Integrating sphere microscopy to quantify losses and limits in nanoscale solar cells

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system with a ratiometric response to Cu(II) and Zn(II) concentrations for assessing metal toxicity in environmental samples. Towards that end, we have begun to carefully characterize the interactions of Cu(II), Zn(II), and other metal ions with a monodisperse PNIPAm homopolymer. The interactions of metal ions with pure PNIPAm is relatively unstudied despite decades of PNIPAm research. To more easily observe a metal's influence on PNIPAm's phase transition and aggregation, we have developed a light scattering strategy using a perpendicular detection fluorometer. By measuring Second Order Scattering intensities and applying a Mie theory interpretation we are able to monitor *in situ* particle aggregation on the 10 to hundreds of nanometer scale in a comparable manner to more expensive instrumentation. We found that when raised above the Lower Critical Solution Temperature linear NIPAm homopolymer (M_n = 8.4 and 10.3 kDa) aggregated to larger particles sizes when in the presence of Cu(II) and Zn(II). Binding interactions directly between PNIPAm and Cu(II) were confirmed using equilibrium dialysis. The observed size trends were rationalized as a function of metal ion concentration according to a metal crosslinking scheme.

INOR 1151

Atomically precise Organomimetic Cluster Nanomolecules (OCNs)

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We have developed a new approach to rapidly assemble atomically precise, highly tunable organomimetic cluster nanomolecules (OCNs) *via* perfluoroaryl-thiol $\mathrm{S_NAr}$ chemistry. Specifically, we demonstrate how perhydroxylated dodecaborate clusters perfunctionalized with rigid, size-tunable pentafluoroaryl-terminated linkers can efficiently undergo 12-fold substitution with various thiolated molecules such as polymers, peptides, and saccharides at room temperature under mild conditions. The resulting OCNs exhibit high structural stabilities under biologically relevant conditions due to the full covalency of these nanomolecules. Furthermore, using a glycosylated OCN as a model, we demonstrate how one can use the developed strategy to rationally design and construct OCNs capable of binding proteins with dramatically enhanced affinities through multivalency.

INOR 1152

Bottom-up synthesis and self-assembly of atomically precise pristine and nitrogen-doped graphene nanoribbons

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Electronic properties of graphene nanoribbons (GNRs) can be tuned by their doping with heteroatoms, such as nitrogen. This possibility has been extensively studied theoretically, but only a few experimental attempts to synthesize nitrogen-doped GNRs (N-GNRs) by bottom-up approaches have been reported. This talk will be focused on the recently developed bottom-up solution method for gram quantities of narrow GNRs and N-GNRs that are less than 2 nm wide and have atomically precise armchair edges. The method is based on Yamamoto coupling of presynthesized molecular precursors followed by cyclodehydrogenation using Scholl reaction. GNRs and NGNRs were characterized by a number of microscopic (STM, AFM, SEM, TEM) and spectroscopic (XPS, UPS/IPES, UV-vis-NIR, IR and Raman spectroscopy) techniques. GNRs and N-GNRs have large electronic bandgaps, which makes them promising for applications in field-effect transistors with high on-off ratios and photovoltaic devices.

Also discussed in this talk will be self-assembly of GNRs and N-GNRs. We demonstrate that the substitutional doping with nitrogen atoms can trigger the hierarchical self-assembly of nanoribbons into highly ordered structures. This phenomenon is observed both on metal surfaces and in an unrestricted three-dimensional (3D) solution environment. On a surface, N-doping mediates the formation of hydrogen-bonded GNR sheets. In solution, sheets of side-by-side coordinated N-GNRs can in turn assemble via van der Waals and π-stacking interactions into 3D stacks, a process that ultimately produces macroscopic crystalline structures. The optoelectronic properties of these semiconducting NGNR crystals are determined entirely by those of the individual nanoscale constituents, which are tunable by varying their width, edge orientation, termination, and so forth. The atomically precise bottom-up synthesis of bulk quantities of basic N-GNR units and their subsequent self-assembly into crystalline structures suggests that the rapidly developing toolset of organic and polymer chemistry can be harnessed to realize families of novel carbon-based materials with engineered properties.

INOR 1153

Integrating sphere microscopy to quantify losses and limits in nanoscale solar cells

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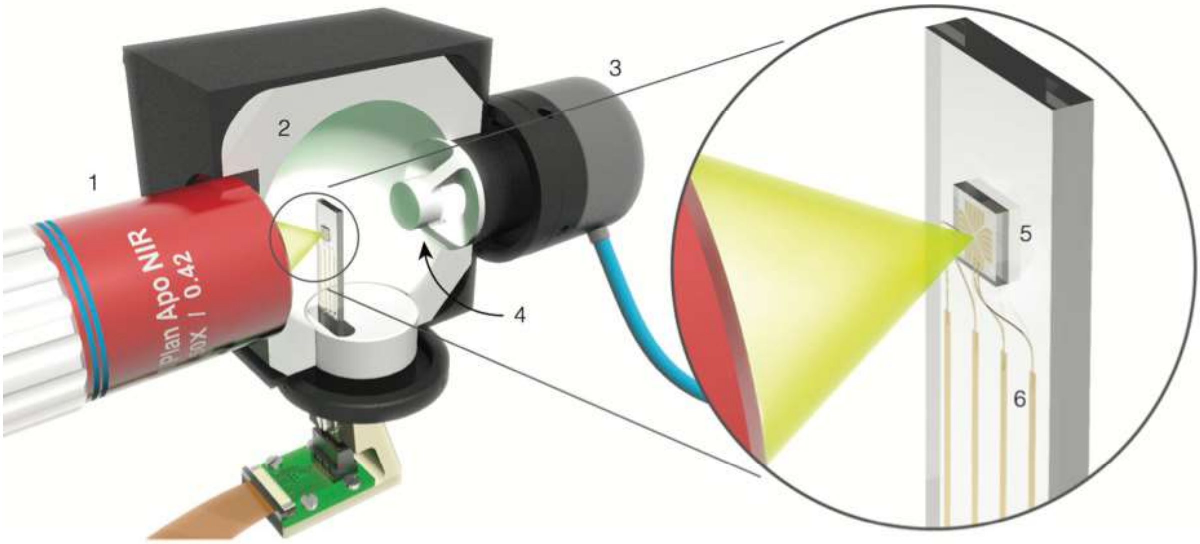
Nanophotonic engineering holds great promise for photovoltaics: the record conversion efficiencies of nanowire solar cells are increasing rapidly, and the record open-circuit voltage has already surpassed the record planar equivalent. Single nanowire devices provide an ideal platform to study how nanophotonics affects photovoltaics.

Characterization of such nanoscale devices, however, is very complicated. For example, the standard definition of power conversion efficiency no longer applies for these devices, because the nanowire can absorb light from an area much larger than its own size. Additionally, the thermodynamic limit on the photovoltage is a priori unknown and may be very different from that of a planar solar cell. To solve these problems a suitable quantitative absorption spectroscopy technique is required that can be applied to single nanostructures. To date such a technique does not exist, because quantitative absorption spectroscopy can only be performed on non-scattering nanostructures (extinction spectroscopy) or when all absorbed power is turned into heat (photothermal spectroscopy).

Here we introduce a new spectroscopy technique, integrating sphere microscopy, which enables direct determination of the absorption cross section of single nanostructures. The technique combines an integrating sphere, the standard for absorption measurements on ensembles of nanoparticles, with a long working distance microscope objective to achieve high spatial resolution. To demonstrate this technique, we investigate a single InP nanowire solar cell and determine for the first time the spatially resolved quantitative absorption, internal quantum efficiency (IQE), and photoluminescence quantum yield (PLQY). We use these intrinsic metrics to place its performance on an absolute thermodynamic scale and pinpoint performance loss mechanisms. For our record device we measure a photocurrent collection efficiency of >90% and an open-circuit voltage (850 mV) that is 73% of the thermodynamic limit (1.16 V).



INOR 1154

Approaching the hole mobility limit of GaSb nanowires

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Recently, high-mobility GaSb nanowires have received tremendous attention for high-performance p-type transistors for various applications; however, due to the difficulty in achieving thin and uniform nanowires, there is limited report till now addressing their diameter-dependent properties as well as their hole mobility limit in this important one-dimensional material system, in which all these are essential information for the deployment of GaSb NWs in practical operations. In this work, by employing our newly developed surfactant-assisted chemical vapor deposition (*Nature Comm.* 5, 5249, 2014), high-quality and uniform GaSb NWs with controllable diameters, spanning from 16 to 70 nm, are successfully prepared, enabling the direct assessment of their growth orientation and hole mobility as a function of diameter while elucidating the role of sulfur surfactant and the interplay between surface and interface energies of NWs on their electrical properties. The sulfur passivation is found to efficiently stabilize the high-energy NW sidewalls of (111) and (311) in order to yield the thin NWs (i.e. < 40 nm in diameters) with the dominant growth orientations of <211> and <111>, whereas the thick NWs (i.e. >40 nm in diameters) would grow along the most energy-favorable close-packed planes with the orientation of <111>, supported by the approximate atomic models. Importantly, through the reliable control of sulfur