Thermal Transport Modeling on Low-Dimensional Semiconducting Nanostructures

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Low-dimensional semiconducting materials, such as one-dimensional and two-dimensional materials, have attracted extensive research interest recently due to their promising applications in electrical energy generation and thermal management. For low-dimensional semiconducting materials, controlling their size, shape, composition and surface chemical functionalization is of importance in controlling their thermal transport behavior since the characteristic lengths inherent to the phonon scattering are often strongly coupled with these extrinsic sizes of these materials.

In this talk, we present our recent works in using various modeling and simulation methods to study the thermal transport properties of several low-dimensional semiconducting nanostructures [1-6]. First, we report our work of using linearized Boltzmann transport equation by incorporating the phonon-surface coupling to the study the effects of the size, surface roughness and composition on the transport properties of $Si_{1-x}Ge_x$ nanowires. Next, we will report our work of using non-equilibrium molecular dynamics to study the thermal transport properties of (1) core-shell Si/amorphous Si nanowires focusing on the geometry factor and strain engineering; (2) MoS_2 sheet and nanoribbons focusing on the geometry effects; and (3) silicene focusing on the effect of isotopic doping and strain engineering. Then, we will report our work of using first-principles method based on density functional perturbation theory and non-equilibrium Green function method to study the phonon scattering and thermal transport behavior of MoS_2 nanoribbons focusing on the intrinsic umklapp scattering mechanism. Finally, we will discuss briefly on the basic principles of using phononic engineering to modulate the thermal transport properties of low-dimensional materials for thermoelectric applications.

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Understanding fracture in Si anodes: Experiments and Simulations

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Si is the most promising anode for next generation Li-ion batteries, as it can provide capacities that are 3-10 times greater than that of current graphitic anodes. The limiting factor in commercializing these promising anodes is the 300% volume expansion and subsequent fracture that they experience during Li-insertion. This talk will present new experiments and simulations that go hand-in-hand and allow the development of design criteria that predict the most promising configurations that will limit damage and allow for stable electrochemical cycling. It is noted that high resolution electron microscopy is used to obtain the fracture patterns after Li-insertion, while finite element simulations can simulate these patterns.

Exotic phase group IV nanoparticles and Si-ZnS nanocomposites: new paradigms to improve the efficiency of MEG solar cells

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The efficiency of nanoparticle (NP) solar cells may substantially exceed the Shockley-Queisser limit by exploiting quantum confinement enhanced multi-exciton generation (MEG). However, (i) quantum confinement tends to increase the electronic gap and thus the MEG threshold beyond the solar spectrum and (ii) charge extraction through NP networks may be hindered by facile recombination. Using *ab initio* calculations we found that (i) Si and Ge NPs with exotic core structures such as BC8 or ST12 exhibit lower gaps and MEG thresholds than particles with diamond cores, and an order of magnitude higher MEG rates [1]. (ii) We also investigated Si NPs embedded in a ZnS host matrix and observed complementary charge transport networks, where electron transport occurs by hopping between NPs and hole transport through the ZnS-matrix (cf. Figure 1) [2]. Such complementary pathways may substantially reduce recombination, as was indeed observed in recent experiments. We employed several levels of theory, including DFT with hybrid functionals and GW calculations.

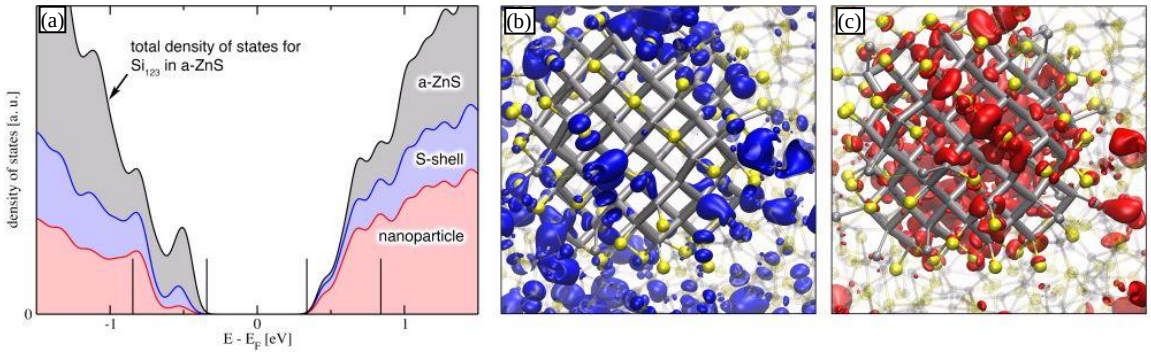

Figure 1: (a) Electronic density of states of the Si nanoparticle and host a-ZnS matrix for a sample of $Si_{123}Zn_{188}S_{201}$, partitioned into contributions from the nanoparticle, the surface shell (S-shell) and the host matrix (a-ZnS). Isodensity plots of the sum of square moduli of the states at the top of the valence band (blue) and bottom of the conduction band (red) are shown in (b) and (c), respectively. The sums were performed over an energy interval of 0.5 eV, as indicated by vertical bars in (a).

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PEC H_2 production: is it PV + electrolysis or not?

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A photoelectrochemical (PEC) hydrogen production device converts solar energy into chemical energy as H_2 gas. Typically, photoelectrode surface is decorated with co-catalyst such as Pt nano particles since the surfaces of known efficient photo absorber materials, such as III-V semiconductors or CIGSe, do not exhibit good catalytic activity for hydrogen evolution reaction (HER). The photo absorber material will absorb photons and generate photo-excited electrons and holes, which, in turn, will drive HER where Pt co-catalyst plays a role of lowering the HER activation barrier. The observation that a high efficiency PEC device seems to require good co-catalyst implies that the underlying conversion mechanism may be a combination of photovoltaic and electrolysis, which will make a PEC device modeling as simple additive: an efficient and corrosion resistant photo absorber with the correct band alignment to H_2/O_2 redox potential combined with a good co-catalyst for HER.

In 2013, it was reported that addition of a disk shaped Pt co-catalyst on a silicon based Metal-Insulator-Semiconductor (MIS) PEC device significantly enhances HER not only on the Pt co-catalyst but also on its surrounding area of SiOx surface [1]. Subsequently, based on ab-initio simulations of interfaces between water and III-V semiconductors, it was proposed [2] that certain types of semiconductor photo absorber surface, when it is in contact with electrolyte, might exhibit a good proton transport at the interface, and if, such a surface has a low activation barrier for Heyrovky step (the second step of HER), it will play a synergetic role with co-catalyst: a consistent picture with the aforementioned experimental observation [1]. Note that a catalyst such as Pt is known to have a low Volmer step (the first step of HER) activation barrier, while semiconductor (photo absorber) surfaces tend to have high Volmer step activation barriers.

In the presentation, we would like to discuss about a new design strategy, which will take advantage of the proposed synergetic effect between co-catalyst and photo-absorber surface.

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Efficiency assessment of novel materials based flexible thermoelectric devices

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In recent years, body heat energy scavenging has become a great source of interest as a power supply for autonomous systems, especially in the area of wearable electronics. The main issue regarding the materials currently used for room temperature thermoelectric applications is their reported health hazardousness [1]. The aim of this study is thus to propose a solution for flexible thermoelectric generators based on novel non health hazardous materials. For this purpose, we study the thermoelectric properties of the tetrahedrite group of materials (figure 1).

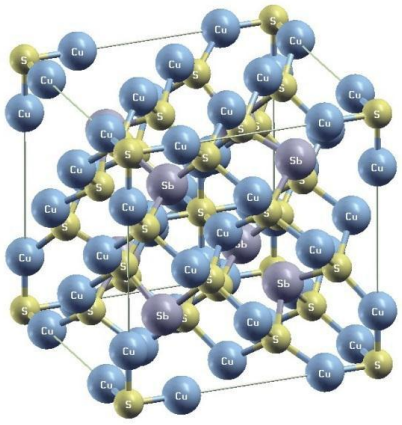

Figure 1: Crystal structure of $Cu_{12}Sb_4S_{13}$

A first step is to understand how doping helps improving the electrical properties of $Cu_{12}Sb_4S_{13}$ using an ab initio Density Functional Theory approach, with the open source code Quantum Espresso [2], through the analysis of the electronic structure (electronic band structure and density of states).

The Seebeck coefficient as well as the electrical conductivity as a function of temperature are calculated by solving the Boltzmann transport equation using the BoltzTrap code [3].

An interesting way of fabricating low cost flexible devices is by using printing techniques as it enables the processing of flexible substrates under standard temperature and pressure conditions. Besides the technological challenges (ink preparation, printing parameters control, post treatment…), it is necessary to evaluate the efficiency of an "ideal" printed device. In this context, a virtual prototype of a flexible thermoelectric device with an innovative design will be described and evaluated thanks to the COMSOL Multiphysics (Finite Elements Modeling) software. The impact of the electrical contact resistance will be taken into account in the model as it is a key parameter for device efficiency improvement.

The presented work will thus demonstrate a strategy for evaluating novel materials as potential replacements to bismuth telluride based alloys for room temperature thermoelectric applications and provide some insights into the development of flexible devices based on those materials.

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Better photovoltaic performance through randomized nanowires

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Radial junction nanowires are expected to give a higher performance than planar solar cells. This is due to enhanced optical path length for absorption and shorter distance for excitons to travel to interfaces where they can dissociate. We have optimised, with respect to geometrical parameters, solar cells consisting of nanowires with TiO2 cores and CdSe shells embedded in conducting polymer. Optical scattering and absorption is studied using Finite-Difference Time-Domain (FDTD) simulations. From this we obtain the generation rate of electron-hole pairs as a function of position, which is input into a charge transport model. We found that nanowires absorb more light when placed randomly rather than in a periodic array.

Synergistic Behavior of Tubes, Junctions and Sheets Imparts Mechano- and Thermo-Mutable Functionality in 3D Porous Multifunctional Boron Nitride Nanostructures

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One-dimensional (1D) Boron Nitride nanotube (BNNT) and 2D hexagonal BN (*h*-BN) are attractive for demonstrating fundamental physics and promising applications in nano/microscale devices. However, there is a high anisotropy associated with these BN allotropes as their excellent properties are either along the tube axis or in-plane directions, posing an obstacle in their widespread use in technological and industrial applications. Herein, we report a series of 3D BN prototypes, namely Pillared Boron Nitride (PBN), by fusing single wall BNNT and monolayer *h*-BN aimed at filling this gap. We use density functional theory and molecular dynamics simulations to probe the diverse mechano- and thermo-mutable properties of PBN prototypes, followed by tensile experiments on 3D printed thought-model specimens. Our results demonstrate that the synergistic effect of the tubes, junctions, and sheets imparts cooperative deformation mechanisms and phonon transport processes, which overcomes the intrinsic limitations of the PBN constituents, thus providing a number of superior characteristics including 3D balance of strength, toughness and thermal transport, emergence of negative Poisson's ratio, and elimination of strain softening along the armchair orientation (**Figure 1**). These features, combined with the ultrahigh surface area and lightweight structure, render PBN as a 3D multifunctional template for applications in graphene- based nanoelectronics, optoelectronics, gas storage and functional composites with fascinating in-plane and out-of-plane tailorable properties. Specifically, the ultrahigh surface area (> 2200 m^2/g) could be apromising venue for energy storage and delivery.

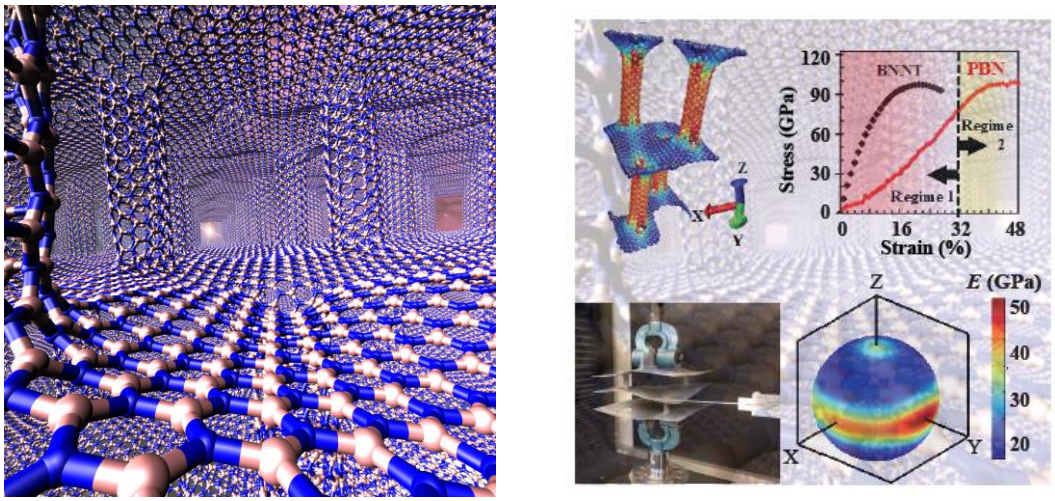

Figure 1. Pillared Boron nitride is a 3D porous multifunctional nanostructure exhibiting unique mechano- and thermo-mutuble properties with ultra-high surface area.

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Ab initio lattice thermal conductivity in pure and doped half-Heusler thermoelectric materials

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Half-Heusler phases are promising intermetallics for applications in thermoelectric generators. Optimization of their thermal transport properties is essential to improve their overall conversion efficiency [1]. Our goal is to perform a theoretical evaluation of thermal transport properties directly from first-principles calculations for various pure and doped half-Heusler compounds. The electronic structures are modeled in the framework of the density functional theory (DFT) [2]. The *ab initio* thermal properties are deduced from harmonic and anharmonic interatomic force constants calculations using finite size displacements method. Many-body perturbation theory is used for calculating the phonon-phonon interactions which yields the lifetime of phonons as function of momentum and band index [3]. Finally, thanks to a direct solution to the phonons Boltzmann transport equation [4] we computed the *ab initio* thermal conductivities, which are found in good agreement with the experimental data.

As a second step, we study specific localized impurities and size-controlled nanoparticles as they can lead to better thermal transport properties enhancing the thermoelectric efficiency [5,6,7,8]. In order to calculate the thermal conductivity in presence of localized defects, we developed a model to account for substitution defects and disorder in half-Heusler phases using perturbation theory and configurational analysis. Our results provide good insights for understanding the behavior of the thermal conductivity, which will be useful to guide experimental work to find pathways to improve the thermoelectric figure of merit of these materials.

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