Nanogenerators, self-powered systems, blue energy, piezotronics and piezophotonics – A recall on the original thoughts for coining these fields

Zhong Lin Wanga,b,c

a School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245, United States
b Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing 100083, China
c College of Nanoscience and Technology, University of Chinese Academy of Sciences, Beijing 100049, China

A B S T R A C T

In my research in the last 20 years, a few fields have been coined in the area of energy and electronics during the course of studying piezoelectric-semiconductor nanostructures. These fields are now attracting a worldwide interest and become the focuses of a few communities. This paper reviews the background and initial ideas based on which we introduced the following original concepts and effects: piezoelectric nanogenerators; self-powered systems; hybrid cell; nano energy; triboelectric nanogenerators; pyroelectric nanogenerators; piezotronics; piezo-phototronics; piezophotonics; tribotronics; blue energy; energy for the new era, and entropy for energy utilization. This paper serves as a record of how these fields were started. Finally, a perspective is given regarding to the energy for the new era, application of nanogenerators, piezotronics and self-powered systems.

1. Introduction

From 1983 to 1999, my research was mainly focused on fundamental theory and new techniques related to transmission electron microscopy (TEM). During which, I think that I have done a number of significant researches that worth to be summarized here. First, we proposed the reflection electron energy loss spectroscopy for studying the surface chemical compositions in TEM (1985–1988) [1]. Secondly, we studied the plasmon excitation of supported small particles (1985–1995) [2], which is laterly called plasmonics in recent years. Thirdly, I was the first who proposed that thermal diffuse scattering is the major contributor to the high-angle annular dark field imaging in scanning transmission electron microscopy (or Z contrast imaging) [3,4]. The theoretical idea I proposed is now well received by the microscopy community for quantifying Z-contrast imaging. Forth, I analytically proved that the image/diffraction calculation done in the “frozen lattice” model in the semi-classical theory for describing electron-phonon interaction in TEM is identical to the result calculated using full phonon dispersion dynamics in quantum scattering theory [5], which is now important for quantifying the ultra-high resolution electron imaging. Finally, I first approved that the off-axis electron holography is an energy filter that can filter off even phonon scattered electrons in electron diffraction and imaging (1992) [6].

Since I joined Georgia Tech in 1995, I started to develop the techniques for measuring the mechanical property and electrical transport properties of a single carbon nanotube inside a TEM, which is the beginning of the in-situ nanomechanics and in-situ transport. These two areas are now active research fields for TEM.

By 1999, I fully realize that the samples and materials used for my TEM studies were mostly provided by others, and my tasks were studying the materials structure and growth mechanisms. The only outcome is publishing some research papers, and I own no intellectual properties. I decided to synthesize nanomaterials myself, so that I can fully use my own expertise in materials characterization. Back to then, the most active nanomaterials being studied were nanoparticles, carbon nanotubes and silicon nanowires. I decided to synthesize one-dimensional oxides. Luckily, we published the first landmark paper in 2001 on oxide nanobelts [7], which sets my foundation for carrying out the study of ZnO nanostructures for about 20 years, from fundamental growth mechanisms to novel properties and to novel applications. This paper has been cited for over 5000 times! This is a turning point of my research from TEM to nanomaterials synthesis.

The objective of this paper is to give a review on the original thoughts we had for coining a number of fields initiated during the course of studying ZnO based energy, electronic and photonic devices and applications Fig. 1. I only present the background under which the ideas were created rather than give a lengthy review on their current progresses. Many papers published in this special issue are the results of these original ideas.

2. Piezoelectric nanogenerators (2005–)

In 2004, we used an atomic force microscopy to characterize the Young’s modulus of vertically aligned ZnO nanowires by simply
deflecting the nanowires under an applied mechanical force. The Young’s modulus was calculated using the Hook’s law. After we published the first paper, I decided to probe the piezoelectric properties of ZnO nanowires, which is known to be piezoelectric. My basic assumption was to convert tiny mechanical deformation energy into electric energy, based on which, the piezoelectric coefficient can be derived if all of the input mechanical energy was converted into electric power. However, the experimental results indicated that the derived value was about two orders of magnitude smaller than what we expected. I suddenly realize that I made a mistake in my assumption, because energy conversion can never be at 100% efficiency. By the afternoon of Sept. 20, 2005, I simply switched my idea from measuring the piezoelectric coefficient to energy conversion using ZnO nanowires. The device was first named nanogenerator (NG) [8], which now has been cited for over 4000 times. This is a milestone that changed my research direction from characterizing the nanodevices were rather large. I made an analogy whose tail is chained with an ‘elephant’, which is the power source. Although the nanodevice is small but the big power source makes the entire system rather bulky. My initial idea was if we could get rid of the big power source and use the energy harvested from the environment to power the nanodevice sustainably, so that the system would be very small – a nanosystem.

The original idea of developing piezoelectric nanogenerator (PENG) was to explore the possibility of building self-powered systems [10], by which we mean that a system is self-sufficient in energy by harvesting energy from its working environment. This is possible because the power consumption of electronic devices drops, and the output of energy harvester increases. For today’s communication, the devices can be in standby mode or active mode, during the former the device can acquire energy from its working environment, and then used it up in latter. The self-powering idea was first proposed in the 2006 paper on nanogenerators. Self-powering is a major idea that can make the system to operate sustainably, which is now well received in many fields in the area of sensor networks, internet of things and implantable in-vivo medical devices.

4. Hybrid cell (2009-)

Various types of energy are available in the working environment of a device, such as solar, mechanical, thermal and electrochemical. With considering the mobility of a nanosystem, the availability of energy from its working environment can vary from time to time and from place to place. Relying on one type of energy may not be sufficient for the sustainable operation of the device, such as the instability of solar energy, and low power of thermalelectrics. During the course of developing PENG, I was wonder if one device can simultaneously harvest two or more different types of energy. This idea was first realized experimentally in 2009 by harvesting mechanical and solar energy using a hybrid cell [11]. Later, the idea was further developed for harvesting multiple types of energy and the same type of energy using two different approaches. I can still recall that the first couple of papers on hybrid cell were rather hard to be accepted for publishing, because it was not familiar to the referees and editors.

5. Nano energy

The field of nano energy was phrased as early as 2005, but I did not push it forward as a field until 2011. I was invited by Elsevier to editor a journal in energy in early of 2011, and I decided to call the journal Nano Energy. Nano energy is about the harvest, storage and effective utilization of energy in our living environment using nanomaterials, nanodevices and nanosystems. As of now, nano energy includes but not limited to nanogenerators, fuel cells, solar cell, energy storage, thermalelectrics, photocatalysis, water splitting and more. It is an active and important field that has drawn a lot of research interest.

6. Triboelectric nanogenerators (2011-)

Triboelectric nanogenerator (TENG) was invented during the course of searching for high output PENG. In early of 2011, our research was focused on integrating layered PENGs for enhancing the output current. In several occasions in 2008 and 2009, we have observed that the output of a PENG reached even 3–5 V, but based on the performance of the PENG we had then, the device could only reach about 1 V. The high output was observed for some devices but not all of the devices. The results puzzled me and I doubted it, and we suspicious if the results were due to artifacts. I simply dismissed the results.

It was until March of 2011 that we observed such “abnormal” signals again. In this time, the lucky thing was that we did not ignore the results and the same time did not believe in the result, instead, we took a close look at the devices that showed an unexpected output. Our examination of the devices showed that there was a little air gap between the piezoelectric layer and the polymer layer used for packaging, which cause them to be in contact and separation when compressed periodically, which suggests that the results could be produced by contact electrification (triboelectric). To verify our hypothesis, we tried over 20 different materials and fabricated hundreds of devices without using piezoelectric materials by repeatedly measuring their output voltages when they are in serial and anti-serial and their output current when they are in parallel and antiparallel (Fig. 2). The results showed that the received data are truly from triboelectric. This later led to the first invention of triboelectric nanogenerators [12]! The development of TENG is surprisingly fast, because of its high output, easy to fabricate, diverse choice of materials, and low cost. TENGs have revolutionary applications for harvesting energy from human activities, rotating tires, mechanical vibration and more, with great applications in self-powered systems for personal electronics, environmental monitoring, medical science and even large-scale power [13].

7. Pyroelectric nanogenerator (2012-)

Thermalelectric effect is well known that uses the temperature
gradient along a thermoelectric material for power conversion. On the other hand, a time variation of temperature of a piezoelectric material can also induce a polarization due to the anisotropic property of the material. This effect is called the pyroelectric effect. We used this effect to build the first pyroelectric nanogenerator in 2012 [14].

8. Piezotronics (2006-)

In our first paper on nanogenerator in 2006, I proposed the mechanism that the current we observed was due to the forward bias of a Schottky barrier between the Pt AFM tip and the ZnO nanowire once it is subjected to mechanical deformation, which produces a piezoelectric potential across the width of the nanowire. After we published the first paper on PENG, I realized that the presence of the piezopotential across a bent nanowire can function as a gate voltage applied across a nanowire based field effect transistor. This means that the transport property along the nanowire can be “controlled” by a strain induced piezoelectric potential. Following this idea, we carried out two experiments, one is the measurement of the transport along a ZnO nanowire once it is subjected to an axial strain [15], and the other is the transport across a Pt-ZnO interface once the nanowire is subjected to a transverse bending at one end [16]. From these two experiments, the presence of piezopotential in ZnO is verified experimentally. Based on such a judgement, the concept of piezotronics was proposed in fall of 2006 [17]. I had an invited talk in fall MRS meeting, during which I changed the title of my talk into “nanogenerators and nanopiezotronics”, which was reported by CE&N as the first report of piezotronics in media [18]. Later, the idea of piezotronics evolves to vertically aligned nanowire arrays by introducing the gating effect of piezoelectric charges at the ends of the nanowires [19], and an array of nanowires as matrix [20]. Recently, piezotronic effect has also been observed for 2D materials [21], and it is a general effect for the third generation semiconductors, such as GaN.

The design of piezotronics fundamentally changes the design of traditional CMOS transistor in three ways: the gate electrode is eliminated so that the piezotronic transistor only has two leads; the externally applied gate voltage is replaced by an internally created piezopotential so that the device is controlled by the strain applied to the semiconductor nanowire rather than gate voltage; the transport of the charges is controlled by the interface at the electrode-nanowire interface rather than the channel width. Piezotronics has potential applications in human-computer interfacing, smart MEMS, nanorobotics and sensors, but the current research is still focusing on fundamental science.

9. Piezo-phototronics (2010-)

In 2009, we experimentally found that the Schottky barrier height at a metal-semiconductor contact can be raised by negative piezoelectric charges distributed at the interface, and decreased by the irradiation of laser due to the increased free carrier density. In such a case, the effect of piezoelectricity can be counted for by laser excitation [22]. In the second paper, we have used the piezoelectric effect to tune the height of the Schottky barrier in order to optimize its sensitivity as photodetector [23]. This is introduced as the piezo-phototronic effect, which is to utilize the piezoelectric polarization charges at the interface for effectively tune the charge carrier separation or recombination process in optoelectronics.

The most important progress in the field is the utilization of piezo-phototronic effect to tube a ZnO-GaN based LED [24] and array of LEDs [25]. We first proposed that the presence of a layer of piezoelectric polarization charges at the interface can create a local energy dip within the carrier depletion zone of a pn junction, which can effectively
increase the electron-hole recombination rate for enhancing LED efficiency by a factor of 4.25. Later, piezo-phototropic effect has been used to enhance the efficiency of various solar cells, efficiency of photon detectors.

10. Piezophotonics (2008-)

In 2008, I published a review article entitled “Towards self-powered nanosystems: from nanogenerators to nanopiezotronics” [26], in which I first theoretically predicted that, owing to the presence of the piezoelectric potential, “the trapped charges can drop from the vacancy/surface states back to the valence band, possibly resulting in photon emission. This process is proposed as a piezoelectric-induced photon-emission effect”. This prediction was later observed by two groups [27,28], which is now the piezophotonic effect. This field is rather small, but it makes the three circles coupling in Fig. 4 complete.

11. Tribotronics (2015-)

As inspired by the ideas of gating effect of the piezoelectric potential, the surface charges induced by contact-electrification (triboelectricity) can also serve as a gate voltage for controlling the carrier transport in a FET device. This can be an effective means for converting a biomechanical action into an electronic control, which was the original idea for introducing the tribotronics [29]. As of now, various tribotronic functional devices have been developed, such as tribotronic tactile switch, memory, hydrogen sensor and phototransistor.

12. Blue energy (2014-)

In March 2014, we were heavily involved in developing various approaches for TENGs, but the main purpose was looking for powering small electronic devices. One of the TENGs we made was to use a shell-core structure for harvesting water wavy energy. I began to think that if we could form a network by linking millions of such ball shape TENGs, and float such network on the surface of water. The fluctuation of water surface can generate power, possibly large power. The output of each sphere is a random pulse in respond to the water wave, but after rectification, the output of millions of such ball TENGs in parallel can be statistically a DC output. My rough estimation indicates that we can easily achieve MW power by an integration of such TENGs. The output has less dependence on weather, day and night, and it occupies no land. We should call such energy “blue energy”, because it harvests energy from blue ocean [30].

A key advance made in fall of 2015 was that, by comparing the output of an electromagnetic generator with that of TENG, we realize that TENG has the most important advantages of high output power at low frequency f (< 5 Hz) [31]. The output power of an electromagnetic generator is proportional to \(f^2\), while that of a TENG is proportional to \(f\) and its output voltage is high and is almost independent of frequency. In such a case, TENG is ideal for harvesting low-frequency, “random” vibration energy introduced by water wave in ocean. Therefore, TENG has the unbeatable advantage of relative high efficiency at low-frequency. We anticipate that the blue energy dream will be realized soon [32].

Furthermore, a network can be constructed using TENGs for harvesting energy from gentle wind in our living environment and in desert, which cannot be achieved using conventional blade based wind power generator that works only when the wind speed reaches a certain value. This is a big advantage for TENG because it gives a much higher output even when the wind is in the level of breeze.
13. Energy for the new era and entropy for energy utilization (March 2017–)

The phrase of “new energy” and “green energy” have been used for many years, which largely refer to solar energy, wind energy and heat energy. In the new era of internet of things, sensor networks, big data, robotics and artificial intelligence, the world needs billions of small, mobile and largely distributed energy sources. But such energy sources are impossible to be supplied by batteries, due to recharging problem and maintenance. It is vitally important to use the idea of “self-powering”. To characterize the energy required for our near future technology, I introduced the idea of “energy for the new era” in order to distinguish the distributed energy sources from the well-known new energy used in the community [33]. I hope that the idea of new era energy will be well received in the near future.

Phrasing of the energy for the new era is an application of entropy in energy science. Tracking back to the technology revolution in human society, the first most important invention was the steam engine in 1781, which was the first of transforming thermal/heat energy into mechanical energy, making it possible of using a machine to replace human labor. The second most important invention was the electromagnetic generator by Faraday in 1831. A conjunction of heat engine and electric generator makes it possible to convert thermal energy into electric power. The original fuel for this process was coal, later oil and nuclear reaction, which are referred as high quality “ordered” energy. The function of a power plant is to convert such high quality energy provided by coal or oil into electric power, which is transmitted via power lines to thousands of factories and families. This is a process of energy transmission from a concentrated place such as a power plant to distributed unites, in where the energy is either being used for lighting, cooling or wasted as heat. Although the total energy is conservative but it is dispersed in our environment, which is referred as low quality “random” energy. This is an irreversible process and is a result of maximizing entropy. This is a process that we utilize energy in traditional term.

Now, as we enter into the era of internet of things, billions of things have to be hooked up with sensors for various measurements, controls and data transmission, we need billions of small power units. If all of these power units were provided by power plants or energy storage units such as batteries, most of the internet of things will be impossible according to Cisco’s study! A possible solution is to use the self-powering by harvesting random energy from our living environment, so that the devices can be sustainably driven. This is an approach for using energy in the new era.

As the high quality and “ordered” fossil energy (coal, oil) slowly vanishing for its high usage in electricity generation in power plants, global warming and climate changes are inevitable due to the conservation of total energy and the increase of entropy as governed by thermodynamics. In the era of IoT, the units that are required to be powered are mobile, changing and largely distributed with huge numbers; in comparison to traditional house powering, these units are called “random”. Harvesting energy from environment to power these “random” units is an effective approach. This is to follow the law of maximizing entropy to meet the needs of IoT new era. In a simple analogy, we use the “ordered” energy from power plants to power the “ordered” needs of our society such as factories and transportation systems, and we use the “random” energy to power the “random” units for IoT.

14. Theory of nanogenerators

The principle of the classical electromagnetic generator is based on electromagnetic induction, and the observed current is called conduction current. However, the theory for nanogenerator is different. In the
Maxwell's displacement current, the main term $\varepsilon \partial E/\partial t$ given by Maxwell in 1861 gave the birth of electromagnetic wave in 1886, which is the foundation of wireless communication, radar and later the information technology. On Oct. 21, 2016, I suddenly realized that the polarization charge density $P_s$ introduced by the surface charges owing to either piezoelectric effect or triboelectric effect was missing in the displacement current. Then, I added a term of $\partial P_s/\partial t$ in the Maxwell's displacement current, which is just the experimentally observed current of the nanogenerator [34]. This means that the nanogenerators are the applications of Maxwell's displacement current in energy and sensors, forecasting the applications of Maxwell's equations in energy and sensors.

Nanogenerator was first invented by using nanowires for energy conversion, and this was why it was called nano-generators. But as now, nanogenerator represents an energy technology that is based on the Maxwell’s displacement current regardless if we use nanowires or not. Displacement current is not the current created by flow of free charges but time variation of electric field and the polarization of media. The principle of nanogenerator is distinctly different from the principle of electromagnetic generator, which is governed by conduction current.

15. Perspectives

As the world is marching into the era of internet of things, sensor networks, big data, functional robotics and artificial intelligence, the world needs a new kind of energy that would power billions of mobile and widely distributed devices. This type of energy is different from the traditional power grid, because each has a small power but the number is huge, with the characteristics of mobile and widely distributed. This type of energy is coined as "energy for the new era".

The nanogenerator we first discovered in 2006 opens a new chapter for the energy for the new era, especially with the invention of the TENG in 2012. It is fast reaching various corners of research. Nanogenerators mainly have four applications (Fig. 3). First, it is a great choice as the poor sources for micro-nano systems, which could be critical for the internet of things and sensor network. Once we can integrate millions of TENGs into a networks, it is highly possible to harvest large-scale energy from ocean and gentle wind. This is the blue energy dream. Thirdly, the most accessible usage is as self-powered sensors, which can cover a large area related to motion, medical science, trigger and agitation, especially in the area of robotics and security. Lastly, since the output voltage of TENG is rather high and it is independent of the operation frequency, it can be used as a high voltage source for various applications, such as microplasma, mass spectrometry, electrospraying and more [35].

The third generation semiconductors are dominated by GaN, ZnO and SiC, which are distinct from the first and second generations of semiconductors in crystal structure and of course in properties. With considering the hexagonal and non-central crystal symmetric of GaN and ZnO family, the piezotronic effect and piezo-phototronic effect are inevitably in device designs and their operations (Fig. 4). The tuning of piezoelectric properties at the interface introduces a new mechanism for designing new type of transistors. The effectiveness of piezotronic and piezo-phototronic effects at room temperature is another advantage for their practical applications in conventional electronic and photonic devices. The two-terminal piezotronic transistors are potentially useful for sensors, robotics and artificial intelligence. The piezo-phototronic effect could be utilized for improving the efficiency of commercial LEDs and solar cells. We anticipate that the piezotronic effect can tune spin transport, single electron transport and even topological insulators.

The introduction of self-powering is a paradigm shift for sensors. Most of the current sensors are passive and they donot function if there is no power. In the last 50 years, the road map of electronics has been focused on miniaturization following the Moore’s law. Solid state electronics has made it possible to integrate billions of components on a single chip, which sets the foundation for improving reliability, reducing size, increasing calculation speed, reducing power consumption and more. The second revolutionary advance is the development of wireless/mobile communication technology. By conjunction with optical fiber based information transfer and high performance computing, the development of internet has changed every corner of our life. Thirdly, in the last decade, adding functionality to mobile devices has closely linked to medical science and security, so that one can fully utilize modern sensor technology, big data, robotics and artificial intelligence. This is the era of functionality and intelligence. If we can make the sensors and possibly systems self-powered or partially self-powered, the systems can operate suitably and continuously without interruption. We anticipate that a paradigm shift from the passive sensor to the self-powered sensor would have the same significance as communication changing from wired to wireless, a game change! Regarding to whatever technology, one thing is true, no electronics works without electric power! Therefore, the last huge drive is to make devices self-powered if possible. The above discussions are summarized in Fig. 5 as four major technological drives toward information technology and IOT: miniaturized integrateability; wireless portability, functionality, and self-powerability.

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