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Review on Nanomaterials and Their Utilization in the Recovery of Waste Mechanical Energy by Using Piezoelectric Nanogenerators

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Abstract - **Nano scale materials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers. A nanometer is one millionth of a millimeter- approximately 100,000 times smaller than the diameter of a human hair. Nanomaterials are of interest because at this scale unique optical, magnetic, electrical, and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine, and other fields. Energy harvesting from the environment is one of the core features of a functional, self-sufficient nanosystem. Self-powered nanosystems combine the nanogenerator with functional nanodevices in order to harvest mechanical energy from the environment into electricity to power nanodevices. It can work independently, without any other external power sources.Piezoelectricity is the electric charge that accumulates in certain solid materials (such as crystals, certain ceramics, and biological matter such as bone, DNA and various proteins) in response to applied mechanical stress.Energy harvesting (or power scavenging) refers to capturing energy from environment, surrounding system or any other source and converting it into a usable form of energy to develop self-power system that doesn't need external power supply e.g. piezoelectric process. In order to harvest the waste mechanical energy during various processes, piezoelectric properties of different materials such as ZnO can be utilised in order to convert the waste mechanical energy into electrical energy which could further be used.**
Keywords: **Nanomaterials, Waste Mechanical Energy, Piezoelectricity, ZnO**

I. INTRODUCTION

Nanoscale materials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers. A nanometer is one millionth of a millimeter - approximately 100,000 times smaller than the diameter of a human hair. Nanomaterials are of interest because at thisscale unique optical, magnetic, electrical, and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine, and other fields. Some nanomaterials occur naturally, but of particular interest are engineered nanomaterials (EN), which are designed for, and already being used in many commercial products and processes. They can be found in such things such as sunscreens, cosmetics, sporting goods, stain resistant clothing, tires, electronics, as well as many other everyday items, and are used in medicine for purposes of diagnosis, imaging and drug delivery [1]. Engineered nanomaterials are resources designed at the molecular (nanometer) level to take advantage of their small size and novel properties which are generally not seen in their conventional, bulk counterparts [2]. The two main reasons why materials at the nano scale can have different properties are increased relative surface area and new quantum effects. Nanomaterials have a much greater surface area to volume ratio than their conventional forms, which can leadto greater chemical reactivity and affect their strength. Also at the nano scale, quantum effects can become much more important in determining the materials properties and characteristics, leading to novel optical, electrical and magnetic behaviors [1]. Tailoring the properties of materials on a molecular level offers the potential for improvement in device performance for applications across the entire range of human activity: from medicine to cosmetics and food, from information and communication to entertainment, from earth-bound transport to aerospace, from future energy concepts to environment and climate change, from security to cultural heritage [3].The nanogenerator was first invented in 2005 by Prof. Zhong Lin Wang. It uses the piezoelectric potential of nanomaterial generated under strain in order to drive free electrons to flow back and forth in an external circuit[4]. Piezoelectricity is an electromechanical effect resulting from a linear coupling between mechanical stress and strain on the one hand and electric field and displacement field on the other. The name originates from the Greek word piezos meaning "pressure" and expresses the observation that electricity is generated on applying pressure to a piezoelectric material [5].

II. LITERATURE REVIEW

Xiang *et al.,* [28] studied Hexagonal [0001] non passivated ZnO nanowires with diameters up to 2.8 nm with density functional calculations. The authors find that ZnO nanowires have larger effective piezoelectric constant than bulk ZnO due to their free boundary. For ZnO nanowires with diameters larger than 2.8 nm, the effective piezoelectric constant is almost a constant. Surprisingly, the effective piezoelectric constant in small ZnO nanowires does not depend monotonically on the radius due to two competitive effects. Moreover, the quantum confinement effect results in larger band gaps of bare ZnO nanowires compared to that of bulk ZnO.

Zhong Lin (Z.L.) Wang *et al.*, [29] developed an innovative approach that uses ultrasonic waves to drive a nanogenerator built from an array of vertically aligned ZnO nanowires. An array of aligned ZnO nanowires is covered by a zigzag silicon electrode coated with platinum. The platinum coating not only enhances the conductivity of the electrode but also creates a Schottky contact at the interface with the ZnO that functions like a p-n junction or diode. The nanowires were grown on gallium nitride substrates, which served as a common electrode for directly connecting with an external circuit. The asymmetric piezoelectric potential across the width of a ZnO nanowire and the Schottky contact between the metal electrode and the nanowire are the two key processes for creating, separating, preserving, and outputting the charges. The DC nanogenerator is driven by ultrasonic waves. Once the wave is on, a nanogenerator measuring $2mm^2$ delivers a current output of 30nA. The design is new, cost-effective, and meets the stipulated requirements. The approach provides a basis for optimizing and improving the performance of the nanogenerator for its applications in nanotechnology.

Zhu *et al.*, [30] reported a flexible high output nanogenerator (HONG), based on a lateral ZnO nanowire array for harvesting mechanical energy, for driving small commercial electronic component. The electrical output of a single layer of the HONG structure reached a peak voltage of 2.03 V and a current of 107 nA with a peak power density of 11 mW/cm^3. The energy generation efficiency was 4.6%. The generated electric energy was successfully used to light up a commercial light-emitting diode (LED). The authors also predicted that the peak output power density of 0.44 mW/cm^2 and a volume density of 1.1 W/cm^3 could be realized by optimizing the density of the nanowires on the substrate and using multilayer integration.

Hu *et al.*, [31] integrated a nanogenerator onto a tire inner surface and scavenged mechanical energy from the deformation of the tire during its motion. The nanogenerator directly powers a liquid crystal display (LCD) screen.

Cha *et al.*, [32] fabricated a sound-driven piezoelectric ZnO nanowire-based nanogenerator and obtained an AC output voltage of about 50 mV. Systematic investigations on the power generating performance of sound driven nanogenerators clearly support that the measured output voltage originated from the sound driven nanogenerator. This study shows that sound can be one of promising energy sources when using highly efficient nanogenerators based on piezoelectric nanowires.

Xu and Wang [33] developed a fully integrated, solid state, compact hybrid cell (CHC) that comprises "convoluted" ZnO nanowire structures for concurrent harvesting of both solar and mechanical energy is demonstrated. The compact hybrid cell is based on a conjunction design of an organic solid state dyesensitized solar cell (DSSC) and piezoelectric nanogenerator in one compact structure. The CHC shows a significant increase in output power, clearly demonstrating its potential for simultaneously harvesting multiple types of energy for powering small electronic devices for independent, sustainable, and mobile operation.

Di Liu *et al.*, [34] proposed next-generation TENG, which realizes constant current (crest factor, ~1) output by coupling the triboelectrification effect and electrostatic breakdown. Meanwhile, a triboelectric charge density of 430 $\mu C\ m^{-2}$ is attained, which is much higher than that of a conventional TENG limited by electrostatic breakdown. The novel DC-TENG is demonstrated to power electronics directly. The findings not only promote the miniaturization of self-powered systems used in Internet of Things (IoTs) but also provide a paradigm-shifting technique to harvest mechanical energy.

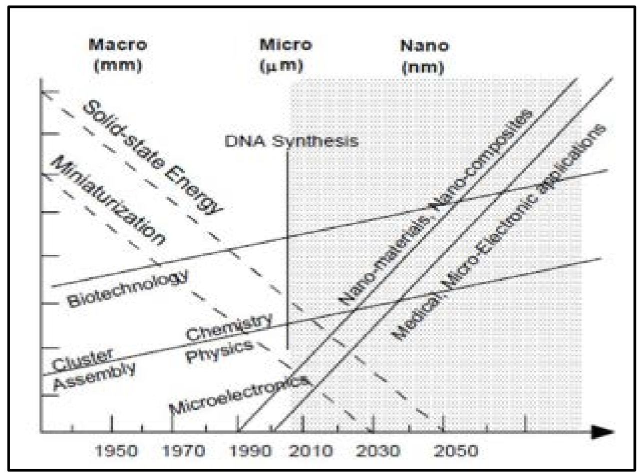

Fig. 1 Evolution of Nano technology[2]

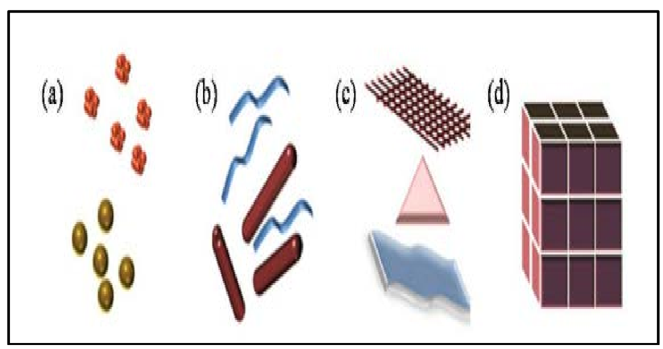

Fig. 2 Classification of Nanomaterials (a) 0D spheres and clusters, (b) 1D nanofibers, nanowires, and nanorods, (c) 2D nanofilms, nanoplates, and networks, (d) 3D nanomaterials

III. BENEFITS OF NANOMATERIALS

1. *Durability:* Nanomaterials can be processed with thermoplastic tougheners to improve strength, ductility, glass transition temperature, and/or conductivity [6].
2. *Purification:* New processes remove residue impurities in nanomaterials that cannot be taken out by conventional processes, resulting in more reliable and predictable composites [6].
3. *Processability:* Groundbreaking techniques such as electro spinning make composites tougher without

interfering with other composite processing characteristics or reducing performance [6].
4. *Versatility:* Advances such as "fuzzy veil" construction can be functionalized either to enhance bonding with the matrix or to alter its electrical and/or thermal conductivity [6].

IV. NOVEL APPLICATIONS OF NANO MATERIALS

These materials have created a high interest in recent years by virtue of their unusual mechanical,electrical, optical and magnetic properties. Some examples are given below

1. Nanophase ceramics are of particular interest because they are more ductile at elevated temperatures as compared to the coarse-grained ceramics [1].
2. Nanostructured semiconductors are known to show various non-linear optical properties [7].
3. Nanostructured semiconductors are used as window layers in solar cells [8].
4. Nanosized metallic powders have been used for the production of gas tight materials, dense parts and porous coatings [1].
5. Cold welding properties combined with the ductility make them suitable for metal-metal bonding especially in the electronic industry [9].
6. Single nanosized magnetic particles are mono-domains and one expects that also in magnetic nanophase materials the grains correspond with domains, while boundaries on the contrary to disordered walls. Very small particles have special atomic structures with discrete electronic states, which give rise to special properties in addition to the superparamagnetism behavior. Magnetic nanocomposites have been used for mechanical force transfer (ferro-fluids), for high density information storage and magnetic refrigeration [10].
7. Nanostructured metal clusters and colloids of mono- or plurimetallic composition have a special impact in catalytic applications. They may serve as precursors for new type of heterogeneous catalysts (Cortex-catalysts) and have been shown to offer substantial advantages concerning activity, selectivity and lifetime in chemical transformations and electrocatalysis (fuel cells). Enantio selective catalysis was also achieved using chiral modifiers on the surface of nanoscale metal particles [10].
8. Nanostructured metal-oxide thin films are receiving a growing attention for the realization of gas sensors (NOx, CO, CO2, CH4 and aromatic hydrocarbons) with enhanced sensitivity and selectivity. Nanostructured metal-oxide (MnO2) finds application for rechargeable batteries for cars or consumer goods. Nanocrystalline silicon films for highly transparent contacts in thin film solar cell and nano-structured titanium oxide porous films for its high transmission and significant surface area enhancement leading to strong absorption in dye sensitized solar cells [11].
9. Polymer based composites with a high content of inorganic particles leading to a high dielectric constant are interesting materials for photonic band gap structure [12].

V. RECENT DEVELOPMENTS IN THE FIELD OF NANOMATERIALS

This section highlights recent developments, from nanoporous polymers to graphene quantum dots, from concepts for designing magnetic properties to nanoplasticity and to the remarkable mechanical properties of a novel type of nanowires, just to mention some of the developments described.

1. One recent development in the field of nanomaterials is the ability not only to tailor the properties of nanomaterials (to achieve custom-designed, "tailor-made" values of certain properties) but to *tune* these properties. Tunable materials allow to change the properties of these materials reversibly and in a controlled manner after fabrication, e.g., by applying an electric field [13].
2. Another remarkable development is the discovery of "nanoglasses", based on the idea of introducing internal interfaces on the nanometer scale not between crystalline structures (leading to nanocrystalline materials) but between non-crystalline, amorphous or glassy structures. These glasses differ structurally from present-day glasses and thus are expected to open the way to an age of glass-based technologies comparable to the contemporary, primarily crystalline-based, technologies [13].
3. In one patented technology, NASA researchers invented a process in which the exfoliation of hexagonal boron nitride (useful as a lubricant and found in substances from cosmetics to pencil lead) is facilitated by converting a set of chemicals into a set of oxide nanoparticles [6].
4. Scientists discovered a novel method to purify nanomaterials by dissolving excess reactants and catalysts in a metal chloride salt. Eliminating these residual impurities allows these nanomaterials to be more reliable and predictable, particularly in the production of boron nitride nanomaterials and nanomaterial-based polymer and ceramic composites [6].
5. In addition to advances in nanomaterial production, new ways have been developed to use nanomaterials in fabrication. One technique involves selectively placing organically modified clays into an aromatic/alkoxy blended resin to create a nanocomposite that has increased strength and stiffness without sacrificing toughness in the cured epoxy [14].
6. Another patented technology centers on a new method of coating, which uses a cylindrical (or other) array of electrospinning needles to continuously apply a coating of nanofiber material to the surface of a composite precursor material.In order to upgrade polymer matrix composites (PMCs), a method forincorporating fibers into a PMC structure has been developed. The applications for nanomaterials are proliferating [6].

Nanomaterials are already in commercial use, with some having been available for several years or decades. The range of commercial products available today is very broad, including stain resistant and wrinkle-free textiles, cosmetics, sunscreens, electronics, paints and varnishes. Nano coatings and Nano composites are finding uses in diverse consumer products, such as windows, sports equipment, bicycles and automobiles. There are novel UV-blocking coatings on glass bottles which protect beverages from damage by sunlight, and longer-lasting tennis balls using butyl-rubber/nano-clay composites. Nanoscale titanium dioxide, for instance, is finding applications in cosmetics, sun-block creams and self-cleaning windows, and nanoscale silica is being used as filler in a range of products, including cosmetics and dental fillings [15].

VI. UTILISATION OF NANOMATERIALS IN RECOVERY OF WASTE MECHANICAL ENERGY

Mechanical energy is one of the most ubiquitous energies that can be reused in our surroundings. The sources of mechanical energy can be a vibrating structure, a moving object, and vibration induced by flowing air or water [16]. The energies related to induced vibrations or movement by flow of air and water at large-scale are wind energy and hydroelectric energy, respectively, which are not well investigated. Instead, the mechanical energies or so-called “low level” vibrations and movements are taken much into consideration as of now [16]. In a model of the nanogenerator mechanism, piezoelectric potential is created from nanowires strained externally.Using thousands of nanowire, a gentle straining produced an output of 1.2 volts, capable of powering an LED display [17]. NGs can be developed using three different approaches, namely, triboelectric, piezoelectric and pyroelectric. Among these, the piezoelectric approach is widely used, because vibrations attracted many researchers as a renewable power source, owing to its excellent environmental adaptability and high robustness [18].

Piezoelectric materials (ZnO, PZT) present unique properties in their internal crystal array structures. Upon external disturbance, such as a vibration or mechanical wave, a voltage drop occurs because the internal atoms may not be symmetrically aligned. These unique characteristics, shared across all piezoelectric materials, allow for the generation of electricity through mechanical stress [19].

TABLE I MECHANICAL ENERGY DERIVED FROM VARIOUS BODILY FUNCTIONS AND THE THEORETICAL CONVERSION TO ELECTRICAL ENERGY THAT COULD BE GENERATED VIA PIEZOELECTRICITY [19]

Activity	Mechanical Energy	Electrical Energy
Blood Flow	0.93 W	0.16 W
Exhalation Flow	1.00 W	0.17 W
Breath	0.83 W	0.14 W

The future of integrated nanodevices exists as self-sufficient nanosystems. Advancements in nano generation via piezoelectricity are a promising solution to a problem that will help us sense, control, communicate, and actuate responses in nanosystems.

VII. HISTORY OF DEVELOPMENT OF NANOGENERATORS

The nanogenerator was first invented in 2005 by Prof. Zhong Lin Wang.The first paper on nanogenerators was published in Science, in 2006, by Prof. Zhong Lin Wang and Dr.Jinhui Song. It demonstrates the fundamental working principle of nanogenerators, by bending a ZnO nanowire using an Atomic Force Microscope (AFM) tip. Additionally, in that paper, the idea of a self-powered nanosystem was put forward [20].

In 2007, DC nanogenerators, driven by ultrasonic waves, were reported [6]. In 2008, a type of fiber-based nanogenerator, which can harvest the low frequency and weak mechanical movement energy in the environment were reported in Nature; this nanogenerator was also a wearable unit. To conquer the challenges of increasing output voltage, an AC nanogenerator was reported in 2009, in Nature Nanotechnology. Additionally, a type of integrated nanogenerator was invented and reported on in 2010 in Nature Nanotechnology; the output voltage in the nanotechnology is greater than 1 V, which means that the nanogenerator’s output can be rectified, stored, and further used to power devices. Then, many kinds of nanogenerators have been reported and their applications greatly expanded [4].

In 2012, Prof. Zhong Lin Wang’s group reported the first organic-material-based triboelectirc nanogenerator. It uses the electrostatic charges created on the surfaces of two different materials during physical contact and separation in order to generate induced charges to harvest mechanical energy into electricity. After its invention, the development of the fundamentals of this kind of triboelectric nanogenerator’s was rapid, which quickly pushed its applications in a wide range of fields [20]. With the great progress of these two kinds of nanogenerators (piezoelectric nanogenerator and triboelectric nanogenerator), self-powered nanosystems are being developed very rapidly.

VIII.UTILISATION OF PIEZOELECTRIC PROPERTIES OF ZnO IN ONE DIMENSIONAL ARRAY

Piezoelectric nanogenerators can be developed using aligned ZnO nanowire arrays. This is a potential technology for converting mechanical movement energy (such as body movement, muscle stretching, blood pressure), vibration energy (such as acoustic/ultrasonic wave), and hydraulic energy (such as flow of body fluid, blood flow, contraction of blood vessel, dynamic fluid in nature) into electric energy for self-powered Nano systems. The word piezoelectricity means electricity resulting from pressure and latent heat[20].The piezoelectric effect results from the linear electromechanical interaction between the mechanical and electrical states in crystalline materials with no inversion symmetry[21]. The piezoelectric effect is a reversible process: materials exhibiting the piezoelectric effect (the internal generation of electrical charge resulting from an applied mechanical force) also exhibit the reverse piezoelectric effect, the internal generation of a mechanical strain resulting from an applied electrical field. The wurtzite ZnO material exhibits excellent piezoelectric property along 1 direction because of the noncentrosymmetric structure [22].

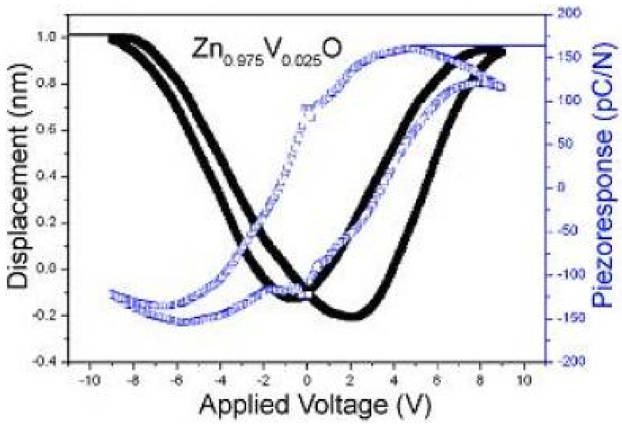

Fig. 3 Representative D-V curve and the piezoresponse hysteresis loop of $Zn0_{.975}V_{0.025}O$ films[23]

IX. ZnO AS PIEZOELECTRIC MATERIAL

As a piezoelectric material, ZnO has various advantages

1. It has the strongest piezoelectric response among the tetrahedrally-bonded semiconductors [25].
2. It is structurally simple and easy to fabricate.
3. ZnO films are compatible with semiconductor processes, and therefore have been widely used as sensors and actuators in micro-electromechanical systems and as SAW and BAW devices in the field of communications [26].
4. Doping with Al and Ga can improve the quality and conductivity of ZnO films. Co-doping can induce room-temperature ferromagnetism in Co-doped ZnO films [27].

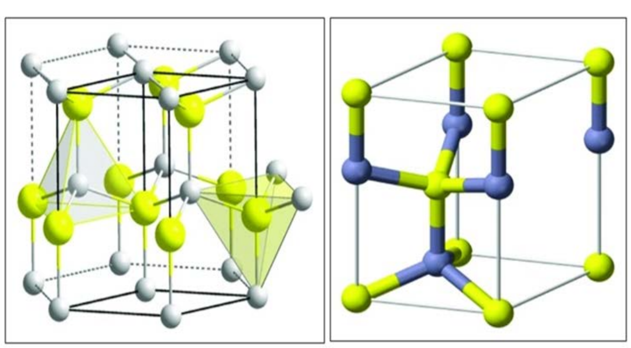

Fig. 4 ZnO structure: (a) the wurtzite structure model (b) the wurtzite unit cell. The O2- and Zn2+form a tetrahedral unit, and the entire structure lack central symmetry.

X. CONCLUSION

Nanomaterials has the potential for revolutionizing the ways in which materials and products are created and the range and nature of functionalities that can be accessed. It is already having a significant commercial impact, which will assuredly increase in the future. By taking advantage of quantum-level properties, Molecular Nanotechnology MNT allows for unprecedented control of the material world, at the nanoscale, providing the means by which systems and materials can be built with exacting specifications and characteristics. Nanomaterials are being used and could be more effectively exhausted in future by using different technologies for utilising the waste mechanical energy making the systems more energy efficient. The inherent piezoelectric property of ZnO, combined with other properties like the variety of nanostructures morphologies, the possibility to synthesize it by cost effective methods, makes ZnO an interesting material with potential for developing innovative devices. Different types of NGs based on ZnO nanostructures have been intensively developed, and studied for testing under different kinds of low frequency mechanical deformation.

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