香山科學會議

第448次学术讨论会

压电电子学和纳米发电机发展前沿

The Frontier of Piezotronics and Nanogenerators

基于压电势的纳米压电物理学的基础研究和相应的跨多学科应用

香山科学会议448次学术讨论会筹备组

2012年12月5日-7日

北京·香山饭店

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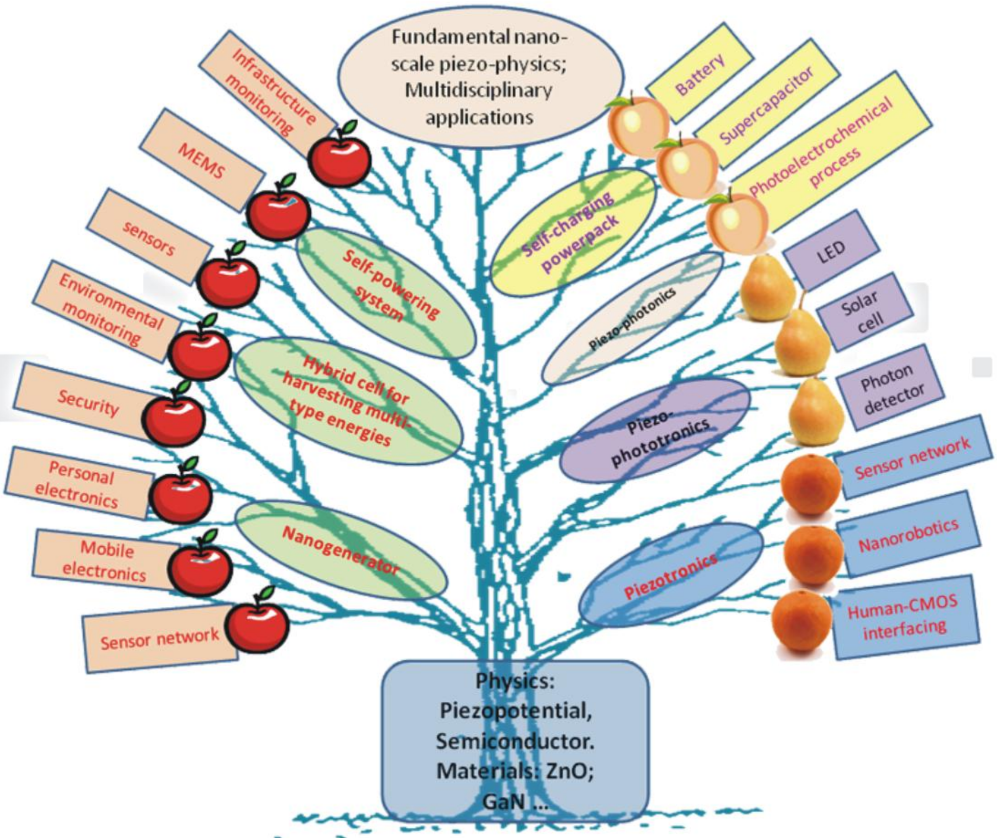

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压电电子学和纳米发电机发展前沿

The Frontier of Piezotronics and Nanogenerators

会议执行主席：

王中林、王占国、周军、秦勇

会议中心议题：

1、用于自供能系统的纳米发电机

2、纳米发电机及其理论

3、压电电子学

4、压电电子学和压电光电子学

Content

Brief Introduction 1

Schedule 5

Theme review report

Zhong Lin Wang
Nanogenerators and piezotronics-from fundamental science to unique applications..9

Central Topic: The Frontier of Piezotronics and Nanogenerators

Sang-Woo Kim
Transparent, flexible, stretchable nanogenerators based on multi-dimensional piezoelectric nanomaterials..11

Xudong Wang
Piezotronic effect in electrochemical processes and soar energy conversion.......13

Dapeng Yu
Bending strain modification on the emission energy and electronic fine structure of the ZnO nano/microwire – Additional evidences to support the piezotronic effect 16

Central topic 1：Nanogenerators for self-powered systems

Liwei Lin
Electrospun piezoelectric nanogenerators...17

M. Mouis, R. Hinchet, G. Ardila, L. Montès
Prospects of GaN nanowires for mechanical energy harvesting-characterization of piezoelectric properties and modelling...19

Keon Jae Lee
Flexible energy harvesting and storage systems 22

Seung-Wuk Lee
Virus-based piezoelectric energy generation 24

Fengru Fan
Flexible triboelectric generator and highly sensitive pressure sensor 29

Jun Zhou
Mechanical-electrical devices base on ZnO piezoelectric fine-wire 33

Yong Qin
High performance flexible nanogenerators 35

Central Topic 2：Nanogenerators and theory

Christian Falconi
Nano-piezoelectricity: from theory to high-performance devices 37

Max Migliorato
Linear and non linear piezoelectricity in novel semiconductor devices 40

Wanlin Guo
Novel mechanical-electric coupling effects in one- and two-dimensional nanostructures 43

Zhong Lin Wang and Yan Zhang
A new method to improve solar cell: Piezo-phototronics effect 44

Central Topic 3：Piezotronics

Gregory S. Rohrer
Influence of polarized interfaces on photochemical reactions 47

Yue Zhang
Nanoscale behavior and failure of ZnO nanomaterials and devices 50

Central Topic 4：Piezotronics and Piezo-phototronics

Chuan-Pu Liu and Nai-Jen Ku
Piezoelectronics and nanogenerators of obliquely-aligned InN nanorod arrays . 54

Hongqi Xu
Piezoelectric photovoltaics with core-shell nanowire arrays 57

Xuedong Bai
Piezotronic effect of nanowires probed by in-situ transmission electron microscopy 59

Jianhua Hao
Dual-modal emission source of thin-film structure based on piezo-phototronic effect 63

Youfan Hu
The applications of piezophototronics: from ZnO nanowire to GaN thin film 66

Qing Yang, Ying Liu, Wenhui Wang, Zhong Lin Wang
Piezo-phototronics: Principle and its applications in flexible optoelectronic and renewable energy 70

Caofeng Pan and Zhong Lin Wang
Enhanced Cu_2S/CdS coaxial nanowire solar cells by piezo-phototronic effect 73

Brief Introduction

The Xiangshan Science Conferences (XSSC) was initiated by the former State Science and Technology Commission, now the Ministry of Science and Technology of China (MOST). It was officially inaugurated in 1993 under the joint sponsorship of MOST and the Chinese Academy of Sciences (CAS). It also draws support from the National Natural Science Foundation of China, the Academic Divisions of CAS, the Chinese Academy of Engineering, the Ministry of Education of China, the former State Commission of Science, Technology & Industry for National Defense, the General Armament Department of the People's Liberation Army, China Association for Science and Technology, and Ministry of Health. XSSC promotes multi- or inter-disciplinary research, overall comprehensive studies, innovative thinking and knowledge innovation by creating a relaxed environment for academic exchanges, upholding the spirit of free academic discussion, and giving priority to scientific frontiers and their future development. The execute chairman will be responsible for the conference. Research Review, Thematic Talks and Further Discussion are three basic ways to explore new developments and future in science.

Ever since the wide range applications of laptop computers and cell phones, seeking of power sources for driving portable electronics is becoming increasingly important. The current technology mainly relies on rechargeable batteries. But in the near future, micro/nano-systems will be widely used in health monitoring, infrastructure and environmental monitoring, internet of things and defense technologies; the traditional batteries may not meet or may not be the choice as power sources for the following reasons. First, with the increasingly shrinkage in size, the size of the total micro/nano-systems could be largely dominated by the size of the battery rather than the devices. Second, the number and density of micro/nano-systems to be used for sensor network could be large, thus, replacing batteries for these mobile devices becoming challenging and even impractical. Lastly, the power needed to drive a micro/nano-system is rather small, in the range of micro- to milli-Watt range. To meet these technological challenges, active research is being carried out in nanogenerators for developing self-powering nanotechnology, aiming at harvesting energy from the environment to power the micro/nano-systems-based sensor network. Ever since the first nanogenerators were demonstrated by using piezoelectric effect in 2006, a great interest has been excited worldwide for developing various approaches for energy harvesting using piezoelectric, triboelectric, thermal electric and pyroelectric effects.

The fundamental principle of piezotronics was introduced by Zhong Lin Wang in 2007. Due to the polarization of ions in a crystal that has non-central symmetry in materials such as the wurtzite structured ZnO, GaN and InN, a piezoelectric potential *(piezopotential)* is created in the crystal by applying a stress. Owing to the simultaneous possession of piezoelectricity and semiconductor properties, the piezopotential created in the crystal has a strong effect on the carrier transport at the interface/junction. *Piezotronics* is about the devices fabricated by using the piezopotential as a “gate” voltage to tune/control charge carrier transport at a contact or junction. *Piezo-phototronic effect* is to use the piezopotential to control the carrier generation, transport, separation and/or recombination for improving the performance of optoelectronic devices, such as photon detector, solar cell and LED. The functionality offered by piezotroics and piezo-phototronics are complimentary to CMOS technology. An effective integration of piezotronic and piezo-phototronic devices with silicon-based CMOS technology, unique applications can be found in areas such as human-computer interfacing, sensing and actuating in nanorobotics, smart and personalized electronic signatures, smart MEMS/NEMS, nanorobotics and energy sciences.

In order to understand the fundamental science of piezotronics and nanogenerators and promote their technological applications in various fields, Xiangshan Science Conference will be held in Beijing Fragrant Hill Hotel on Dec. 5-7, 2012 with the theme of “The Frontier of Piezotronics and Nanogenerators”. Many internationally well known scientists from China, US, UK, France, Italy and Korea in the fields have been invited to deliver invited talks in the following major themes: nanogenerators for self-powered systems, nanogenerators and theory, piezotronics, and piezotronics and piezo-phototronics.

Executive Chairman of the conference:

Zhong Lin Wang	Professor	Beijing Institute of Nanoenergy and Nanosystems, CAS
Zhanguo Wang	Researcher	Institute of Semiconductors, CAS
Jun Zhou	Professor	Huazhong University of Science and Technology
Yong Qin	Professor	Lanzhou University

Theme review report:

Nanogenerators and piezotronics – from fundamental science to unique applications	Zhong Lin Wang

Central topic reports:

Transparent, flexible, stretchable nanogenerators based on multi-dimensional piezoelectric nanomaterials	Sang-Woo Kim
Piezotronic effect in electrochemical processes and solar energy conversion	Xudong Wang
Electrospun piezoelectric nanogenerators	Liwei Lin
Prospects of GaN nanowires for mechanical energy harvesting-characterization of piezoelectric properties and modeling	M. Mouis
Linear and non linear piezoelectricity in novel semiconductor devices	Max Migliorato

Xiangshan Science Conference advocates equal academia and encourage questioning extant theory to promote expressing different opinions and unconventional thinking without requirement to reach a consensus. This conference will be aimed at creating a multidisciplinary and loose environment in order that the past word and future development trend of science and cut-edge analysis in key issues and solutions can be freely discussed and new growth point disciplines can bi explored. The ration of discussion time to report time is generally 1-1.2:1.The conference requires speaking concisely, which should not present too much published achievement but the latest information, trends and new ideas based on past research.

Schedule

December 4, 2012 (Tuesday): Registration

Registration: 8:30-18:00

Reception Dinner: 18:00-20:30

December 5, 2012 (Wednesday)

Conference hall: Fragrance Containing Hall，Fragrant Hill Hotel

Executive Chairman: Zhong Lin Wang, Zhanguo Wang, Yongqin, Jun Zhou

8:30	Welcome address by Xiangshan Science Conference	Bingxin Yang
8:40	Opening Speech Self-introduction by everyone	Zhanguo Wang
9:00	*Coffee Break and Photo taken*	

Central Topic: The Frontier of Piezotronics and Nanogenerators

Executive Chairman: Zhanguo Wang, Zhong Lin Wang, Yong Qin, Jun Zhou

9:30	Nanogenerators and piezotronics – from fundamental science to unique applications	Zhong Lin Wang
10:15	Transparent, Flexible, Stretchable Nanogenerators based on multi-dimensional piezoelectric nanomaterials	Sang-Woo Kim
10:45	Piezotronic effect in electrochemical processes and soar energy conversion	Xudong Wang
11:15	Bending strain modification on the emission energy and electronic fine structure of the ZnO nano/microwire – Additional evidences to support the piezotronic effect	Dapeng Yu
11:45	Discussion *Free speech, each time no more than 5 minutes*	
12:15	*Lunch*	

Central Topic：Nanogenerators for self-powered systems

Executive Chairman: Zhong Lin Wang, Zhanguo Wang, Yong Qin, Jun Zhou

14:00	Electrospun piezoelectric nanogenerators	Liwei Lin
14:30	Prospects of GaN nanowires for mechanical energy harvesting - characterization of piezoelectric properties and modelling	Mireille Mouis
15:00	Flexible energy harvesting and storage systems	Keon Jae Lee
15:30	*Coffee Break*	

Central Topic：Nanogenerators for self-powered systems

Executive Chairman: Yong Qin, Zhanguo Wang, Zhong Lin Wang, Jun Zhou

15:45	Virus-based piezoelectric energy generation	Seung-Wuk Lee
16:15	Flexible triboelectric generator and highly sensitive pressure sensor	Fengru Fan
16:40	Mechanical-electrical devices base on ZnO piezoelectric fine-wire	Jun Zhou
17:05	High performance flexible nanogenerators	Yong Qin
17:30	Discussion *Free speech, each time no more than 5 minutes*	
18:30	*Banquet(Multi-Functional Hall)*	

December 6, 2012 (Thursday)

Conference hall: Fragrance Containing Hall，Fragrant Hill Hotel

Central Topic：Nanogenerators and theory

Executive Chairman: Jun Zhou, Zhanguo Wang, Zhong Lin Wang, Yong Qin

8:30	Nano-piezoelectricity: from theory to high-performance devices	Christian Falconi
9:00	Linear and non linear piezoelectricity in novel semiconductor devices	Max Migliorato
9:30	Novel mechanical-electric coupling effects in one- and two-dimensional nanostructures	Wanlin Guo

9:55	A new method to improve solar cell: Piezo-phototronics effect	Yan Zhang
10:20	*Coffee Break*	

Central Topic：Piezotronics

Executive Chairman: Zhanguo Wang, Zhong Lin Wang, Yong Qin, Jun Zhou

10:35	Influence of polarized interfaces on photochemical reactions	Gregory S. Rohrer
11:05	Nanoscale behavior and Failure of ZnO nanomaterials and devices	Yue Zhang
11:35	Discussion *Free speech, each time no more than 5 minutes*	
12:15	*Lunch*	

Central Topic：Piezotronics and Piezo-phototronics

Executive Chairman: Yong Qin, Zhanguo Wang, Zhong Lin Wang, Jun Zhou

14:00	Piezoelectronics and nanogenerators of obliquely-aligned InN nanorod arrays	Chuan-Pu Liu
14:30	Piezoelectric photovoltaics with Core-Shell nanowire arrays	Hongqi Xu
15:00	Piezotronic effect of nanowires probed by in-situ transmission	Xuedong Bai
15:25	*Coffee Break*	

Central Topic：Piezotronics and Piezo-phototronics

Executive Chairman: Jun Zhou, Zhanguo Wang, Zhong Lin Wang, Yong Qin

15:40	Dual-modal emission source of thin-film structure based on piezo-phototronic effect	Jianhua Hao
16:05	The applications of piezophototronics: from ZnO nanowire to GaN thin film	Youfan Hu
16:30	Piezo-phototronics: Principle and its applications in flexible optoelectronic and renewable energy	Qing Yang
16:55	Enhanced Cu_2S/CdS coaxial nanowire solar cells by piezo-phototronic effect	Caofeng Pan

17:20 Discussion

Free speech, each time no more than 5 minutes

18:30 *Dinner*

December 7, 2012 (Friday)

会议室：蕴香厅

执行主席：王占国、王中林、周军、秦勇

中心议题：重大科学前沿问题及潜在突破方向综合讨论

8:30	纳米发电机的技术应用	王中林
9:15	讨论（自由发言，每人每次不超过 5 分钟，可以多次发言）	
10:30	休息	
10:45	压电电子学重大科学前沿问题及可能的潜在应用	王中林
11:30	讨论（自由发言，每人每次不超过 5 分钟，可以多次发言）	
12:15	午餐	

Nanogenerators and piezotronics － from fundamental science to unique applications

Zhong Lin Wang

Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing

School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta USA

Developing wireless nanodevices and nanosystems is of critical importance for sensing, medical science, environmental/infrastructure monitoring, defense technology and even personal electronics. It is highly desirable for wireless devices to be self-powered without using battery. Nanogenerators (NGs) have been developed based on piezoelectric, trioboelectric and pyroelectric effect, aiming at building self-sufficient power sources for mico/nano-systems. The output of the nanogenerators now is high enough to drive a wireless sensor system and charge a battery for a cell phone, and they are becoming a vital technology for sustainable, independent and maintenance free operation of micro/nano-systems and mobile/portable electronics. This talk will focus on the fundamentals and novel applications of NGs.

For wurtzite and zinc blende structures that have non-central symmetry, such as ZnO, GaN and InN, a piezoelectric potential (*piezopotential*) is created in the crystal by applying a strain. Such piezopotential can serve as a “gate” voltage that can effectively tune/control the charge transport across an interface/junction; electronics fabricated based on such a mechanism is coined as *piezotronics*, with applications in force/pressure triggered/controlled electronic devices, sensors, logic units and memory. By using the piezotronic effect, we show that the optoelectronc devices fabricated using wurtzite materials can have superior performance as solar cell, photon detector and light emitting diode. Piezotronics is likely to serve as a “mechanosensation” for directly interfacing biomechanical action with silicon based technology and active flexible electronics. This lecture will focus on the fundamental science and novel applications of piezotronics in sensors, touch pad technology, functional devices and energy science.

References:

1. 《自驱动系统中的纳米发电机》，王中林著，科学出版社，2012
2. 《压电电子学与压电光电子学》，王中林著，科学出版社，2012

Transparent, Flexible, Stretchable Nanogenerators Based on Multi-dimensional Piezoelectric Nanomaterials

Sang-Woo Kim

School of Advanced Materials Science and Engineering, SKKU Advanced Institute of Nanotechnology, Sungkyunkwan University (SKKU), Republic of Korea

Nanogenerators based on piezoelectric semiconductor nanostructures are very promising for the miniaturization of power packages and self-powering of nanosystems used in implantable bio-sensing, environmental monitoring, and personal electronics. New strategies for the dramatic enhancement of the power generation to commercialize the nanogenerators are indispensable for not only self-powered body-implantable nano/micro-systems, but also portable devices such as commercial LCDs, LEDs, etc with low operating power consumption. For realizing highly efficient nanogenerators, morphology control of piezoelectric semiconducting nanostructures is one of the most important issues.

Graphene could be a platform to serve as a substrate for both morphology control and direct use of electrodes due to its ideal monolayer flatness with π electrons. As a first issue systematic studies regarding vertically well-aligned ZnO nanowires and nanowalls obtained by controlling Au catalyst thickness and growth time without inflicting significant thermal damage on the graphene layer during thermal chemical vapor deposition of ZnO at high temperature of about 900℃ will be presented. Further, I demonstrate that a piezoelectric nanogenerator that was fabricated from the vertically aligned nanowire-nanowall ZnO hybrid/graphene structure generates a new type of direct current through the specific electron dynamics in the nanowire-nanowall hybrid. As a second issue, the first use of thermally stable cellulose paper and stretchable fiber as substrates for foldable, stretchable and thermally stable piezoelectric nanogenerators to overcome the problem of unstable electrical output from plastic-based nanogenerators due to thermal induced-stress.

Enhancing the output power of a piezoelectric nanogenerator is essential in applications as a sustainable power source for wireless sensors and microelectronics. As a third issue, I will present a novel approach that greatly enhances piezoelectric power generation by introducing a p-type polymer layer on a piezoelectric semiconducting thin film. Holes at the film surface greatly reduce the piezoelectric potential screening effect caused by free electrons in a piezoelectric semiconducting material. Furthermore, additional carriers from a conducting polymer and shift in the Fermi level help in increasing the power output. P3HT was used as a p-type polymer on piezoelectric semiconducting ZnO thin film, and PCBM was added to P3HT to improve carrier transport. The ZnO/P3HT:PCBM-assembled piezoelectric power generator demonstrated 18-fold enhancement in the output voltage, and tripled the current, relative to a power generator with ZnO only at a strain of 0.068%. The overall output power density exceeded 0.88 W/cm^3, and the average power conversion efficiency was up to 18%. This approach offers a breakthrough in realizing a high-performance flexible piezoelectric energy harvester for self-powered electronics.

Additionally, I will present a flexible hybrid architecture designed to harvest mechanical and solar energies, either separately or simultaneously. By using ZnO with intrinsically coupled piezoelectric and n-type conductive properties, a flexible hybrid energy scavenger is naturally created without any crosstalk and an additional assembling process, thus totally differing from a simple integration of two different energy generators. The piezoelectric output signals from our hybrid cells are originally AC type, but they can be controlled to DC-like type by tailoring mechanical straining processes both in a dark and under a light illumination. Based on such controllability of a piezoelectric output behavior, the performance of the hybrid cell is synergistically enhanced by the contribution of piezoelectric generator, compared with the output power generated independently from the solar cell part under normal indoor level of illumination.

Piezotronic Effect in Electrochemical Processes and Soar Energy Conversion

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The piezotronic effect describes the coupling of piezoelectric polarization and the intrinsic electric field in a space charge region for the purpose of tuning charge transport behaviors of semiconductor materials and devices. The bases of modern technology (information processing, energy conversion and energy storage systems) all make use of how electrons flow through a circuit. In a heterojuction, the effect of the energy state discontinuity is profound, with the electronic conduction properties taking on a character that is exquisitely sensitive to the magnitude of the discontinuity. It is via this means that the electronic properties of the ensemble can be dominated by the electron properties of the interface. It then follows axiomatically that the electronic properties of the ensemble can be tailored by precise modification of the interfacial energetics. To that end the piezotronic effect has a significant influence on the heterostructure's electronic properties, which requires either one of the materials composing the heterjunction must be piezoelectric or a material within the near vicinity must be piezoelectric. It is thus advantageous that many of the materials used in the heterojunction devices listed previously are themselves piezoelectric, these include AlN, GaN, ZnO, CdS, SiC etc. The precise application of mechanical deformation to the heterostructure results in a piezoelectric potential which can tailor the electronic properties of the interface. The merit of this approach is that it allows for a device to be composed of materials which are still individually optimized for their specific bulk electronic properties while allowing the independent optimization of their heterointerface.

We first discuss barrier-height engineering of a heterogeneous semiconductor interface manifested by a PEC half-cell, where the influence of the remnant piezoelectric polarization on the photocurrent of water splitting was studied as a function of strain applied to the anode. The PEC anode consists of a thin film of piezoelectric ZnO deposited on a transparent ITO electrode. Photocurrent was enhanced when the ZnO anode was subjected to a tensile strain, which was attributed to the barrier height reduction at the ITO-ZnO interface induced by remnant piezoelectric polarization. Effective barrier height change demonstrated a linear relation with mechanical strain. The piezotronic effect has also been applied to the ZnO/PbS quantum dot (QD) heterojunction for engineering the interfacial band structure and depletion region. This method escalated the solar energy efficiency by 30% when a relatively small strain -0.25% was applied to the QDSC under low-intensity illumination. The enhancement of short circuit current and efficiency was mostly due to the expansion of depletion region in PbS, as a result of piezoelectric polarization-induced charge redistribution at the ZnO/PbS interface. Change of open circuit voltage was less significant and consisted of two components: photocurrent-related quasi Fermi level shifting and remnant piezopotential at the ZnO/ITO interface. The PV performance became less responsive to piezoelectric polarization under higher illumination intensity due to the compensation from trapped photoexcited charges at the interface. Both approaches endow us new insights for improving the efficiency of solar energy conversion by piezotronic band structure engineering without altering the interface structure or chemistry.

In addition to band structure engineering, piezoelectric potential can be directly applied to electrochemical processes – piezocatalysis. This provides a direct pathway for mechanical to chemical energy conversion. By straining a piezoelectric PMN-PT [$Pb(Mg_{1/3}Nb_{2/3})O_3$-$32PbTiO_3$] beam in water, we experimentally demonstrated that piezoelectric potential can raise the energy of electrons at the surface of piezoelectric material (or electrode) to such a level that is sufficient to drive proton reduction reactions within its immediate vicinity. The hydrogen evolution rate was exponentially dependent upon the magnitude of piezoelectric potential, consistent with the application of the Bulter-Volmer relationship. The piezocatalytic efficiency (~0.2% – ~2.4%) was found to depend sensitively upon the length of straining state, consistent with the limitations imposed by electrochemical reaction kinetics in the DI water environment. $NaNO_3$ electrolyte was used to investigate the effect of capacitive charging losses, which were found to be substantial and detrimental to the piezocatalytic efficiency. The results embolden a new and promising strategy for mechanically tailoring interface energetics and chemistry.

Bending Strain modification on the emission energy and electronic fine structure of the ZnO nano/microwire － Additional evidences to support the piezotronic effect

Dapeng Yu
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Piezotronic effect in nanowire structures has led to the discovery of nanowire nanogenerators, which is approaching inductrial application scaling. Here we provide additional evidence to support the Piezotronic effect which is based on the bending deformation of the semiconductor nanowires. High special/energy resolution cathodoluminescence (CL) spectroscopy enables us to make precise investigation on the optical/electronic fine structures in nanostructures. The linear distribution of strain gradient from tensile to compression in bent ZnO nano/microwires provides ideal conditions to address the modification of the electronic structures by strain in semiconductor materials. Radial line scan of the CL spectroscopy along bent ZnO wires at liquid helium temperature shows very fine excitonic emission structures, which demonstrates systematic red shift towards the increase of tensile strain, and blue shift as well as excitonic peak splitting towards the increase of compressive strain. Strain-gradient is found to dominate the overall red-shift of the emission energy at a pure bending configuration.

Electrospun Piezoelectric Nanogenerators

Liwei Lin
Department of Mechanical Engineering, UC Berkeley, USA

A self-powering system that harvests its operating energy directly from the environment/body movement is an attractive proposition for sensing, personal electronics and security applications. Developments in the miniaturization of portable and wireless devices have created large interests for new power sources that are scalable with the size of the systems as well as viable to provide power without a recharging process or replacement. Recent work in the field of nanomaterials towards engineering effective materials and structures, have shown that such energy sources could be realized by scavenging energy from ambient environments (solar, thermal, mechanical vibration, etc.). In particular, the use of piezoelectric generators as a robust and simple solution for mechanical energy harvesting has attracted lots of attention. It could potentially meet both requirements of energy independence and scalability. First reports of energy scavenging using zinc oxide (ZnO) nanowires have drawn a tremendous interest. By coupling the semiconducting and piezoelectric properties, mechanical strains could be converted into electricity using nanoscale structures. Numerous research groups have reported research results in the field of nanogenerators and a multitude of different approaches have been proposed. Based on their physical forms they can be categorized as film-based, nanowire-based and nanofiber-based nanogenerators. Due to their simplicity of fabrication by spin-on or thin-film deposition methods, film based versions are currently most readily available form of nanogenerators. A created strain due to the bending or compression of the film is the origin of the energy creation. Nanowire-based nanogenerators are typically made out of a semiconducting material such as ZnO, ZnS, GaN, and CdS. These piezoelectric materials build up an internal potential when strained by an AFM tip, zig-zag electrodes or a compliant substrate. In addition to the inorganic nanowires and thin films, the third group of nanogenerators is based on nanofibers. Among the materials that are often applied is PZT, which is a ceramic material that exhibits an exceptionally efficient piezoelectric energy conversion. Nanofiber-based nanogenerators using organic materials have recently been introduced. Flexibility, lightweight, biocompatibility and availability in various thicknesses and forms make them a particularly interesting candidate for wearable or implantable energy harvesting devices.

This talk will focus on recent results of single and arrayed nanogenerators made of polyvinylidene fluoride (PVDF) via the in-situ stretching and poling process by means of electrospinning. Results show that energy conversion efficiency of nanogenerator could be 10 times higher than large scale structures made of the same material. Furthermore, electrospinning of fibers can be applied for numerous materials with high controllability and large throughput. The obtained fibers, often fabricated from PVDF or PZT in the case of nanogenerators, are highly flexible and have high energy conversion rates. This makes them well suited for integration in implantable and/or flexible devices, textile applications, sound driven generators etc. The tremendous variety for fiber based nanogenerators makes them promising research topics as various groups have developed prototypes of nanogenerators. Although these results proof the feasibility of the fabrication of nanogenerators, further developments are required before fiber based nanogenerators could be used in practical applications. Nevertheless, the capability of demonstrating electrospun nanofiber as possible power generator could have a profound impact in various application areas, including energy harvesting, strain sensing, and actuation sources.

Key words: Electrospinning, nanofiber, nanogenerator, piezoelectric

Prospects of GaN nanowires for mechanical energy harvesting - characterization of piezoelectric properties and modelling

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With this presentation, our goal is to show that mechanical harvesting by semiconducting nanostructures is not necessarily a simple extrapolation to nanoscale of the MEMS approaches. Indeed, the mechanical energy available in usual environment, such as from body motion, blood pressure vibration, machine vibrations or shocks is mainly generated at low frequencies or randomly. In order to harvest this energy effectively with nanoscale structures such as piezoelectric nanowires, it is necessary to reconsider the operation principle of the harvesting device core itself. [1] Some experimental prototypes have already been demonstrated in the literature, using ZnO [2], PZT [3], PVDF [4] or GaN [5]. In a second section, we will explain in more details what can be expected from such nanowire based harvesting device, based on simulation. [6] General optimization guidelines will be provided. Scaling trends will be given, showing that scaling to NEMS structures allows similar energy to be harvested with smaller forces, and that the theoretical energy that can be extracted is compatible with that required by autonomous systems. However, the properties of most piezoelectric materials are rather badly known, especially at nanoscale, where they must often be inferred, at best from thin film properties. There is thus a need for precise and reliable characterization. ZnO and PZT are the favourites among the usual piezoelectric materials in terms of expected efficiency at a given scale. Despite their smaller piezoelectric properties, GaN and related materials feature interesting properties for integrated applications. Near field characterization was used to probe their mechanical, piezoelectric and piezotronic properties. The AFM tip was used to force a strain within the nanowire and to measure, at the same time, the generated voltage or current. [7, 8] For small diameter nanowires, transverse forces were used. Measurements were carried out on GaN nanowires grown by the Plasma-Assisted-MBE technique on (111) Silicon wafers [9]. Experimental results will be shown and qualitatively explained with the support of multi-physics simulation. It was observed experimentally that the piezoelectric potential generated under bending could be enhanced by engineering the nanowire structure with an axial GaN/AlN heterostructuration.[7] This result has very important implications in terms of applications.

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[1] G. Ardila, R. Hinchet, M. Mouis, L. Montès. Scaling Prospects in Mechanical Energy Harvesting using Piezoelectric Nanostructures. IEEE International Semiconductor Conference Dresden-Grenoble, Sept. 2012, 24-26.

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Flexible Energy Harvesting and Storage Systems

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Energy harvesting technologies converting external sources (such as thermal energy, vibration and mechanical energy from the nature sources of wind, waves or animal movements) into electrical energy is recently a highly demanding issue in the materials science community for making sustainable green environments. In particular, fabrication of usable nanogenerator attract the attention of many researchers because it can scavenge even the biomechanical energy inside the human body (such as heart beat, blood flow, muscle stretching, or eye blinking) by converging harvesting technology with implantable bio-devices. Herein, we describe two separate procedures suitable for generating and printing a lead-free $BaTiO_3$ based thin film nanogenerator and nanocomposite generator on plastic substrates to overcome limitations appeared in conventional flexible ferroelectric devices. First, flexible thin film nanogenerator was fabricated by transferring the $BaTiO_3$ thin film from bulk substrates and its piezoelectric properties of ferroelectric devices were characterized. Second, we report the nanocomposite generator (NCG) for achieving a simple, low-cost, and large area fabrication based on $BaTiO_3$ nanoparticles (NPs) and graphitic carbons (CNT or RGO). From the results, we demonstrate the highly efficient and stable performance of new forms of nanogenerator and the integration of bio-eco-compatible ferroelectric materials may enable innovative opportunities for artificial skin and energy harvesting system. Finally, an all-solid-state bendable LIB is demonstrated on plastic substrate using a new universal transfer approach based on sacrificial mica substrates. This flexible LIB combining with nanogenerator will realize all flexible energy harvesting and storage system in the future.

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Virus-Based Piezoelectric Energy Generation

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Research Summary

The development of novel energy sources that do not emit carbon dioxide is one of today's greatest global challenges. The scale of this challenge is so immense that the incremental improvements provided by existing scientific and engineering approaches are not sufficient to secure our energy future. Meeting these rising energy demands will require a new paradigm for generating, storing, and using energy with performance levels exceeding those of current technologies. Recently, we developed novel, scalable energy converting biomaterials using genetically engineered M13 bacteriophages (viruses). The M13 virus possesses features that make it very attractive as a building block for energy generating materials (Fig.1). M13 is a long-rod shaped bacterial virus composed of a single-stranded DNA that is encapsulated by 2700 copies of the major coat protein, pVIII. pVIII has an alpha helical structure with a dipole in the carboxyl- to amino-terminal direction; covering the viral surface periodically with 5-fold helical symmetry and no inversion center. This structural

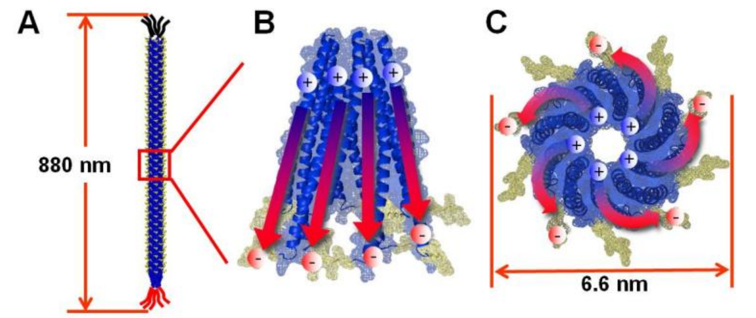

Fig.1 Schematic diagram of piezoelectric M13 phage structure. (A) The phage is 880 nm in length and 6.6 nm in diameter. The phage is covered by ~2700 copies of pVIII proteins and has 5 copies of pIII (red-line)and pIX proteins (black-line) at both ends. (B) Side view of the aligned charged dipole structure from ten major coat proteins in the phage showing the α-helical structures with dipole moments pointing from the N-terminus to C-terminus. (C) Vertical cross-sectional view of the phage showing the 5-fold rotational and 2-fold screw symmetry. The colored arrows represent the coat protein dipoles from positive (blue) to negative (red).

arrangement enables M13 to act as a piezoelectric nanofiber that can convert mechanical energy to electric energy and *vice versa*. In addition, M13 can replicate in large quantities through amplification in bacteria. Due to its monodisperse long-rod shape, M13 can self-assemble into periodically ordered two- and three-dimensional structures. Recently, we verified the molecular level piezoelectric properties using piezoresponse force microscopy techniques and fabricate the prototype of the devices.

In-plane phage piezoelectric properties: We characterized the in-plane piezoelectric properties of the phage using PFM techniques. We first fabricated a monolayer of micro patterned phage thin films on a Au substrate through PDMS assisted self-assembly processes. We then characterized the in-plane piezoelectric response of the monolayer phage thin films using a direction-dependent PFM experiment (Fig. 2A). AFM topography images and height profiles show that the phage are uniformly covered on the cysteamine patterned areas with a 1 μm width and an ~8 nm thickness. AFM phase images showed an in-plane piezoelectric response in the axial direction ($d_{14\ parallel}$) of the phage when scanned parallel to the phage length. The bright and dark contrast within the AFM phase image (Fig. 2B) comes from the randomly oriented directional phage dipoles in the monolayer phage thin film. In order to characterize the direction dependence of the piezoelectric response of the phage, we also performed in-plane PFM measurements ($d_{14\ vertical}$) by rotating the sample 90 degrees to scan the phage film in the vertical direction. In the vertical scanning direction, we could not observe the similar phase contrast in the AFM phase image (Fig. 2C) compared with what was

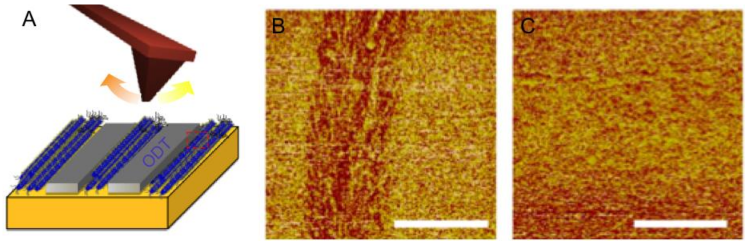

Fig.2 In-plane piezoresponse of phage film. (A) Schematic of in-plane piezoresponse measurement. Single layer of phages were assembled on ODT/Cysteamine-patterned Au substrate. (B) In-plane PFM phase signal. The torsional motion was detected while applying AC signal to the AFM tip (Fig. 2A, left). (C) In-plane PFM phase signal of 90°-rotated sample. The same are as Fig 2D was taken after rotating the sample by 90° while maintaining the scanning direction. Scale bars are 1 μm.

observed in the parallel scanning direction. We believe that the observed reduced phase contrast was caused by the radial arrangement of the pVIII major coat protein through the phage body which canceled the phage piezoelectric responses in the lateral PFM measurement.

Characterization of out-of-plane phage piezoelectric properties: We characterized the out-of-plane piezoelectric response of multi-layer phage films. We first grew self-assembled phage films on Au substrates (Fig.3A) and then quantitatively measured the piezoelectric responses of the self-assembled phage films. With the stepwise increase of applied AC voltage from 1 to 10 V applied to the phage film, we could observe a corresponding stepwise increase in amplitude throughout the sample. The phage film exhibited an electromechanical coupling coefficient of d_{33} = 7.72 pm/V. As for the control, we also measured PPLN and collagen, which exhibit d_{33} of 13.22 pm/V, and 1.14 pm/V respectively (Fig. 3B and C). Through the genetic engineering of phage with different amounts of negative charge incorporation from one negative charge to four negative charges on

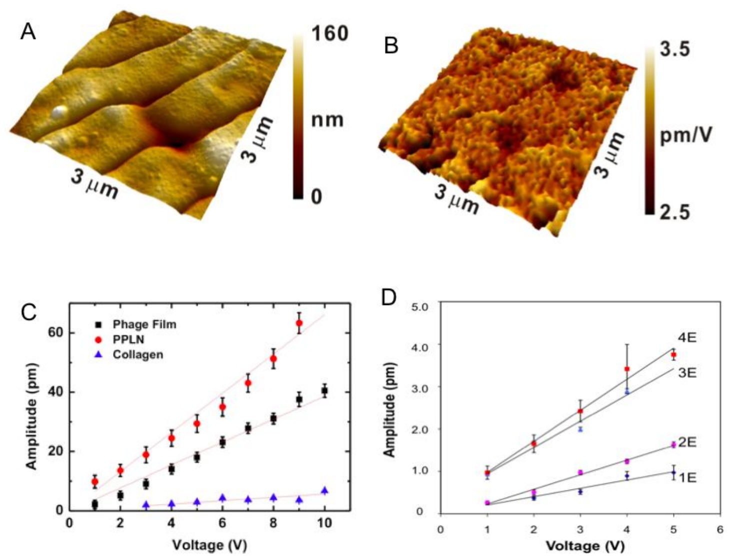

Fig.3 Out of plan piezoelectric properties of the phage. (A) AFM topography image of a region (3um x 3um) of highly ordered phages. (B) The effective piezoelectric coefficient deff image of the same region as (A). The d_{eff} shows relatively lower value on the grooves. The piezoresponse of phage film in comparison to periodically poled lithium niobate (PPLN) and collagen film. We obtained the effective piezoelectric coefficient d_{eff} ~ 3.86 pm/V for the phage film. The PPLN and collagen showed d_{eff} ~ 6.61 pm/V and ~0.57 pm/V, respectively. (D) Trends of the piezoelectric response dependent on additional negative surface charge incorporation from one glutamate (1E) upto four glutamate (4E)

each pVII coat protein (1E, 2E, 3E and 4E; E=glutamate), we could obtain an increased strength of the piezoelectric response (Fig. 3D).

Piezoelectric energy generation devices: Using 4E-phage films, we fabricated phage-based piezoelectric energy generators. The phage-based generator consisted of a ~1 cm^2 multilayer phage film sandwiched between two metal electrodes (Fig. 4A). Periodic mechanical loads were applied to the phage-based piezoelectric generators using a dynamic mechanical test system and the resultant electrical signal output was characterized by measuring the short-circuit current, open-circuit voltage, and charge (Fig. 4B). When applying a rectangular compressive load (Fig. 4C) at 6 sec intervals, the signal showed two peaks of reverse polarity which corresponded to the pressing and releasing motion of the mechanical test system. From this experiment, we typically observed peak values of ~4 nA for the short-circuit current (Fig. 4D). This peak current level could be tuned by adjusting the strain and strain rate (Fig. 4E & F). The peak current increased

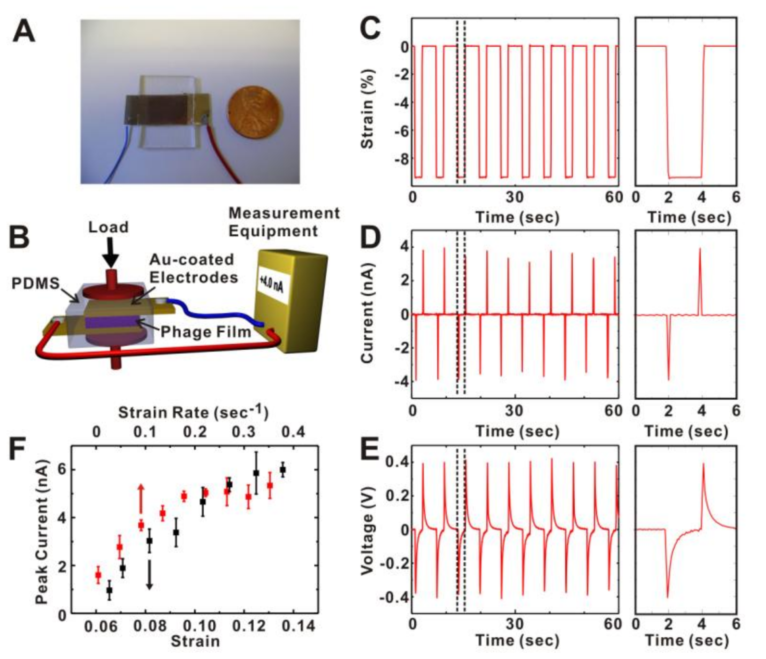

Fig.4. Characterization of phage-based piezoelectric energy generator. (A) Photograph of a phage-based generator. (B) Schematic diagram of the piezoelectric electric energy generation measurement setup. A mechanical load was applied to the device while monitoring the voltage and current. (C) Applied mechanical strain onto the device, (D) short-circuit current signal, and (E) open-circuit voltage signal from the phage-based generator. The two vertical dotted lines highlight the instance of pressing (left line) and releasing (right line) of the load. (F) Dependence of the phage-based generator peak current amplitude on strain and strain rate. Strain is defined as the ratio of the device vertical displacement to the initial device thickness.

linearly for strains from 0.06 to 0.1 and strain rates from 0 to 0.4 sec^{-1}. As a result, we were able to enhance the current output up to 6 nA.

In summary, we have developed a piezoelectric energy converting biomaterial from a self-replicating bacterial virus, M13 phage. We verified the chemical and physical structure-dependent biopiezoelectric properties of the phage using piezoresponsive microscopy techniques and fabricated piezoelectric generators to produce electrical energy up to 6 nA and 400 mV. Future improvement of our phage-based energy generator will be the development of parallel connected devices to achieve high electric energy output and the combination of microfabricated electrodes and self-assembly of phage thin films to improve efficiency. Additional modifications to enhance phage dipole strength, such as chemical modification or inorganic dopant incorporation will be developed. As a result, we believe the development of our phage-based piezoelectric nanofibril material could play an important role in addressing future energy challenges.

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Flexible Triboelectric Generator and Highly Sensitive Pressure Sensor

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Energy harvesting and conversion devices using nanotechnology have received increasing interest recently because they are likely to play a vital role in building and driving self-powered nanodevices and nanosystems. Since the first piezoelectric ZnO nanogenerator was reported in 2006, various nanogenerators (NGs) based on functional piezoelectric materials have been demonstrated [1-3]. They show high power output performance owing to their special nature and reasonable device design. In particular, such smart devices have been confirmed that can drive a commercial LED, small liquid crystal display, and even self-powered wireless system. Generally speaking, all the approaches that can generate electric charges, separate positive and negative charges, and use the potential generated by them to drive a flow of free electros can be the selection for electric generators, including electromagnetic, piezoelectric, pyroelectric, and even electrostatic effects.

The general physical process for energy conversion has three important steps: charge generation, charge separation, and charge flow. These steps were accomplished in piezoelectric nanogenerators (NGs) by employing the piezoelectric potential created under strain. Alternatively, triboelectric associated electrostatic phenomena are most common phenomena in our daily life, from walking to driving, but it has been ignored as an energy source for electricity. It will be practical if we can use the electric charges/potential generated by a tribological process to generate electricity.

Recently, we have developed a flexible triboelectric generator (TEG) using all-polymer based material [4]. By stacking two thin polymer films made of Kapton and polyester (PET), a charge generation, separation, and induction process can be achieved through a mechanical deformation of the polymer films as a result of the triboelectric effect. A typical TEG is fabricated with two polymer sheets made of materials having distinctly different triboelectric characteristics, with metal films deposited on the top and bottom of the assembled structure. Once subjected to mechanical deformation, a friction between the two films, owing to the nano-scale surface roughness, generates equal amount but opposite signs of charges at two sides, respectively. Thus, a triboelectric potential layer is formed at the interface region, which serves as a charge "pump" for driving the flow of electrons in the external load if there is a variation in the capacitance of the system. Such a flexible polymer TEG gives an output voltage of up to 3.3 V at a power density of ~10.4 mW/cm^3.

The integration of flexible and transparent characteristics is an important component in the new organic electronic and optoelectronic devices. Therefore, building flexible transparent energy conversion and storage units plays a key role in realizing fully flexible and transparent devices. To achieve this, through rational design, we demonstrated a new high-output, flexible and transparent NG [5]. Compared with the above-described work, three approaches were employed in this research: (i) replacing Kapton film with transparent PDMS film, (ii) replacing Au electrodes with transparent ITO electrodes, then the entire structure is flexible and transparent, and (iii) fabricating various PDMS pattern arrays to enhance the friction effect, resulting in a high-output generator. We have fabricated three types of regular and uniform polymer patterned arrays (line, cube and pyramid) to improve the efficiency of the NG. The power generation of the pyramid-featured device far surpassed that exhibited by the unstructured films, and gave an output voltage of up to 18 V at a current density of ~0.13 A/cm^2, which is four times as high as that of the previously reported triboelectric generator.

Furthermore, the as-prepared NG can be applied as a self-powered pressure sensor for sensing a water droplet (8 mg, ~3.6 Pa in contact pressure) and a falling feather (20 mg, ~0.4 Pa in contact pressure) with a low-end detection limit of ~13 mPa. Our pressure sensor has a different principle compared with reported plastic pressure sensor. First, our sensor is a self-powered device and based on the power generation rather than the capacitance change induced by pressure. Second, the response signal of our sensor is a sharp peak instead of a state curve, which exhibits a fast response and no hysteresis with the fast switching of the sensor. The voltage output signal has no significant degradation up to 10 Hz, which demonstrates the fast and deterministic response of the pressure sensor.

The flexible triboelectric generator is a simple, low-cost, readily scalable device that can convert random mechanical energy in our living environment into electricity using conventional flexible/foldable polymer materials. This technology has a great potential for scaling up to power mobile and personal electronics used in environmental monitoring, personal medical networks, electronic emergency equipment and other self-powered systems.

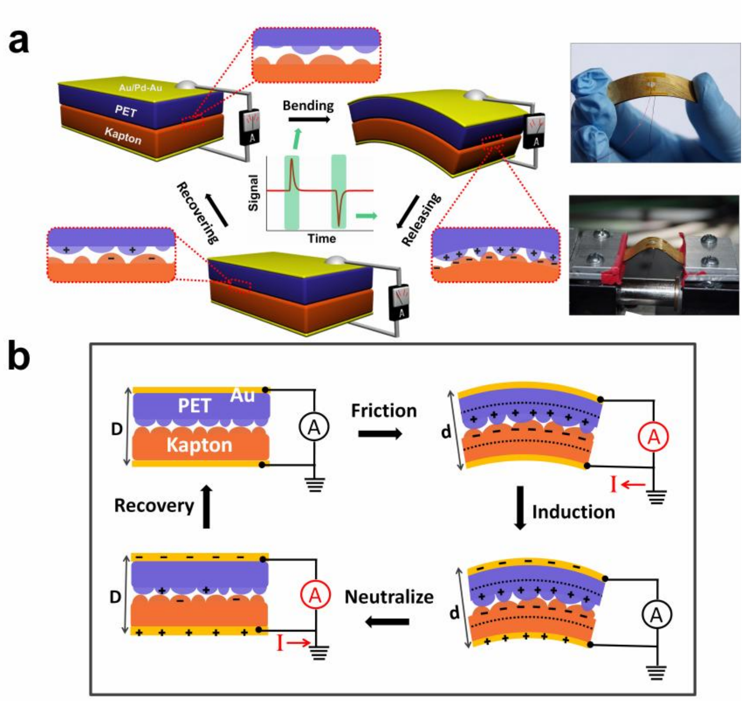

Fig.1 Schematic illustration of the structure and working principle of the triboelectric generator [4].

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Mechanical-electrical devices base on ZnO piezoelectric fine-wire

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Piezotronics is a new field integrating piezoelectric effect into nanoelectronics, the working principle of which relies on the piezoelectric potential created inside a nanowire under straining, which can serve as the gate voltage for fabricating a new type of device. We firstly demonstrated a mechanical-electrical trigger using a ZnO piezoelectric fine-wire (PFW) (microwire, nanowire). Once subjected to mechanical impact, a bent PFW creates a voltage drop across its width, with the tensile and compressive surfaces showing positive and negative voltages (Fig.1), respectively. The voltage and current created by the piezoelectric effect could trigger an external electronic system, thus, the impact force/pressure can be detected.

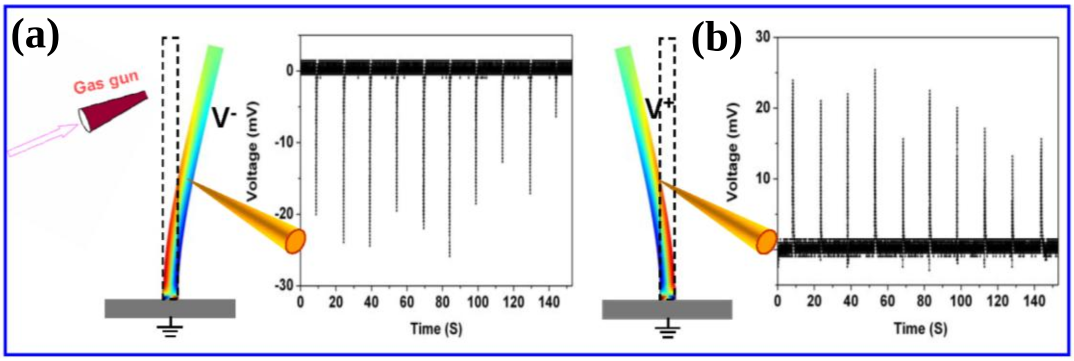

Fig.1 Self-generated voltages as directional triggers based on a single piezoelectric wire. Direct measurements of the asymmetric voltage distribution on the tensile and compressive side surfaces of a ZnO wire. (**a**) By placing a metal tip at the right-hand side and blowing Ar pulses at the left-hand side, negative voltage peaks of ~25 mV were observed once the pulse was on. (**b**) By quickly pushing and releasing the wire at the right-hand side by a metal tip, a positive voltage peak of ~25 mV was observed for each cycle of the deflection. The frequency of the deflection was once every 15 s.

In addition, strain sensors based on individual ZnO PFWs have been demonstrated (Fig.2). The PFW has Schottky contacts at its two ends but with distinctly different barrier heights. The I-V characteristic is highly sensitive to strain due to mainly the change in Schottky barrier height (SBH), which scales linear with strain. The change in SBH is suggested owing to the strain induced band structure change and piezoelectric effect. The experimental data can be well described by the thermionic emission-diffusion model. A gauge factor of as high as 1250 has been demonstrated.

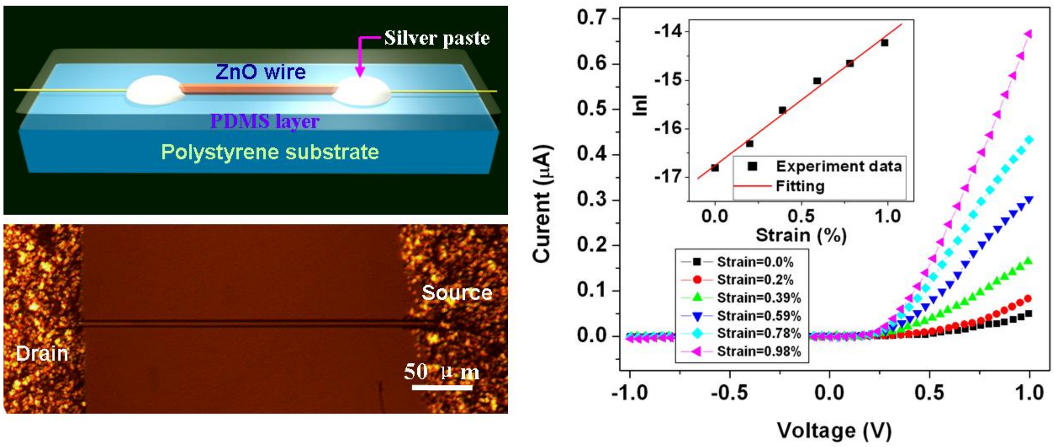

Fig.2 (a) Schematic of a single ZnO PFW based strain sensor device. (b) Optical image of a strain sensor device. (c) *I-V* characteristics of device under different strain. Inset is the dependence of ln *I* (in unit of ampere) on the applied strain.

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High Performance Flexible Nanogenerators

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Flexible nanogenerators play a vitally important role in harvesting tiny and wide frequency mechanical movements in the surrounding environment to power nanodevices. To increase the output of nanogenerator while keeping its flexibility and energy harvesting ability in wide frequency, we developed a technology to fabricate lead zirconate titanate (PZT) textiles in which nanowires are parallel with each other. [1] This kind of textiles are suitable for flexible and wearable nanogenerators. The nanogenerator made up of one piece of PZT textile can generate 6 V output voltage and 45 nA output current, which are large enough to power a liquid crystal display (LCD) and a UV sensor. When many pieces of PZT textiles are stacked in a mode to make all nanowires parallel with each other, they can be made into a flexible nanogenerator with ultrahigh output voltage of 209 V and output current density of 23.5 $\mu A/cm^2$, which are sufficiently powerful to instantaneously lighten a commercial light-emitting diode (LED) without the energy storage process.[2] At last, based on PZT nanowire textile, a new magnetic force-driven contactless nanogenerator (CLNG), with no contact between nanogenerator and mechanical movement source, will be demonstrated. The CLNG can harvest the mechanical movement energy in a non-contact mode to generate electricity. Its output voltage and current can be as large as 3.2 V and 50 nA respectively, which are sufficient to power up a liquid crystal display (LCD). [3] The new kind of nanogenerator has potential to wirelessly power the in vivo functional devices, which will expand the application of nanogenerator.

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Nano-piezoelectricity: from theory to high-performance devices

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Piezoelectricity at nanoscale can enable the fabrication of devices with unprecedented performance for energy harvesting, mechanical sensing/actuation, biomedical devices, optoelectronics, and more. In fact, compared with traditional piezoelectric materials, quasi one-dimensional piezoelectric nanostructures can be highly deformed by very small forces, exhibit outstanding mechanical properties, and can have substantially higher piezoelectric coefficients. Moreover, in some materials, notably in zinc oxide, there are other possibly crucial advantages: the piezoelectric and semi-conductive properties coexist; the nanostructures are likely to be non-toxic and bio-compatible, and can be grown on almost arbitrary and large-area substrates by simple, low cost, low temperature, and CMOS/MEMS-compatible processes. In fact, only few years after the first reports from Prof. Zhong Lin Wang [1,2], piezoelectric nanodevices have already shown an extremely high potential and have opened entirely new classes of applications [3]. However, there is likely a large room for further improvements. In particular, despite significant progresses in the theoretical understanding of piezoelectricity at nanoscale have already resulted in significantly better devices, the available models are rather simple and do not allow aggressive design optimization.

Therefore, in this presentation I will synthetically discuss how the interplay between semiconductive and piezoelectric properties [4], the position of contacts [5], the type of mechanical input [5,6], the shape, the electrical boundary conditions [7], and the charge transport properties [8] can crucially determine the piezopotential, the mechanical-to-electrical conversion efficiency, and the on-off ratio. These theoretical considerations can be crucial for designing piezo-nanodevices with substantially higher piezopotential, mechanical-to-electrical conversion efficiency, and on-off ratio. As an example, a laterally deflected piezoelectric nanowire with a total bottom contact is expected to result in a lower piezopotential and mechanical-to-electrical conversion efficiency because the total bottom contact may, ideally (i.e. if the contact is made of an ideal metal), zero the piezopotential in the region of maximum strain [5]; on the contrary, in the case of a purely vertical compression the strain is uniformly distributed over the entire length of the piezoelectric nanowire, thus resulting in substantially higher piezoelectric potential and mechanical-to-electrical conversion efficiency [5], a theoretical result which has already been validated by many experiments [9]. As another example, the mechanical-to-electrical static conversion efficiency of vertically compressed nanowires is almost independent of strain at small strains and increases at higher strains, thus confirming that the ability of nanostructures to withstand extreme deformations without fracture may be a key for increasing the efficiency of nanogenerators. As another example, in the case of floating electrodes, non-homogeneous doping and/or non-homogeneous sections may break the anti-symmetry of the piezopotential and, for instance, piezo-semiconductive nanowires with truncated conical shape may be useful for nanogenerators, piezotronics, and piezophototronics [7]. Novel results on modeling of quasi-1D piezoelectric nanostructures will also be presented.

In the final part of the presentation I will highlight what is missing for allowing an optimized design of piezoelectric nanodevices. In fact, several potentially crucial properties can not yet be accurately taken into account, either at theoretical level or by numerical calculations, including parasitic impedances, scaling of the electro-mechanical properties (Young modulus, piezoelectric coefficients,…), and transient phenomena.

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Linear and Non Linear Piezoelectricity in Novel Semiconductor Devices

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Piezotronics is a term coined in by Prof Zhong Lin Wang (*Georgia Institute of Technology, Atlanta, USA*) and describes the exploitation of strain and deformation internal polarization fields in polar semiconductors. Such fields already find applications in transducers and micropositioner devices but are also know to be present in GaN based light emitting diodes and lasers. Being a property of polar semiconductors it is present in both III-V and II-VI compounds, such as the technologically import ZnO. For many years piezoelectricity was included in the design of devices only to first order. In recent years a great deal of evidence, both model and experimental data, has been generated that such effects need to be included to at least second order [1-3]. The inclusion of such non linear effects produces surprising and non intuitive results, notably the generation of fields of opposite polarity compared to the prediction of linear piezoelectricity and the possibility of enhancing the piezoelectric polarization by a factor of 5-10 under particular deformations. In this presentation we will show the evidence for non linear effects and discuss the possible applications to light emitting diodes, quantum dot emitters and energy harvesting devices.

Our theory of Non Linearities, based on accurate quantum mechanical calculations and a tight binding formulation of the elastic and dielectric properties of zincblende and wurtzite crystals, is capable of highlighting and correctly predicting the polarization properties of several polar semiconductors under strain.

Such technique relies on correctly estimating the anion-cation displacement that polar semiconductors undergo when stress is applied along a polar direction of the crystal. It is such displacement in fact that breaks the natural symmetry of mostly the covalent but partially ionic sp^3 orbitals of the 5 atom complexes that form into tetrahedrons. Such symmetry in bulk zincblende semiconductor crystals results in the overall electronic charge being redistributed equally and uniformly shared among the 4 bonds. Once the symmetry is broken and the bond lengths of the cation-anion atom pairs become non-equivalent, charge redistribution takes place while breaking the charge neutrality observed in bulk systems at equilibrium. The sudden appearance of electrical dipoles on the atomic scale manifests itself as the macroscopic effect known as piezoelectric polarization, often experimentally observed indirectly from the way it affects electronic, vibrational and optical properties of devices. Piezoelectric fields of 10^2 to 10^3 KV/cm are commonly reported in the literature. So far we used our methodology on various zincblende and wurtzite semiconductors and the highlights of our findings are:

(a) We have resolved the mystery surrounding the apparent lower compared to bulk values of the piezoelectric coefficient in InGaAs/GaAs (111) grown Quantum Wells by accounting non linearities in the strain dependence of the piezoelectric coefficients.

(b) We have studied the piezoelectric coefficients of pseudomorphically strained InAs and GaAs semiconductors and showed a high level of tunability in external pressure resulting in change of polarity from negative to positive for the piezo field of InAs grown on a GaAs substrate. Furthermore we showed also how the polarization fields could be increased by up to 6 times the bulk values for external pressures creating strain in the range from 0 to 10%.

(c) We have applied the same methodology to wurtzite III-N and their alloys, revealing much smaller Spontaneous Polarization effects than previously reported, while observing much larger values of the total (spontaneous + strain induced) polarization compared to linear models, therefore highlighting the large effect of Non Linear Piezoelectricity in wurtzite semiconductors

(d) We have also recently generalized the study of zincblende InGaAs materials compared to our own previous work to reveal the exact expansion to non linear terms needed to accurately describe non linear piezoelectric effects and found that cubic terms need to be included (unpublished, manuscript in preparation) in the generalized equation for the piezo coefficients:

$$e_{lm} = e_{lm}^{0} + \sum_{n=1}^{3} e_{lnm}\varepsilon_n + \sum_{n|n'=1}^{3} e_{lnn'm}\varepsilon_n\varepsilon_{n'} + \sum_{n|n'|n''=1}^{3} e_{lnn'n''m}\varepsilon_n\varepsilon_{n'}\varepsilon_{n''}$$

The significance of our work is that by incorporating our unique and well tested ability of evaluating non linear polarization in the design of composite semiconductor structures we will in the near future be able to propose layouts were the piezoelectric fields, i.e. the ‘engine’ inside PEHs devices, can be suitably enhanced, greatly increasing, possibly by a factor of 2, the ability of such devices to convert mechanical energy into an electrical potential difference.

In this presentation we will also show how knowledge of non linearities in the piezoelectric field in materials such as wurtzite InGaN leads to new areas of exploitation for optical devices such as quantum sources of entangled photons or novel light emitting diodes with significantly increase efficiency.

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Novel Mechanical-Electric Coupling Effects in One- and Two-dimensional Nanostructures

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At nanoscale, matters show distinctly different behaviors from their bulk materials mainly due to the strong coupling between the local fields of matter consisting of electronic structures, charge, orbital and spin states and external applied fields. Such nanoscale multifield couplings can turn very common materials into functional nanomaterials with tunable properties we expected for piezotronics and nanodevices. Here we discuss several novel mechanical-electric coupling effects in one- and two-dimensional nanostructures based on first principle theory.

1) Piezoelectric and electrostrictive effect of nanotubes (CNTs, BNNTs, graphene sheets)
2) Piezoelectric, flexoelectric and flexoelectronic effects of nanowires (uniaxial deformed and bent NWs)
3) Exceptional mechanical-electric coupling effects in 2D nanostructures, and possiblility to extend piezotronics to piezospintronics or piezooptotronics.

Such extraordinary mechanical-electric coupling effects in low-dimensional nanostructures open up new vistas in functional devicesfor efficient energy conversion, nanogenerators, self-powering flexible devices and novel functional systems.

A new method to improve solar cell: Piezo-phototronics effect

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Abstract

For solar cell design, there are two approaches to optimize the solar cell performance: developing new energy efficiency material and designing new structure. The inner-crystal piezopotential in piezoelectric semiconductor materials, such as ZnO, GaN, InN and CdS, can effectively tunes/control the carrier separations and transport processes at the vicinity of a p-n junction or metal-semiconductor contact, which is called the *piezo-phototronic effect*. The presence of piezoelectric charges at the interface/junction can significantly affect the performances of photovoltaic devices, especially for flexible and printed organic/inorganic solar cell fabricated by piezoelectric semiconductor nano/microwires. This is new method to improve solar cell, and offer the new way to design photovoltaic devices.

The basic structure of typical nano/microwire solar cells is a p-n junction or metal-semiconductor (M-S) contact. The working principle of the solar cell is to use the built-in electric field in the depletion region to assist the separation of electron-hole pairs generated by incident photons. The piezoelectric charges created at the junction area under strain can effectively tune/control the solar cell performance. The piezopotential significantly modify the band structure at the interface, resulting in a control over the carrier generation, separation and transport at the p-n junction or M-S interface, which is the piezo-phototronic effect.

Piezoelectric Solar Cell Based on p-n Junction

According to our theoretical work about piezotronic effect, an ideal p-n junction is taken as an example to understand the unique property of an PSC. There are two typical effects in a piezoelectric semiconductor material under applied external stress:

piezoresistance effect and piezotronic effect. Piezoresistance effect is about the strain induced change in bandgap, density of states and/or mobility. Piezoresistance is mostly a volume effect and it is not sensitive to the reversal of the piezoelectric polarity in the semiconductor, thus, it can be truly considered as a change in resistance of the semiconductor bulk. Although the change in bandgap can affect the saturation current density and the open circuit voltage of a solar cell, the change of bandgap is independent of the sign of piezoelectric charges created at the contact of the device. The second effect is the piezotronic effect, which is about the polar direction dependence of an inner crystal piezoelectric potential arising from the piezo-charges created at the contacts. Owing to the sign reversal of the piezo-charges at the two ends of the device, a non-symmetric effect is induced at the two ends. This means that the output of the solar cell depends on the polarity of the crystal. The open circuit voltage of p-n junction PSC is approximately given by:

$$V_{OC} \approx \frac{kT}{q}\ln\left(\frac{J_{solar}}{J_{pn}}\right) = \frac{kT}{q}\left\{\ln\left(\frac{J_{solar}}{J_{pn0}}\right) + \frac{q^2\rho_{piezo}W_{piezo}{}^2}{2\varepsilon_s kT}\right\} \quad (1)$$

Piezoelectric Solar Cell Based on Metal-Semiconductor Schottky Contact

The metal-semiconductor (M-S) contact is an important component in solar cell devices. The open circuit voltage of an M-S contact PSC can be obtained as:

$$V_{OC} \approx \frac{kT}{q}\left\{\ln\left(\frac{J_{solar}}{J_{MS0}}\right) - \frac{q^2\rho_{piezo}W_{piezo}{}^2}{2\varepsilon_s kT}\right\} \quad (2)$$

Experiment results

In order to verify the theoretical model, p-n type solar cells have been fabricated by using poly (3-hexylthiophene) (P3HT) as a p-type material and the ZnO micro/nanowires as the n-type material. As expected from our theoretical discussion, for the ZnO microwire growing along the [0001] direction that is pointing away from the P3HT-ZnO interface, positive piezoelectric charges are created at the interface of the p-n junction under compressive strain, which result in an increase in open circuit voltage but a drop in the saturation current density. Alternatively, for the tensile strain case, negative piezoelectric charges are created at the p-n junction, which increase the saturation current density but reduce the open circuit voltage.

In summary, we have presented a theoretical model about the piezoelectric effect on solar cell by studying carrier transport in two configurations: the p-n junction and metal semiconductor Schottky contact. The analytical results of current density and open circuit voltage under simplified conditions are derived for understanding the core physics about the piezo-phototronic effect on solar cell output. The theoretically expected results have been verified by experiments. We have presented the basic principle of piezoelectric solar cell: the inner crystal piezoelectric potential inside the region of the junction can be used effectively for enhancing charge separation. The mechanism can be applied to most of junctions for using the built-in electric field in the crystal to separate charges, including p-n junction, metal-semiconductor contact, and heterojunction. Our study not only provides the basic understanding on the piezoelectric effect on the characteristics of a solar cell, but also assists the design for higher performance solar cells.

Influence of polarized interfaces on photochemical reactions

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Particulate semiconductors can be used as relatively inexpensive catalysts to photochemically split water and produced hydrogen. This reaction has been the subject of extensive research for two primary reasons. The first is that hydrogen is a high energy density fuel whose combustion does not produce greenhouse gases. The second is that if sunlight can be used as the source of photons, then the production and combustion of hydrogen would provide a sustainable energy cycle. However, the efficiency of the reaction is too low for the practical synthesis of hydrogen by this route. The main factors that reduce efficiency are related to the small size of the catalyst particles, which are typically less than 100 nm in diameter. The confinement of both the photoexcited electrons and holes and the oxidation/reduction reactions to such a small volume leads to enhanced recombination of photogenerated electron-hole pairs within the particle and the back reaction of intermediate species on the surface of the particle. While one might think a simple solution is to use larger particles, the surface area reduction associated with larger particles leads to reduced reaction rates that quickly offsets any gains that arise from reduced recombination. Considering this situation, it was hypothesized that if particles could be electrically polarized, then the oppositely charged photogenerated charge carriers would be transported in opposite directions. Because of this charge carrier separation, recombination would be less likely. Furthermore, if the oxidation and reduction half reactions occur at different spatial locations, then the rate of the back reaction would be reduced.

The purpose of the paper is to summarize research that was carried out to test this hypothesis. The research relies on the use of ferroelectric materials to provide a source of polarization. However, the ferroelectrics of interest are not stable when illuminated in aqueous solutions. Therefore, to create a practical catalyst, the ferroelectric must be used in a composite structure with a protective titania layer.

It is first shown that polarization arising from ferroelectric domains can influence the photochemical reactivity of metal oxides. The mechanisms of photochemical reactions on $BaTiO_3$ and $BiFeO_3$ surfaces will then be reviewed. [1,2] Next, photochemical reactions on TiO_2 films supported by $BaTiO_3$ and $BiFeO_3$ are considered [3-5]. The findings indicate that polarization within ferroelectric domains influences the motion of photogenerated charge carriers. Because electrons and holes travel in opposite directions in the same dipolar field, oxidation and reduction reactions occur in spatially selective patterns that are determined by the domain structure. Thin film heterostructure experiments have been used to show that the photochemical reactivity of TiO_2 can be enhanced when it is supported on $BaTiO_3$ and $BiFeO_3$. [3-5] The same effect has been translated to high surface area, hierarchically structured catalysts, which evolve hydrogen and degrade dyes at a greater rate than titania alone. [6,7] This is attributed to electron-hole separation in the space charge region of the supporting ferroelectric that reduces recombination and makes more charge carriers available to participate in the reaction.

In the final portion of the presentation, other mechanisms that can be used to create polarization at an interface will be described, including p-n junctions and polar surface terminations. For example, the reactivity of hematite (Fe_2O_3) films supported on $SrTiO_3$, which supports polar terminations, it much greater than bulk hematite. [8]

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Nanoscale Behavior and Failure of ZnO Nanomaterials and Devices

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Owing to their unique electronic, optical and piezoelectric properties, one-dimensional ZnO nanomaterials are envisioned as fundamental building blocks of future electromechanical, optoelectronic, sensing and actuation nanosystems. By employing the *in situ* characterization method, the fundamental principles of the piezoresistance, piezoelectric and the piezo-phototronic effects of ZnO were investigated. Design and fabrication of novel, nanowire/belt based sensors, piezotronic and optical devices will be presented in this report. Moreover, nanoscale failure in the building blocks of a device is inevitable in nanodevice fabrication and operation, which can lead to malfunction and/or even failure of the entire device. So, we pioneered the investigation of nanofailure of ZnO based piezoelectric devices by scanning probe microscopy. This fundamental understanding should pave the way to design optimized nanowire systems for electronic, electromechanical, and optoelectronic applications [1-2].

When ZnO nanocrystal is mechanically deformed, both of the piezoresistance and piezoelectric effects may take place and influence the electrical properties of ZnO nanomaterials. By connecting a Sb-doped ZnO NB with nonpolar growth direction across two electrodes on flexible substrate, we fabricated piezoresistance strain sensor and the corresponding piezoresistance coefficient was obtained [3]. Additionally, nanowire with polar growth direction was used to construct piezoelectric strain sensor to detect movement frequency of AFM tip, the devices were found to have a high sensitivity (about 200%) and a fast response time [4]. These results support the applications of ZnO NWs/NBs in nanopiezoelectric and piezoresistance strain sensors. Furthermore, based on the fundamental principle of piezotronics, piezoelectric field effect transistor and piezoelectric diode were realized with their potential use in logic unit and memorizer [5-6].

In the photoelectric device aspects, we fabricated a high-brightness blue-LED using a ZnO-nanowire array grown on p-GaN. The turn-on voltage is low and the brightness increases with the increase of voltage. The response of the EL intensity to a pulse of 30 V displays good reproducibility and a rapid response. We also investigated the effect of strain on the localized ultraviolet photoresponse in single bent ZnO nanowire. The nanowire has a higher sensitivity at the bent region than that at the straight region. The piezoelectric electric field across the width of the bent nanowire can be neutralized by the photogenerated electron-hole pairs, which could result in the photoresponse enhancement, as presented in Fig. 2 [7-8].

For biosensing application, three kinds of biosensors based on ZnO nanomaterials, traditional electrochemical, FET and HEMT types were fabricated [9-10]. The electrochemical biosensor based on ZnO nanotetrapod displayed a highly sensitive of 28.0 μA cm^{-2} and a detection limit of 1.2 mM. The special four-leg tetrapod-like ZnO nanostructures provide multiterminal charge transfer channels and good electron communication. We also fabricated an enzyme-coated single ZnO nanowire-based FET biosensor for detection of uric acid that could easily detect as low as 1pM, and the response time turns out to be in the order of millisecond. An excellent biosensor with ZnO nanowires-gated AlGaAs/GaAs high electron mobility transistor (HEMT) was used to detect lactic acid with a wide detection range from 0.03 nM to 300 mM, as shown in Fig.3.

For nanosystems with small scale, it is a challenge to study and evaluate the nanodamage and nanofailure because of excessive influencing factors such as voltage, current, and external force/pressure. But, a relatively complete evaluation system to the failure of nanomaterials was urgently needed. Here, we investigated the electrical and mechanical coupling nanodamage in single ZnO nanobelt and nanodevices, also several mechanisms were established to explain the phenomena, as shown in Fig. 4 [11-12].

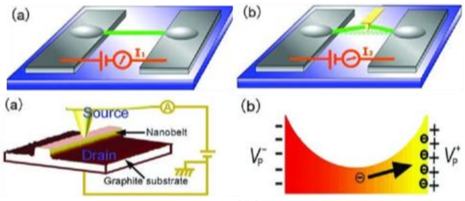

Fig.1 The Schematic view of pizoelectric FET and piezoelectric diode fabricated using nanowires/nanobelts.

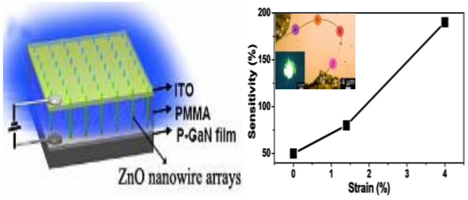

Fig.2 Schematic illustration of the heterojunction LED and the response curve of sensitivity followed strain.

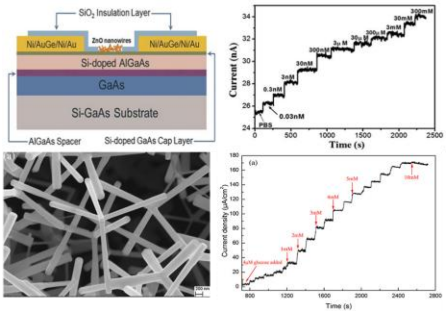

Fig.3 Schematic view of the ZnO nanowires/nanotetrapod-based sensors and the plot of drain current vs. time

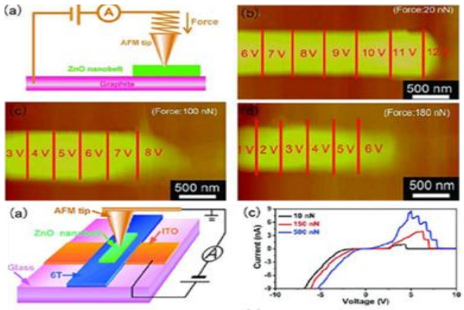

Fig.4 Investigation of electrical and mechanical coupling nanodamage in single ZnO nanobelt and nanodevices

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Piezoelectronics and Nanogenerators of Obliquely-aligned InN Nanorod arrays

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Due to increasing interest on nanogenerators and piezotronics, InN materials are chosen due to the relatively large piezoelectric constant despite the difficulty in growing high quality InN nanorods (NR). However, the quantized surface electron accumulation layers (QSEAL) inherent to InN cause surface band gap, band bending and discrete subband energy states as strong two-dimensional confinements of electrons and their surface dependent electrical and optical properties were rarely studied. Here, we demonstrate how InN can be designed to contribute to these areas not only by the choice of the materials, but also the geometry to maximize the mechanical deformation. Large area single crystalline InN NR arrays aligned obliquely, bounded by top polar {0002} surfaces and semipolar {-1102} side surfaces were grown by molecular beam epitaxy as shown in Fig. 1(a) below. The influences of the QSEALs on electron transport properties are investigated by conductive atomic force microscopy. The nonlinear I-V characteristics of the Schottky junction deviates from the asymmetric rectifying behavior into a nearly Ohmic-like behavior with increasing surface electron sheet concentrations. The Schottky barrier height is also observed to decrease by about 58 meV for the (-1102) plane than the (0002) plane. At larger biases for a Schottky junction, a large amount of electrons tunnel through the barrier corresponding to the sub-energy levels of the (0002) and (-1102) surfaces. The Schottky barrier height increases in conjunction with the deflection force with high current density at large biases because of tunneling. For the piezoelectric properties, the Schottky barrier height can be systematically tuned by varying the tip deflection forces as shown in Fig. 1(b) below. It is shown that the piezoelectric and electric transport properties of InN exhibit a great divergence than ZnO. Therefore, the existence of the QSEALs in InN is one of the biggest challenges in designing InN based electronics and nanogenerators. Figures 2 show the current output by deforming an obliquely aligned InN NR array with a Pt/Ir coated C-AFM tip. In this case, output power can be harvested simply by exerting a normal force on a nanogenerator to create piezoelectric potential across. Several sharp output current peaks observed well correlate with the sites of the InN NRs. As the NR bent by the normal force, negative (positive) piezopotential V^{-} (V^{+}) was created at the compressive (stretch) side of the NW forming a voltage drop across the width of the NW. A positive peak ouptut current appeared when the tip was in contact with the compressed side. The nanogenerators built on this structure can produce an average output direct current of 205.6 nA by only applying the tip deflection force of 3 nN, which can be further increased with larger forces. This work demonstrates the feasibility of using obliquely aligned InN nanorod array for harvesting electricity from ambient environment leading to the realization of self-powered nanodevices.

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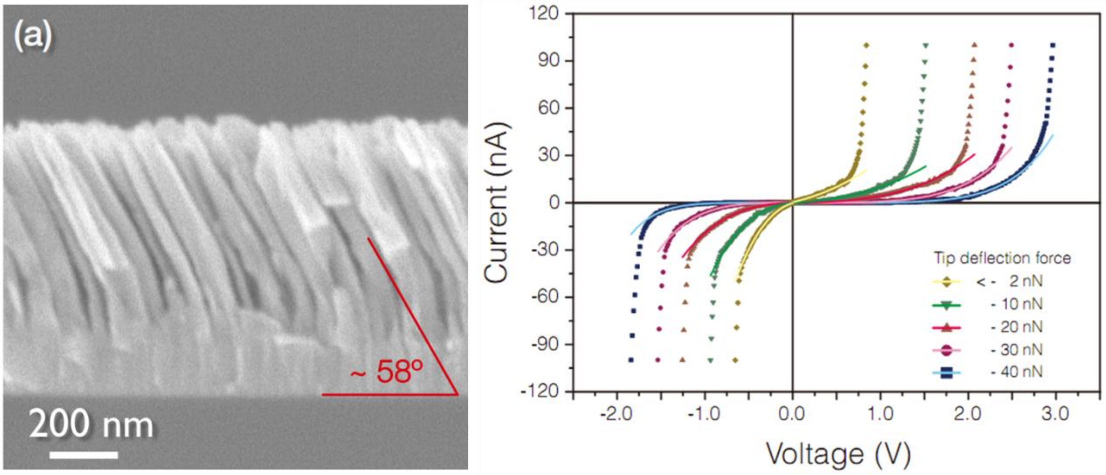

Fig.1 (a) Cross-sectional scanning electron microscopy image of the oblique-aligned InN nanorod arrays (b) Typical I-V characteristics of an InN nanorod at different tip deflection forces.

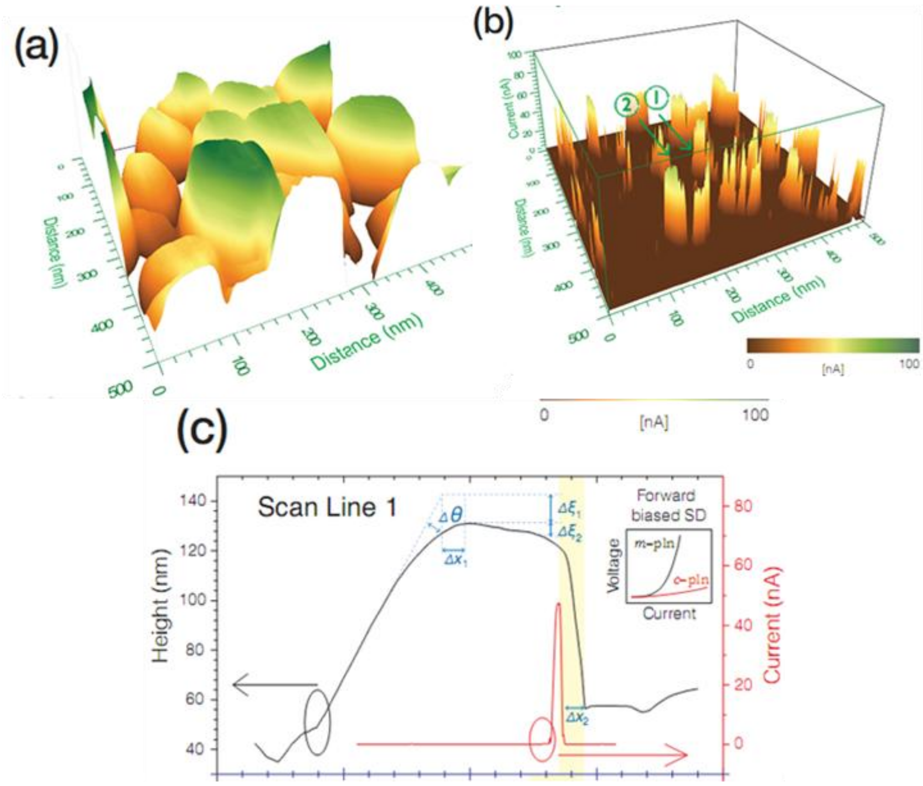

Fig.2 (a) Surface topography and (b) current mapping (The InN NR-to-tip bias is 0 V) images for the obliquely aligned InN NR array. (c) Dual cross section of a InN NR at linescans 1 and 2 of with the topography and current signals superimposed.

Piezoelectric Photovoltaics with Core-Shell Nanowire Arrays

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Compound semiconductors are in general piezoelectric materials. In this talk, I will report on a piezoelectric field generated by the built-in strains in lattice mismatched core-shell compound semiconductor nanowires can be employed for photovoltaic applications [1]. We show, based on fully electroelastically coupled continuum elasticity theory, that lattice-mismatch-induced strain [2,3] in an epitaxial core-shell nanowire gives rise to an internal electric field along the axis of the nanowire. This piezoelectric field results predominantly from atomic layer displacements along the nanowire axis within both the core and shell materials and can appear in both zinc blende and wurtzite crystalline core-shell nanowires. The effect can be employed to separate photon-generated electron-hole pairs in the core-shell nanowires and thus offers a new device concept for solar energy conversion. We have experimentally verified this novel piezoelectric effect by electrical measurements of InGaP/InP core-shell nanowires which are epitaxially grown by metal-organic vapor phase epitaxy. The measurements show clearly a diode behavior as a result of the existence of the axial piezoelectric field in the nanowires. We have also investigated the coupling efficiency of light in the solar spectrum into standing nanowire arrays based on a scattering matrix method [4,5] and found optimal diameters in the photovoltaic application, for which solar energy absorption efficiency higher than the corresponding planar thin film devices can be achieved.

I would like to acknowledge the collaborations with Aizi Jin, Fantao Meng, Erik Trygg, Jesper Wallentin, Magnus T. Borgström, Fredrik Boxberg, Niles Sodergaard, and Nicklas Anttu on this work.

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Piezotronic effect of nanowires probed by in-situ transmission electron microscopy

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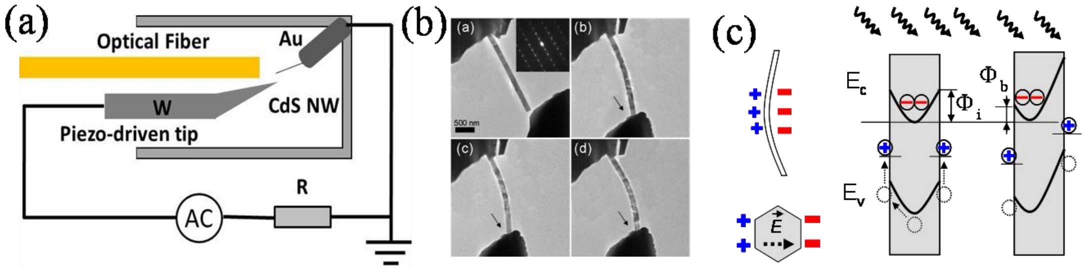
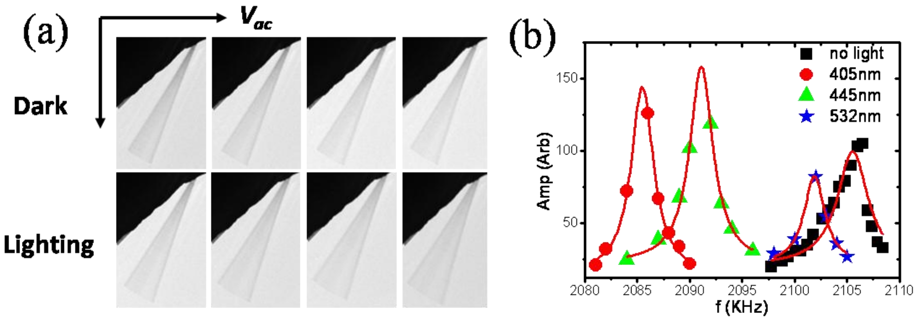
Piezotronics is a new field integrating piezoelectric effect into nanoelectronics, which has attracted much attention for the fundamental research and potential applications. In-situ transmission electron microscopy (TEM) method is powerful in a way that it can manipulate individual piezoelectric nanowires and also directly correlate the atomic-scale structure with piezotronic properties.

In this talk, I will report on the construction and applications of the homemade in-situ TEM electrical and optical holders. The piezotronic effect of ZnO nanowires, including the response of the electrical transport and photoconducting behaviors on the nanowire bending, has been investigated by in-situ transmission electron microscopy (TEM), where the crystal structure of ZnO nanowires were simultaneously imaged. Serials of consecutively recorded current-voltage (*I*-*V*) curves along with an increase of nanowire bending show the striking effect of bending on their electrical behavior. With increasing the bending of ZnO nanowires, their conductance dropped significantly. The changes of electrical parameters, such as resistivity, electron concentration, and carrier mobility, have been retrieved. The electrical transport coupled with the optical and piezoelectric properties of individual ZnO nanowires were studied. It is found that the photocurrent drops and the decay time largely decreases with the increase of bending of ZnO nanowire. The reduction of the conductance is attributed to the charge trapping effect and the reduction of the conducting channel, due to the piezo-induced electric field when the ZnO nanowire is bent. The slow decay tail of the photocurrent is resulted from the surface recombination barrier. With the assistance of electromechanical resonances, the dependence of mechanical quality factor on the resonance amplitude was also studied. The mechanical quality factor of ZnO nanowires largely drops while increasing resonance amplitude. The dynamic nanomechanics of ZnO nanowire is closely related with their piezoelectric effect. These results are significantly important for the fundamental research and technological applications of piezotronics.



(a) Setup of electrical and optical probe inside TEM; (b) In-situ images of ZnO nanowire bending; (c) Model of photo response of the bent ZnO nanowire.

The dynamic nanomechanics of ZnO nanowires were studied inside TEM. The electromechanical resonances of individual ZnO nanowires were induced by alternative current (ac) signals inside a transmission electron micrcrope, which have been used to measure the mechanical quality factors (*Q*) and elastic bending moduli (*E*) of a single ZnO nanowire. The resonance amplitudes were tuned by the applied ac voltages. The results indicate that, *Q* drops as much as ~80% with increasing resonance amplitudes, while *E* slightly decreases (~3%). The mechamism of the amplitude-dependent mechanical properties is discussed. The dynamic nanomechanics of ZnO nanowire is closely related to its piezoelectric effect. This study has implications for the mechanical-related applications of ZnO nanowires, such as nanoresonators and nanogenerators.



(a) Response of electromechanical behavior of CdS nanowire on light illumination; (b) Red shift of resonance frequency under the illumination.

In addition, the optical tuning of electromechanical behavior of resonator based on individual CdS nanowires has been realized by in situ TEM method. It is found that the red shift of resonance frequency of CdS nanowires happened under the light illumination, related with the red shift of resonance frequency, the effective Young's modulus of CdS nanowires reduced. The mechanism will be also discussed in this talk. The extra charge carrier generated by light lowers the Madelung constant and thus lowers the ionic bond energy. The internal energy is lowered and thus Young's modulus is lowered. The resonance frequency of semiconductor nanowires can be tuned by applied light field, which is a significant study on optical-electro-mechanical coupling.

In summary, piezotronic effect, including piezoelectronic and piezo-photoelectronic properties of nanowires have been investigated by construction of electrical and optical probe holder inside TEM, providing an experimental insight into the pioneering field- piezotronics.

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Dual-modal emission source of thin-film structure based on piezo-phototronic effect

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Luminescent materials and devices are central to a wide variety of applications ranging from photonics to biomedicine applications. Light-emitting diodes (LEDs) mostly investigated for flat- panel display and light sources are essentially a p-n junction diode typically made from a semiconductor. The light emission is generated by the direct injection and subsequent recombination of electron-hole pairs in the forward-biased p-n junction. The phenomenon of light emission from such electron-hole pair recombination as a result of minority carrier injection is regarded as injection electroluminescence (EL). A little surprise for us is that very limited work on exploiting EL devices beyond the p-n junction structure has been reported in the last decades. In order to search more EL device type, an important question in this area, both scientifically and technologically, is how to tailor the materials properties and therefore construct a new device structure. Particularly, it should be very attractive if the light source could generate additional signal, offering a novel multi-modal functional source. Inspired by the new concept of piezo-phototronics, we report on the fabrication and characteristics of strain-induced piezoelectric potential stimulated luminescence from ZnS:Mn thin-film grown on piezoelectric $Pb(Mg_{1/3}Nb_{2/3})O_3$-$x$$PbTiO_3$ (PMN-PT) substrate. Compared with previously reported 1D nanostructures, the utilization of thin-film structure would be beneficial to increasing device reproducibility and reducing the fabrication cost because of the mature thin-film fabrication technologies. Additionally, thin-film structure facilitates the integration and patterning of device. More importantly, a multifunctional source capable of generating both light and ultrasound wave is demonstrated using a single system in our work.

The ZnS:Mn thin-film was grown on PMN-PT by pulsed laser deposition. PMN-PT single-crystal features large piezoelectric coefficients and extraordinary high electromechanical coupling factors. These merits also translate into high performance of the ultrasound transducer fabricated with PMN-PT single-crystal. The utilization of piezoelectric PMN-PT substrate in this work provides an effective and precise approach to control over a range of strain state of the thin-films and therefore can realize strain-mediated luminescence. Light-emission is observed from the integrated thin-film structure based on a different working principle than conventional EL. The light-emission of the ZnS:Mn film is caused by the piezoelectric potential, resulting from the converse piezoelectric effect of PMN-PT substrate. The observation confirms that the strain-induced luminescence is essentially a dynamic process when a time varying voltage is applied. Pulsed emissions are observed to response the transient voltages. It is suggested that the emission intensity of luminescence depends on the rate of strain change induced by applied voltage. Strong frequency dependent luminescence from ZnS:Mn/PMN-PT system indicates that the resonance occurs at its nature frequency. Based on the observation on the frequency dependent luminescence, we suggest that PMN-PT working at a resonant frequency can greatly promote the emission. The frequency dependent results further rule out the probability of conventional EL. Such a novel light source can be driven by high-frequency triggering voltage up to MHz. The result provides a clue that it is possible to realize on-chip multi-mode source integrated thin-film phosphors with piezoelectric materials after the observation of light emission from ZnS:Mn film by external applied voltage via the converse piezoelectric effect. Moreover, simultaneous generation of light and ultrasound wave can be observed in this single system. We can tune the luminescence and ultrasound signal of the ZnS:Mn films via a converse piezoelectric effect in PMN-PT upon the application of an ac or dc electric-field. This work offers the potential in developing a dual-modal source combing light and ultrasonic wave for various applications such as hybrid system for tissue diagnosis and medical imaging.

In addition, we also investigate controllable biaxial strain effects on the characteristics of graphene/PMN-PT field-effect transistors (FETs) very recently. Transport properties of graphene are measured via tunable biaxial strain induced by PMN-PT in an *in-situ* and real-time manner. The novel graphene/PMN-PT FET exhibits a large memory window which is promising to practical applications of grapheme-based memory. The strategy proposed here provides one opportunity to *in-situ* dynamically investigate the transport properties of graphene via electric field and piezoelectric-induced biaxial strain effects, simultaneously. The time-dependent strain can lead to the 2D Raman peak shift experiencing several stages, which affects the transport properties of graphene. Hence, biaxial strain may induce the unique behaviors of graphene on PMN-PT, which does not exist in previously reported conventional graphene-based FETs.

The applications of Piezophototronics: from ZnO nanowire to GaN thin film

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Investigation of localized and quantity controllable coupling between different properties in nanomaterials/nanodevices is of great interest and significance. Such work will dramatically boost the understanding of the material, and develop novel nanodevices with new working principle possessing expanded applications. For a material that simultaneously has semiconductor, photon excitation and piezoelectric characteristics, a coupling among these properties is a new research field called "piezo-phototronics". The original idea was first initiated in 2010.[1] It focused on the fundamental physics of coupling effect in nanomaterials. It describes a new principle for controlling the coupling among mechanical, photonic, and electrical properties of nanodevices. The core idea is that the inner-crystal piezopotential can effectively tune/control the carrier generation, transport, separation and/or recombination processes at the vicinity of a p-n junction or metal-semiconductor interface, and thus the electro-optical processes.

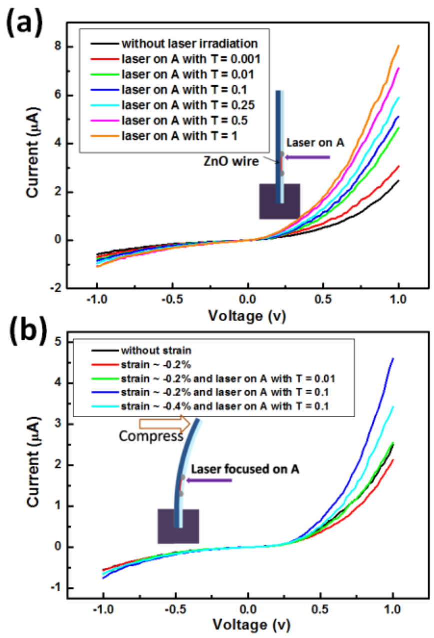

Fig.1 (a) Tuning the I-V transport characteristic of a device by controlling the intensity of the excitation laser focused at contact A via optical filters from transmission coefficient T = 0.001 to 1, without strain. (b) Design and control of the transport properties of the device by coupling the intensity of illuminating laser and the degree of strain in the microwire showing the basic principle of piezo-phototronics.

The first pioneering work we have done is that we realized designing and controlling the electrical transport characteristics of a ZnO micro/nanowire device by localized coupling between piezoelectric and photoexcitation. [1] We fabricated two-end bonded ZnO wire devices to construct a metal-semiconductor-metal structure with Schottky barrier (SB) at the two contacts. Both piezoelectric effect and photoexcitation intensity can tune the I-V transport property of a ZnO microwire device, but they act in opposite directions. The piezoelectric effect tends to raise the height of the local SB at the metal-ZnO contact, while photon excitation using a laser that has energy higher than the band gap of ZnO lowers the SB height. If we refer one end of the device as A, by shining the laser at contact A of the device, as the relative intensity of the laser being changed via optical filters from transmission coefficient T = 0.001 to 1, the I-V curve has been largely tuned (Fig. 1a). Fine tuning of the magnitude of mechanical straining and the intensity of the light illumination can produce a designed shape of the I-V characteristic. Fig. 1b shows the coupled tuning of the two effects on the I-V shape. By choosing a strain of −0.2% and relative light intensity T = 0.01 (green curve), the observed I-V curve matched well to the original I-V curve obtained without applying a strain nor laser excitation (dark curve). This experiment shows that by carefully controlling the relative contributions of the effects from piezoelectricity via strain and photon excitation via light intensity, the local contact can be tuned step-by-step, and thus the transport characteristics of the device were well controlled.

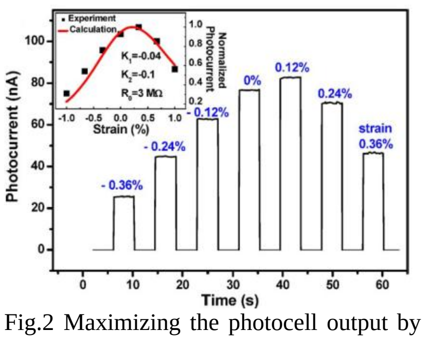

Fig.2 Maximizing the photocell output by piezo-phototronic effect. The output current responses to the strain applied on the device, and gets a maximum value certain point.

Then, we demonstrated the application of piezo-phototronic effect in optimizing the output performance of the photocell. [2] The working mechanism is that by exciting a SB structure using a laser that has photon energy higher than the bandgap of the semiconductor, electron-hole (e-h) pairs are generated at the interface region. If the height of the SB is too high, the generated e-h pairs cannot be effectively separated. If the SB is too low, the e-h pairs are easily recombined even after a short separation. There exists an optimum SB height that gives the maximum output photon current. By using the tuning effect of piezopotential to the SB, we can experimentally find out the optimum choice of the SB height in corresponding to the maximum photon current, as shown in Fig. 2.

As the most popular III-V semiconductor, the electroluminescence (EL) properties of GaN have been extensively investigated for decades for various applications, including LED, laser diodes, flat-panel display devices, etc. Most recently, we present that the EL properties of Mg-doped p-type GaN thin films can be tuned by the piezo-phototronic effect via adjusting the minority carrier injection efficiency at the metal–semiconductor interface by strain induced polarization charges. [3] The external quantum efficiency of the blue EL at 430 nm was changed by 5.84% under different straining conditions which is 1 order of magnitude larger than the change of the green peak at 540 nm, as shown in Fig. 3. The results indicate that the piezo-phototronic effect has a larger impact on the shallow acceptor states related EL process than on the one related to the deep acceptor states in p-type GaN films. This study has great significance on the practical applications of GaN in optoelectronic devices under a working environment where mechanical deformation is unavoidable such as for flexible/printable LEDs.

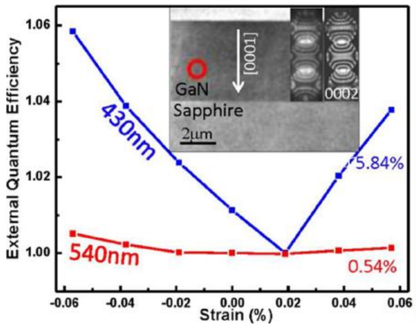

Fig.3 External quantum efficiency of the EL emission at 430 and 540 nm when different strain was applied to the GaN thin film. The insert is the cross-sectional TEM results for the GaN film and the corresponding CBED patterns taken from the red circled areas.

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Piezo-phototronics: Principle and Its Applications in Flexible Optoelectronic and Renewable Energy

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Due to the polarization of ions in a crystal that has non-central symmetry in materials such as the wurtzite structured ZnO, GaN and InN, a piezoelectric potential (piezopotential) is created in the crystal by applying a stress. Owing to the simultaneous possession of piezoelectricity, semiconducting and photonic properties, the piezopotential created in the crystal has a strong effect on the carrier transport at the interface/junction. By utilizing the advantages offered by these properties, new research fields have been created. The piezo-phototronic effect is to use the piezopotential to control the carrier generation, transport, separation and/or recombination for improving the performance of optoelectronic devices, such as photon detector, solar cell and light emitting diode. In the paper, we will introduce the fundamentals and review the updated progress of piezo-phototronics fields. A perspective is given about their potential applications in sensors, human-silicon technology interfacing, MEMS, nanorobotics and renewable energy. The potential applications of piezo-phototronics devices include optoelectronics, sensors, human interface technology, MEMS, nanorobotics and energy sciences.

The first device we show is piezo-phototronic enhanced ZnO NW UV photodetector. The responsivity of a photodetector is directly proportional to photocurrent. As piezopotential can induce barrier height change, we can utilize it to enhance the photocurrent. A theoretical model is constructed to study the piezo-phototronic photodetectors based on single-Schottky and double-Schottky contacted metal–semiconductor–metal (MSM) structures. In this model, we have coupled the photoexcitation and piezoelectric terms into basic current equations to study their influence on the final device performance. The asymmetric characteristic of the piezo-phototronic effect is demonstrated very clearly: the change of current under the same amount of applied strain is opposite when the bias voltage is applied at the opposite direction. However under different illumination power, the photocurrent changes symmetrically with regard to the two Schottky contacts. Then we investigate the effects of the piezopotential on the performance of the photodetector. First, we investigated the effects of piezopotential on the dark current of the photodetector. I-V curves in the dark remained no change under different tensile and compressive strain, which means that piezopotential has very small effect on the dark current. Under light illumination, if c-axis from left hand to right hand, the absolute current at a reverse bias increased step-by-step when applied a variable strain from tensile to compressing. And the effect of strain on photocurrent is much larger for weak light detection than for strong light detection. Correspondingly, the photo responsivity increases with the compressive strain increases. In the experiments, we also found the change of photocurrent and responsivity has an approximately linear relationship with strain. Furthermore, the slope varies with the excitation light intensity.

The most recent research on the application of piezophototronics is piezoelectric enhanced LED. As we know, UV LED has wide applications in chemistry, biology, military and so on, yet they suffer from low external efficiency due to internal reflection in thin films. In this work we enhanced the efficiency by piezophototronics effect. Under an assumption of no-doping or low-doping in ZnO for simplicity, numerically calculated piezopotential distribution in the ZnO microwire shows that a negative potential drop is created along its length when the ZnO microwire is under a-axis compressive strain. The depletion width and internal field may be reduced under this additional component of forward biased voltage. Subsequently, the injection current and emitting light intensity under the same externally applied forward voltage increase when the device is strained. More importantly, by solving Poisson equation with coupling piezoelectric effect, we found that the enhancement of external efficiency may be caused by the localized positive piezopotential near GaN/ZnO interface, which produces carrier trapping channels. Electrons and holes can be temporarily trapped and accumulated in the channels in the conduction and valence band, respectively, subsequently increased hole and electron, resulting in a large increase in emission intensity. Finally, our experimental results have proved this idea of enhancement, and the external efficiency increases as high as more than four times.

The piezopotential have given rise to new research areas of Nanogenerators, Piezotronics and Piezophototronics. Nanogenerator and piezotronics are two way coupling effect. In nanogenerator piezoelectric potential driven transient flow of electrons in external load. Piezotronics is about the devices fabricated using the piezopotential as a “gate” voltage to tune/control charge carrier transport at a contact or junction. The Piezophototronics effect is the three way coupling of semiconductor current transport properties, piezoelectricity and photoexcitation. Piezophototronics effect has been studied experimentally, and has been applied to optimizing photocell output, photodetector sensitivity, and LED emission efficiency. Future applications include optimization of other optoelectronic devices like resonators and organic photonics

Enhanced Cu_2S/CdS coaxial nanowire solar cells by piezo-phototronic effect

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Searching for renewable and green energy is one of the most urgent challenges to the sustainable development of human civilization owing to the threat of global warming and energy crises. Solar is probably the most abundant clean and renewable energy. Semiconductor nanowires (NWs) have a lot of advantages as candidates for photovoltaic (PV) applications [1] due to their large surface-to-volume ratio, better charge collection [2] and the possibility of enhanced absorption through light trapping [3,4]; at the other side, nanowires will cause large surface and interface recombination, which could be overcome by surface passivation [5] and epitaxial growth of p-n junctions [6]. The core-shell geometry of NWs is proposed to be able to enhance the efficiency of charge collection by shortening the paths travelled by minority carriers [5-7], increasing the optical quality of the material [8], or strain engineering of the bandgap [8].

These NWs based PV has also great application in flexible power source compared to bulk materials. In such case, the strain in the NWs, introduced during growth, device fabrication and/or application, is an important issue for piezoelectric semiconductor (like CdS, ZnO and CdTe) based PVs. First, for decreasing electron-hole interface recombination and increasing charge collection efficiency, a single crystal epitaxial *p-n* structure is highly desirable, but these epitaxial hetrojunction NWs introduce static strain as a result of a misfit between the inherent crystal lattices between the core and shell materials. Second, flexible PV devices have been the subject of research for powering flexible electronics and devices [9,10], which inevitably introduce strain during the operation. Although theoretical study has predicted piezoelectric effect on NW PV [11], experimental verification is still unavailable. Thus, our goal here is to study the piezo-phototronic effect on the performance of piezoelectric PV devices made using single crystal epitaxial coaxial structures.

In this presentation, we report the enhanced performance of the piezoelectric n-CdS/p-Cu_2S core-shell NW PV devices by a factor of 70% using the *piezo-phototronic effect*, which could control the electron-hole pair generation, transport, separation and/or recombination at *pn* junction via applied strain, thus tuning the performance of the PV devices: when the p-n junction is parallel to the *c* axis of the NW (configure I), the PV performance enhances with increasing the compressive strain, but decreases with increasing the tensile strain. The concepts of 'piezotronics' and 'piezo-phototronics' were introduced by us in 2007 and 2010, respectively.[12-16] Due to the polarization of ions in a crystal that has non-central symmetry in materials such as the wurtzite structured ZnO, GaN and InN, a piezoelectric potential (piezopotential) is created in the crystal by applying a stress. Owing to the simultaneous possession of piezoelectricity and semiconductor properties, the piezopotential created in the crystal has a strong effect on the carrier transport at the interface/junction. *Piezotronics* is about the devices fabricated using the piezopotential as a "gate" voltage to tube/control charge carrier transport at a contact or junction. *Piezo-phototronic effect* is to use the piezopotential to control the carrier generation, transport, separation and/or recombination for improving the performance of optoelectronic devices, such as photon detector, solar cell and LED.

Such Piezo-phototronics effect offers a new concept for improving solar energy conversation efficiency by designing the orientation of the nanowires and the strain to be purposely introduced in the packaging of the solar cells. This study shed light on the enhanced flexible solar cells for applications in self-powered technology, environmental monitoring and even defensive technology.

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