezotronics have been greatly expanded in the last two years through the demonstration of several nanodevices by Jun Zhou and others in my group in 2008[42,43]. Using a two-end bonded ZnO PFW on a flexible polymer substrate, the strain induced change in I-V transport characteristic from symmetric to diode-type has been observed (Figure 10). This phenomenon is attributed to the asymmetric change in Schottky-barrier heights at both source and drain electrodes as caused by the strain induced piezoelectric po-

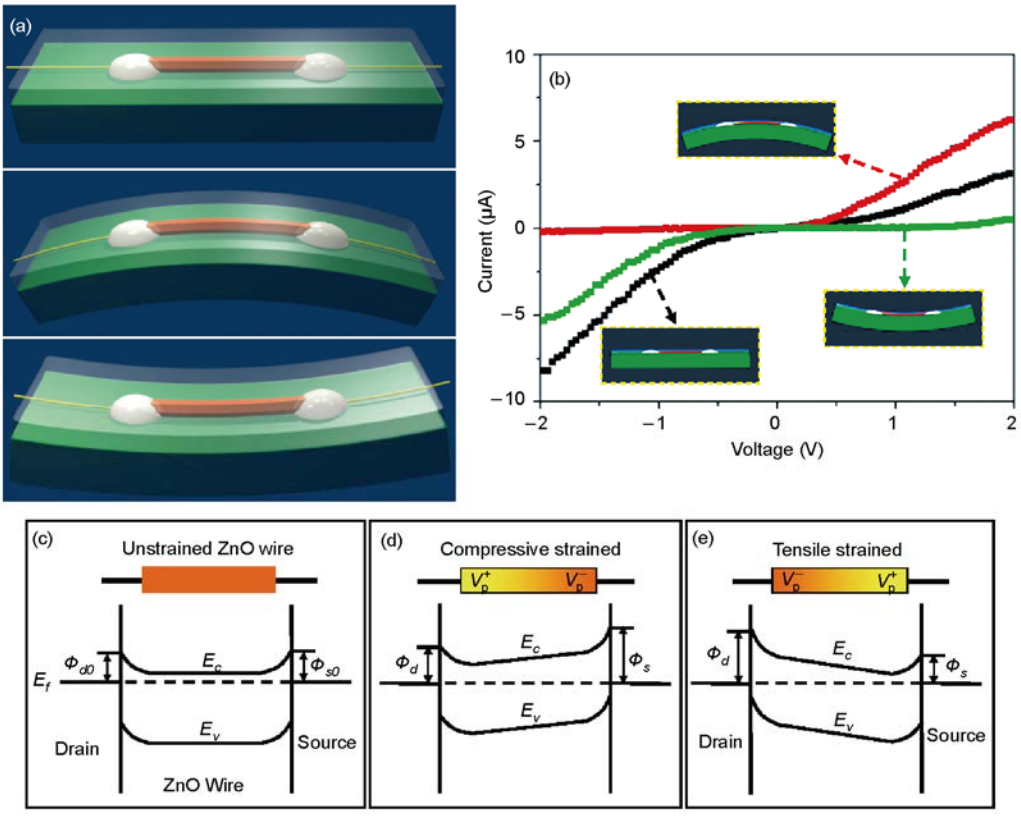


**Figure 10** (a) Polarity switchable piezoelectric diode using a two-end bonded ZnO wire; (b) Typical *I-V* characteristics of the sensor under different compressive strains. Black line is the *I-V* curve without strain. The direction of the blue arrowhead indicates the increasing of applied compressive strain. Schematic energy band diagrams illustrating the Schottky barriers at the source and drain contacts of a unstrained (c), compressive strained (d), and tensile strained (e) PFW, which illustrates the effect of switching the piezoelectric potential either by strain or by wire orientation on the local band structure and SBH.

tential-drop along the PFW. A new piezotronic switch device with an "on" and "off" ratio of ~120 has been demonstrated. This work shows a novel approach for fabricating diodes and switches that rely on a strain governed piezoelectric-semiconductor coupling process. I anticipate that more exciting electronic devices will be fabricated based on the principle of piezotronics.

## 6 Theory of nanogenerator and nanopiezotronics (2007—present)

We have also extensively developed the theory of nanogenerators. My student Yifan Gao has applied the perturbation theory for calculating the piezoelectric potential distribution in a nanowire as pushed by a lateral force at the tip[44]. The calculation shows that the piezoelectric potential in the NW almost does not depend on the $z$-coordinate along the NW unless very close to the two ends, meaning that the NW can be approximately taken as a "parallel plated capacitor". This is entirely consistent to the model established for nanopiezotronics, in which the potential drop across the nanowire serves as the gate voltage for the PE-FET. The maximum potential at the surface of the NW is directly proportional to the lateral displacement of the NW and inversely proportional to the cubic square of its length-to-diameter aspect ratio. By ignoring the doping in NW, the magnitude of piezoelectric potential for a NW of diameter 50 nm and length 600 nm is ~0.3 V when bent by a force of 80 nN. This voltage is much larger than the thermal voltage (~25 mV) and is high enough to drive the metal-semiconductor Schottky diode at the interface between AFM tip and the ZnO NW, as assumed in our original mechanism for the nanogenerators.

In 2008, we have investigated the behavior of free charge carriers in a bent piezoelectric semiconductive nanowire under thermo-equilibrium condition with consideration the finite doping[45]. For a laterally bent n-type ZnO nanowire, with the stretched side exhibiting positive piezoelectric potential and the compressed side negative piezoelectric potential, the conduction band electrons tent to accumulate at the positive side of the nanowire. The positive side is thus partially screened by free electrons but the negative side of the piezoelectric potential preserves. For a typical ZnO nanowire with diameter 50 nm, length 600 nm, donor concentration $N_D = 1\times10^{17}$ cm$^{-3}$ under a bending force of 80 nN, the potential in the positive side is <0.05 V and potential in the negative side is ~ −0.3 V. This potential is strong enough to overcome the threshold at the Schottky barrier between the metal tip and the nanowire. The theoretical results support the mechanism proposed for piezoelectric nanogenerator. The prediction of such theory has been observed experimentally for the p- and n-type NWs[46].

## 7 Nanosensors (2007—present)

ZnO has a great promise for optical applications, such as UV sensors. However, due to the presence of point defects and confined dimensionality, the UV sensitivity of ZnO NWs and NBs is limited. My student Changshi Lao and others demonstrated in 2007 that the UV response of a ZnO NB based sensor was enhanced by close to five orders of magnitude after functionalizing its surface with a polymer that has a high UV absorption ability[47]. This giant enhancement in photoconductance is attributed to the energy levels introduced by the polymer lying in the corresponding band gap and in the conduction band of ZnO, which served as a "hopping" state and increased the excitation probability of an electron to the conduction band. This exciting discovery will greatly impact the applications of ZnO NWs/NBs for UV detection.

Most recently, Jun Zhou and others have proposed a new process for largely enhancing the response and rest time of UV nanosensor[48]. By utilizing Schottky contact instead of Ohmic contact in device fabrication, the UV sensitivity of the nanosensor has been improved by four orders of magnitude, and the reset-time has been drastically reduced from ~ 417 to ~ 0.8 s. By further surface functionalization with function polymers, the reset-time has been reduced to ~ 20 ms even without correcting the electronic response of the measurement system. These results demonstrate an effective approach for building high response and fast reset UV detectors, which is distinct from the traditional approach of using Ohmic contacts.

## 8 Summary

This article reviews my own venturing in discovering, understanding and applying of novel nanostructures of ZnO. The aim is to share our experience in developing the field and our step-by-step progress. Many of our discoveries have been reported by vast majority of media world wide, such as Fox News[49] and CCTV[50]. The paper reporting the first nanobelt has been the top 10 most cited papers in Materials Science. The discovery of nanogenerators is the top 10 world discoveries in science according to academicians of Chinese Academy of Science. The fiber based nanogenerator was elected as one of the top progresses in physics in 2008 by *Physics World*, and as the top 10 scientific discoveries in China in 2008[51,52]. The nanogenerator has been selected as the top 10 sci-fi discoveries that can have the equal importance as the invention of cell phones in 10—30 years, according to *New Scientist*. The nanopiezotronics is the top 10 emerging technologies in 2009 according to *MIT Technology Review*. We will continue to work in the field of ZnO nanomaterials and will develop series of novel devices and power generators that hopefully to be useful for human kinds in one day.

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