1.3.7 Thermoelectrics and thermo-mechanics of individual nanostructures

Classical and quantum transport phenomena together with ultrafast optical response were investigated at the level of individual nano-objects focusing on the study of the combined heat-charge-energy conversion mechanisms and of their applications in the fields of nanoscale thermoelectrics and thermo-mechanics. Nano-objects display peculiar physical properties (e.g. electronic, thermal and mechanical ones) that are intimately related to their composition, structure, morphology, and to the environment. Unveiling the correlation between the morphological and physical properties of nano-objects would boost the engineering of nano-systems with tailored properties, and promote metrology protocols for their characterization, alternative to high-resolution imaging techniques. Recent results on the investigation of the thermoelectric and thermos-mechanical properties of individual nanostructures –semiconductor nanowires and metallic nanodisks - are summarized hereafter.

The advent of nanostructures has opened new perspectives for the creation of innovative thermoelectric (TE) materials that outperform the currently available solid-state converters. We demonstrate high-temperature thermoelectric conversion in InAs/InP nanowire (NW) quantum dots (QDs) by taking advantage of their strong electronic confinement (Fig. 1) [1]. The electrical conductance G and the thermopower S are obtained from charge transport measurements and accurately reproduced with a theoretical model accounting for the multilevel structure of the quantum dot. Notably, our analysis does not rely on the estimate of cotunneling contributions, since electronic thermal transport is dominated by multilevel heat transport. By taking into account two spin-degenerate energy levels we evaluate the electronic thermal conductance k and we investigate the evolution of the electronic figure of merit ZT as a function of the quantum dot configuration, demonstrating $ZT \approx 35$ at 30 K, corresponding to an electronic efficiency at maximum power close to the Curzon–Ahlborn limit.

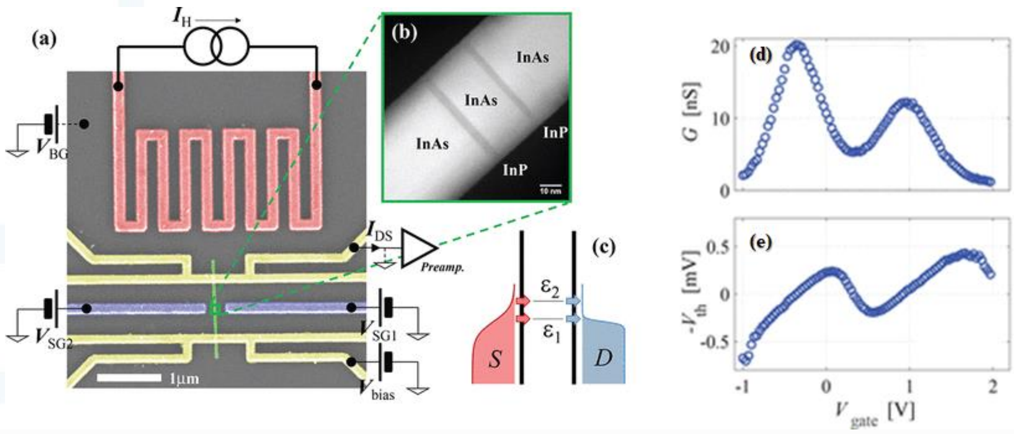

Figure 1. **(a)** SEM of a prototypical device. A local heater (red) is used to establish a temperature difference ΔT between the two ends of the NW (green) embedding an InAs/InP heterostructured QD. The device is fabricated on top of a degenerately doped SiO_2/Si p++ substrate (gray), and a set of Ti/Au electrodes (yellow) can be used both as electrical contacts to the NW and as local resistive thermometers. The QD electronic configuration can be controlled with a pair of side gates (purple) or using the conductive substrate as a backgate electrode. **(b)** TEM of the heterostructured QDs. **(c)** Sketch of the energetics scheme: the QD implements a multilevel system that can mediate heat and charge transport between the source (S) and drain (D), in the presence of thermal and electric bias. Two spin-degenerate levels ε_1 and ε_2 ($\Delta\varepsilon = \varepsilon_2 - \varepsilon_1$) play a relevant role in the regime studied in the experiment. **(d)** Extrapolated conductance G and **(e)** thermovoltage $-V_{th}$ as a function of the applied gate voltage V_{gate} for the first degenerate energy level for an average temperature T_{avg} = 24.9 K and for I_H = 10 mA current feeding the heating serpentine, when the system is in a T_{bath} = 4.2 K thermal bath.

A share of the experimental activities focuses on the development of reliable methods to precisely assess the TE properties of individual nanostructures [2,3]. We exploit noise measurements as an advanced thermometry tool to shine light on diffusive electronic transport in NW-based field effect transistors (FETs) [4,5] in presence of a thermal bias. We also demonstrate an all-electrical platform to measure the thermal conductivity *k* in suspended NW devices [6], using the so-called 3ω-method that relies on self-heating in the presence of an AC current modulation at frequency *ω*. Besides, we combine electrical and Raman measurements to achieve the full figure of merit of single NWs [7]. It is worth to mention that both the latter techniques – 3ω and Raman - can be exploited in combination with new outstanding methods for the field effect control of semiconductors at the micro- and nano-scale, based on the concept of electric double layer field effect transistor. Here, electric fields exceeding 30 MV/cm are built up at the interface between a semiconductor and a layer of tightly packed charged molecules (ions) conformally distributed around the surface of the semiconductor.

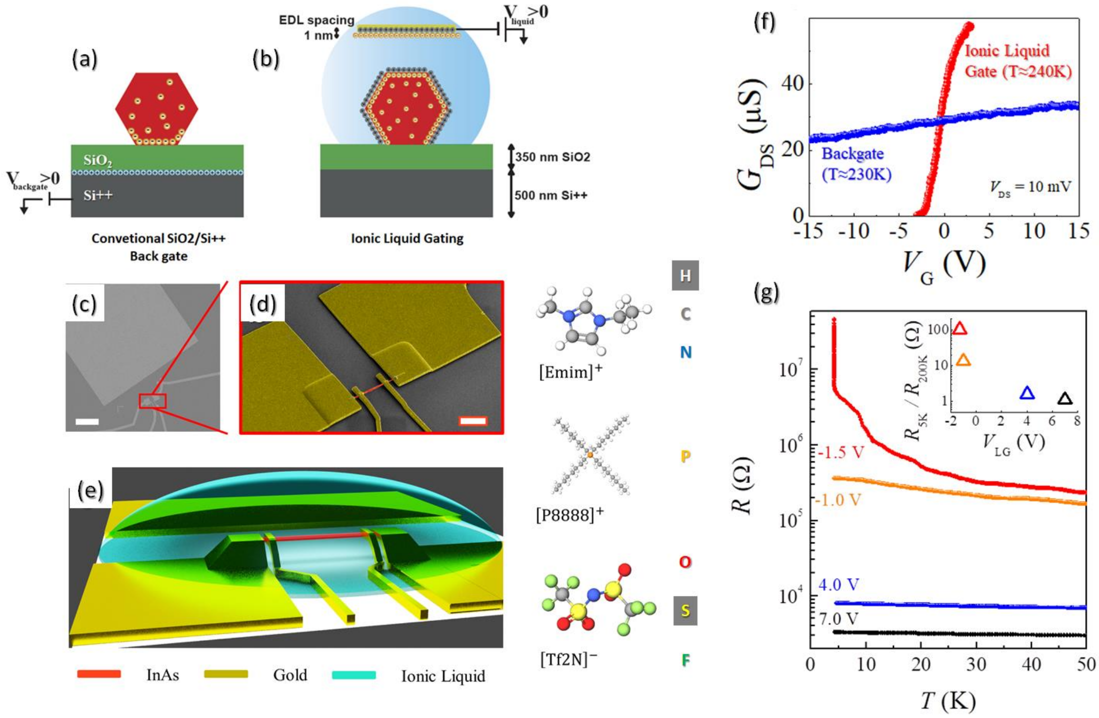

Figure 2. **(a)** Conventional back-gate method compared to **(b)** ionic liquid gating: the latter is conformal and allows to achieve outstanding charge carrier concentration. **(c-d)** scanning electron micrograph of device architecture where an individual NW (red colored) suspended onto a substrate is electrically contacted by four Ohmic contacts and equipped with a large counter-electrode used to polarize the ionic liquid (not shown in the image). **(e)** Pictorial view of the suspended NW-based device surrounded by an ionic liquid droplet used to enable electric double layer transistor operation. The ionic liquid may have a thermal conductivity up to 100 times smaller with respect to the one of the NW and the substrate. **(f)** Red (blue) transconductance corresponds to ionic-liquid gating (back-gating) operation of the NW transistor. **(g)** Temperature dependence of the device electrical resistance indicates the onset of a transition from a semiconducting to a quasi-metallic state.

In this approach, gate media typically consist of a soft-matter system such as a polymer functionalized with mobile ions or an ionic liquid (a salt melt at 300 K).

In this frame, we have demonstrated the operation of a FET based on a single InAs NW gated by an ionic liquid, reporting very efficient carrier modulation with a transconductance value up to 50 times larger with respect to conventional back-gating implemented via the SiO_2/Si++ substrate (Fig. 2).
This opens the way to the exploitation of ionic-liquid gating in nanodevices based on III–V semiconductor NWs [8,9]. Notably, soft-matter systems used as dielectric gate can be properly engineered in order to: (i) be transparent to a wide light wavelength range, thus being compatible with optical techniques; (ii) display a thermal conductivity two orders of magnitude smaller with respect to the one characteristic of solid-state semiconductors (Si, III-V compounds) and insulators (SiO_2), thus being compatible with k measurement using the 3ω-technique. This allows the simultaneous measurements of the electrical and thermal properties of the same nanostructure, and can stimulate novel investigations in the field of nanoscale thermoelectrics.
On the side of thermal-to-mechanical energy conversion at the nanoscale, we have investigated the mechanical vibrations of individual gold nanodots or nanodisks - nanopatterned on a sapphire substrate - using ultrafast time-resolved optical spectroscopy (Fig. 3) [10,11].

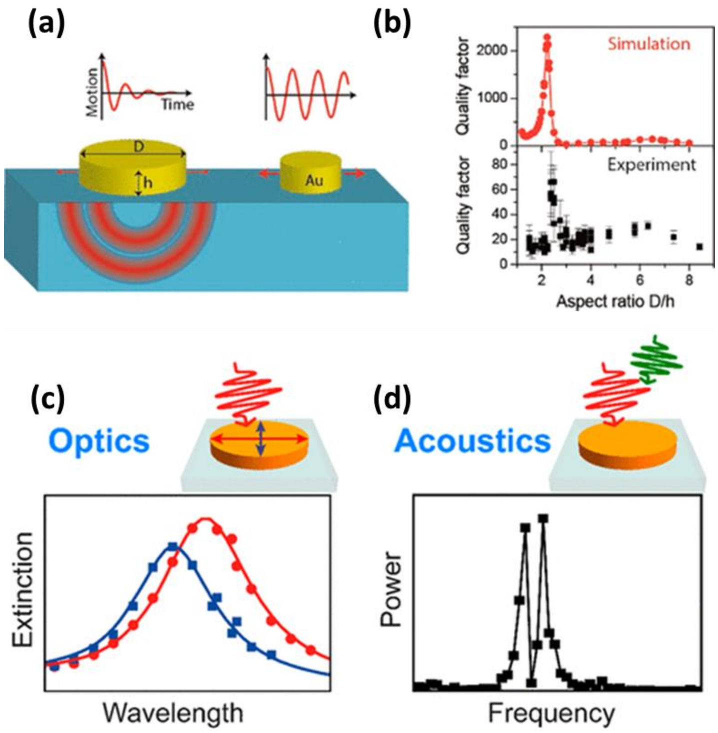

Figure 3. (a) Gold nanodisks are lithographically defined onto a sapphire substrate: the aspect ratio strongly affects the mechanical vibrations upon thermal excitation induced by a laser pulse. (b) Highest quality factor of experimentally detected vibrational modes for different nanodisks aspect ratio. The nanodisks may display circular section or noncircular one, and the presence of a major and a minor axes has an impact on the optical as well as acoustical response: (c) extinction spectra for the two orthogonal polarization directions are shifted in energy, and (d) the Fourier transform of the oscillating part of the time-resolved signal reveals two different resonances.

The number and characteristics of the detected acoustic modes are found to vary with nanodisk geometry. In particular, their quality factors strongly depend on nanodisk aspect ratio (i.e., diameter over height ratio), reaching a maximal value of ≈70, higher than those previously measured for substrate-supported nano-objects. The peculiarities of the detected acoustic vibrations are confirmed by finite-element simulations, and interpreted as the result of substrate-induced hybridization between the vibrational modes of a nanodisk. Moreover, using spatial modulation and pump−probe optical spectroscopies, we have identified the signatures of small morphological anisotropies in the plasmonic and vibrational responses of our nanostructures. In fact, the features of the measured extinction spectra and time-resolved signals are highly sensitive to faint deviations of the nanodisk morphology from a perfectly cylindrical one. An elliptical nanodisk section, as compared to a circular one, lifts the degeneracy of the two nanodisk in-plane dipolar surface plasmon resonances, which can be selectively excited by controlling the polarization of the incident light. This splitting effect, whose amplitude increases with nanodisk ellipticity, correlates with the detection of additional vibrational modes in the context of time-resolved spectroscopy. The analysis of the measurements is performed through the combination of optical and acoustic numerical models. This allowed us first to estimate the dimensions of the investigated nanodisks from their plasmonic response and then to compare the measured and computed frequencies of their detectable vibrational modes, which are found to be in excellent agreement. The results of our studies demonstrate novel possibilities for engineering the vibrational modes of nano-objects, and show that single-particle optical spectroscopies are able to provide access to fine morphological characteristics, representing in this case a valuable alternative to traditional techniques aimed at post-fabrication inspection of subwavelength nanodevice morphology.

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