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**PIEZOELECTRIC NANODEVICES: PRESENT AND FUTURE**

*Sommari degli interventi*

## Piezoelectric transducers from basic definitions to applications

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Piezoelectric materials are widely employed in the field of sensors, sensor systems and actuators. The non symmetric ionic charge of their structure is utilized to get a voltage under strain action and to obtain a deformation as a reciprocal effect, under an applied voltage of a suitable value. This presentation will surf on the basic constitutive equations explaining the intrinsic sensitivity mechanism when a force or a voltage is applied. The noise spectral density for this materials used as a capacitor in general is shown to follow a low different from the Nyquist one, due to the high impedance involved in most applications. Furthermore derivation of the sensitivity values for this kind of materials is presented as a prerequisite for the calculation of the resolution. Some examples of applications are briefly commented in order to show the high potentiality of the piezoelectric materials.

**A Constitutive Theory for Active Fiber-reinforced Composites**

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Electroelastic materials of interest in engineering applications are those capable of a fast and reversible mechanical response to application of an electric field. The implicit coupling of mechanics and electromagnetism has invariably to be strong to be useful, and highly nonlinear, when the displacements and deformations involved are large, as is the case with electroelastic *soft matter*.

To delineate a comprehensive and thermodynamically consistent constitutive theory of electroelasticity is a task for continuum mechanics. Conventionally, the onset of such a theory can be identified with two seminal papers by R.A. Toupin [1] and Tiersten [2]; an account of the theory's recent status is found in [3]; [4] features a comprehensive review focused on dielectric elastomers, an important class of so-called *smart materials*.

To design piezoelectric devices, especially at very small scales, it would be desirable to have an *atomistically-informed theory of electroelastic structures*, just as we have for carbon nanotubes. As today, this goal seems far from being achieved, although many problem-specific theories have been proposed and used successfully. Another such theory, advanced in [5], is the subject of my today talk.

AFCs (Active Fiber-reinforced Composites) are artificial bodies consisting of one or more layers of parallel ceramic fibers embedded in a polymer matrix. In [5], a linear mathematical model for their constitutive response is proposed, by importing certain concepts from the modeling of fibrous living tissues and by regarding an AFC as a special piezoelectric material body whose stored energy is a weighted sum of the stored energies of fibers and matrix.

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**Piezoelectric materials in microelectronic devices and systems**

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Piezoelectric materials are in use in electronic equipment from many years, especially for their feature which makes them be the electrical equivalent of the mechanical harmonic oscillator. With this feature the primary use has been and still is in accurate measure of the time, as can be observed in all quartz watches. With piezoelectric materials are also made very simple and common devices, such as lighters for gas where the mechanical energy is converted into electrical energy at high voltage. More recently and we will show something, the possibility of introducing piezoelectric materials in miniaturized structures, using the techniques developed for microelectronics, has allowed realizing sensors and actuators of extremely small size that they put even more prominence in the properties of electromechanical transduction of all this class of materials.
Some of the emerging applications that make use of the miniaturization of the piezoelectric materials, sometimes used alone or inserted into mixed architectures such as those of MEMS or of silicon integrated circuits, are the following: medical ultrasonic transducers, where an array of piezoelectric actuators sends acoustic waves to obtain ultrasound images of organs within the human body; pressure sensors, where the strength of mechanical deformation of the material is converted into electric signal; energy harvesting, where the electric power generated by the cyclic deformation of the material is stored in batteries or capacitors; mechanical engines, where the mechanical deformation of the piezoelectric material electrically induced is able to implement movement of other parts of the device mechanically coupled; piezoelectric microphones, where the mechanical deformation induced by the acoustic waves that impact on the material, is transformed into an electrical signal; other uses are in the control of head position in the HDD, various solutions for ink jet print heads and other currently emerging applications.

**Piezoelectric effect for improved semiconductor optoelectronics: from laser diodes and single photon emitters to solar cells**

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The piezoelectric (PZ) effect in strained semiconductor heterostructures can be used as an additional degree of freedom in designing novel devices with desired optoelectronic properties. After a brief overview of the field, we discuss how the PZ field in (111)B grown InGaAs/AlGaAs laser diodes improves their performance compared to (100) counterparts, in terms of lower threshold currents observed for all temperatures and cavity lengths. On the other hand, we show that PZ fields in InGaN/GaN heterostructures seriously limit their performance in laser diode applications, restricting the lasing wavelength below 500nm and increasing the threshold current of blue laser diodes by a factor of 4. At another limit of application, we show how the PZ field in InAs/GaAs (211)B quantum dots leads (i) to large antibinding energies of bi-excitons which is promising for single photon emitters at elevated temperatures, and (ii) to negligible exciton fine structure splittings, making these dots good candidates for the fabrication of solid-state entangled photon sources, without the need of any pre-patterning or post-processing step. Finally, we will discuss the possibilities of the PZ effect in designing optimized III-V nanowire heterostructures for photovoltaic applications

**Mechanics of piezoelectric quasi-1D nanostructures**

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The mechanical properties of volume-confined materials differ dramatically from those of conventional bulk samples as the nanoscale is approached. In the context of piezotronic nanogenerators, the unique mechanical properties ZnO 1-D nanostructures represent indeed the truly "enabling factor" of this new innovative technology. Due to their ability to withstand large elastic deformations (reportedly up to 15% strain vs. < 1% in bulk form) without breaking, ZnO nanowires may prove decisive - in terms of energetic efficiency and durability - for the viability of nanogenerators applied to sensors networks, implantable MEMS for biomedical applications, and other remote applications. Accordingly, the accurate measurements of elastic (i.e. Young's Modulus) and failure (e.g. fracture, fatigue, buckling, etc.) properties of ZnO nanostructures as a function of size is crucial for design purposes.

The first part of the talk is devoted to experimental nanomechanics of solids, highlighting metrological issues and current methods to tell intrinsic properties apart from extrinsic ones. In-situ micro-compression experiments on nanopillars are discussed to show how the power-law strengthening trend observed with decreasing size can be understood in the framework of a Weibull-like theory. Apart from individual AFM and TEM-monitored tests, the appealing possibility to perform a collective "statistical" test on a thousand (or a million) of quasi-1D nanowires simultaneously is also presented, as this is of consequence by the viewpoints of (industrial) process control and damage tolerant.

The second part of the presentation deals with the mechanical properties of nanomaterials for energy harvesting and, specifically, of ZnO nanowires. Conflicting reports in literature are pointed out and critically evaluated in the light of more modern approaches and theories. The coupling between mechanical and functional properties is emphasized, also with respect to the challenges it raises for the experimental characterization of actual ZnO nanogenerators.

**Piezoelectric quasi-1D nanostructures for biomedical applications**

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Nanoscale structures and materials have been explored in many biological applications because their novel and impressive physical and chemical properties, that offer remarkable opportunities to study and interact with complex biological processes. Particularly, their high surface/volume ratio, surface tailorability, improved solubility, and multifunctionality open many new possibilities for biomedicine.

In this talk, piezoelectric nanomaterials and their applications in the nanomedicine field will be introduced. Despite their impressive potentials, in fact, they have not yet received significant attention for bio-applications. Our results suggest that the exploitation of piezoelectric nanoparticles in nanomedicine is possible and realistic, and their impressive physical properties can be most useful for several applications, that range from sensors and transducers for the detection of biomolecules, to "sensible" substrates for tissue engineering or cell stimulation. After a short introduction to the major classes of innovative nanoparticles that have gained attention in the recent years, I will focus the attention on the research carried out in our laboratories.

Our group pioneered nanomedicine applications of boron nitride nanotubes (BNNTs), starting from an extensive investigation of their biocompatibility. BNNTs are of significant interest for the scientific community because of their potentially unique and important properties for structural and electronic applications. A BNNT is a structural analogue of a carbon nanotube: alternating B and N atoms entirely substitute for C atoms in a graphitic like sheet, with almost no change in atomic spacing; despite this, carbon and boron nitride nanotubes present many different properties. In this presentation, I show studies on biocompatibility and interactions between BNNTs and living cells. Thereafter, I will introduce potential useful applications of BNNTs as intracellular nanotransducers.

Another class of smart nanoparticles under investigation in our group is represented by zinc oxide nanorod arrays. In the latest years, the use of ZnO nanostructures has been proposed in different biomedical applications, however, to date, only a few contrasting results concerning their biocompatibility can be found in the literature. In particular, the application of the extraordinary piezoelectric properties of ZnO nanostructures has poorly been explored for the culture of electrically excitable cells. Here, I will show experiments about adhesion, proliferation and differentiation of two mammalian cell lines (PC12, as model of neuronal cells, and H9c2, as model of muscle cells) over ZnO nanowire arrays. We demonstrated suitability of these arrays in sustaining cellular functions, and their potential in applications that range from tissue engineering to minimally invasive sensing and/or stimulation.

I will conclude highlighting the challenges of nanomedicine in the next future, confirming the urgent need to exploit the rapid advances in nanomaterials for biomedical applications. The merging of different disciplines such as bioengineering, materials science, chemistry, physics, biology, as well as medicine, will be essential for the successful exploration of the applications of nanomaterials inside cells, and for effective and realistic applications in the clinical practice

**High-Performance Transparent, Flexible, Stretchable Piezoelectric Power Generators Based on Multi-Dimensional Nanomaterials**

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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 oC 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. Finally, ultrahigh power output nanogenerators will be introduced at the presentation site.

**Piezoelectric quasi-1D nanodevices**

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This presentation will summarize why quasi-1D piezoelectric nanodevices can offer breakthroughs in energy harvesting, sensing, actuation, optoelectronics, and biomedical applications.

Afterwards, I will explain how the position of contacts [1], the type of mechanical input [1,2], the shape, the electrical boundary conditions [3], the defects, and the charge transport properties [4] of the piezonanodevices can greatly affect the piezopotential, the conversion efficiency, and the on-off ratio. Additionally, I will discuss the distinction between anti-symmetric and not-anti-symmetric piezo-nano-devices [3]. Based on these theoretical considerations, I will give practical guidelines for designing high performance quasi-1D piezoelectric nanodevices.

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