Design, synthesis and characterization of novel nanowire structures for photovoltaics and intracellular probes

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Semiconductor nanowires (NW) represent a unique system for examining and exploiting phenomena at the nanoscale, and are expected to play a critical role in future electronic, optoelectronic and miniaturized biomedical devices. Modulation of the composition and geometry of nanostructures during growth encodes information or function, thus enabling applications at length scales unattainable with conventional lithography. My Ph.D. work has focused on synthesis of new semiconductor NWs and NW heterostructures and on the development of these structures into proof-of-concept devices such as solar cells and intracellular probes.

New nanowire materials

Despite advances in NW synthesis, progress towards the ab-initio design and growth of hierarchical nanostructures has been limited. In order to encode, for the first time, distinct structural units within a single NW, we have developed a 'nanotectonic' approach that provides iterative control over the nucleation and growth of NWs. We employed this strategy to grow kinked or zigzag NWs wherein the hierarchical NW units are separated by triangular joints. The synthetic approach is general and can be extended to the growth of kinked II-VI and III-V semiconductor NWs. Moreover, while the length and number of straight segments between the triangular joints can be controlled, the crystallographic growth direction is preserved throughout
the synthesis. We also realized dopant-modulated structures, including \( p-n \) diodes and field-effect transistors, with specific device functions precisely localized at the kinked junctions in the NWs\(^8\).
In order to extend further our topographical control over NW growth, we have demonstrated a rational, multi-step approach toward the synthesis of branched NW heterostructures. Single-crystalline semiconductor (IV-IV, III-V, II-VI) and metal branches have been grown on either bare or core/shell NW backbones with explicit control over composition, morphology and doping. Moreover, using the branches as input sources, functional devices such as diodes and field effect transistors (FETs) were demonstrated. Multi-branch-input configurations can lead to more complex nanoscale devices such as addressable light emitting diode arrays, logic circuits and biological sensors. Together, these advances in NW heterostructure synthesis enable a new level of structural and functional complexity at the nanoscale.

**Single nanowire photovoltaics**

Nano-enabled photovoltaics (PV) may hold great promise as next generation solar cells, providing high power conversion efficiencies at low-cost, and may also serve as integrated power solutions for emerging nanoelectronic devices. To being elucidating their intrinsic potential as solar cells, we initiated studies of single NW heterostructures as stand-alone and active PV elements.

The use of single NWs as PV elements presents several key advantages. First, the principle of bottom-up design allows for in situ and precise control of nanomaterial parameters, including chemical/dopant composition, diode junction structure, size, and morphology. Second, single or interconnected NW PV elements can be seamlessly integrated with conventional electronics and/or future nanoscale electronics to provide energy for low-power applications. Third, studies of PV properties at the single NW level permit determination of the intrinsic limits, areas of improvement, and potential benefits of nano-enabled PV.
We demonstrated the first single \textit{p-type/intrinsic/n-type (p-i-n)} Si NW solar cell with a radial core-shell geometry\textsuperscript{10}. Under 1-sun (100 mW/cm\textsuperscript{2}) simulated solar illumination the \textit{p-i-n} Si NW elements yield a maximum power output of 200 pW per NW and an energy conversion efficiency of up to 3.4\%, with stable and improved efficiencies achievable at higher intensities.

**Figure 2, Single nanowire photovoltaics\textsuperscript{10,13}.** A, Schematic of carrier generation and separation in axial (upper) and radial (lower) \textit{p-i-n} NWs. The pink, yellow, and blue regions denote the \textit{p-type}, \textit{i-}, and \textit{n-type} diode segments, respectively. The pink and blue spheres denote the holes and electrons, respectively. B, Dark and light \textit{I–V} curves of a coaxial Si NW device. C, Real-time detection of the voltage drop across a modified Si NW at different pH values. The Si NW pH sensor is powered by a single Si NW photovoltaic device. D, Nanowire AND logic gate powered by two Si NW photovoltaic devices in series.
Significantly, individual and interconnected Si NW PV elements serve as robust power sources to drive functional nanoelectronic sensors and logic gates (Figure 2C, 2D).

We also reported the first experimental realization of axial modulation-doped \( p-i-n \) and tandem \( p-i-n^+ - p^+ - i-n \) Si NW photovoltaic elements\(^{11}\). Under 1-sun simulated solar conditions, optimized \( p-i-n \) Si NW devices exhibited an open circuit voltage (\( V_{oc} \)) of 0.29 V, a maximum short-circuit current density of 3.5 mA/cm\(^2\), and a maximum efficiency of 0.5%. In addition, a novel single Si NW tandem solar cell consisting of the synthetic integration of two photovoltaic elements with an overall \( p-i-n^+ - p^+ - i-n \) structure was prepared and shown to exhibit a \( V_{oc} \) that is on average 57% larger than that of the single \( p-i-n \) device. This result underscores the potential for facile integration of multiple photovoltaic cells at the nanoscale.

The aforementioned coaxial and axial Si NW PV elements provide a new nanoscale test bed for studies of photoinduced energy/charge transport and artificial photosynthesis and might find general use as elements for powering ultra-low power electronics and diverse nanosystems\(^{10-13}\).

**Nanowire cellular probes**

Biomaterials and biomedical devices can broadly impact the life sciences by enabling development of tools for interrogating biological systems and by providing a synthetic replacement for damaged tissues. In this regard, research at the intersection of biology with nanoscience is emerging as a fruitful one in part due to the comparable size scale of nanostructures and functional units in biological systems\(^{14-17,20}\).

We first showed that Si NW field-effect transistor (FET) arrays fabricated on transparent substrates can be reliably interfaced with acute brain slices\(^{15}\). In particular, multiplexed mapping of neural signals with two-dimensional NW FET arrays revealed spatially heterogeneous
functional connectivity in the olfactory cortex with a resolution substantially surpassing previous electrical recording techniques. Our demonstration of simultaneous high temporal and high spatial resolution recording, as well as mapping of functional connectivity, suggests that NWFETs can become a powerful platform for studying neural circuits in the brain.15

Figure 3, Nanoscale intracellular FET probes. A, Schematics of 60° (top) and 0° (middle) multiply kinked nanowires and cis (top) and trans (bottom) configurations in nanowire structures. The blue and pink regions designate the source/drain (S/D) and nanoscale FET channel, respectively. B, SEM image of a doubly kinked nanowire with a cis configuration. L is the length of segment between two adjacent kinks. Scale bar, 200 nm. C, SEM of an as-made device. The yellow arrow and pink star mark the nanoscale FET and SU-8, respectively. Scale bars, 5 µm. D, Electrical recording from beating cardiomyocytes: (i) extracellular recording, (ii) transition from extracellular to intracellular recordings during cellular entrance, and (iii) steady-state intracellular recording. Green and pink stars denote the peak positions of intracellular and extracellular signal components, respectively.
Moving beyond detection of extracellular signals using 2D Si NW FETs, we demonstrated the first electrical recordings of intracellular potential with three-dimensional (3D) Si NW FET probes\textsuperscript{14}. The nanoscale probes are designed and chemically synthesized without lithography to encode an FET device at the apex of a kinked NW. This is achieved through control over \textit{cis-}/\textit{trans-} conformations and modulation doping. Subsequently, the free arms of such kinked nanowires are electrically contacted to free-standing and flexible electrodes. Electrical characterization of the 3D NW probes shows they are robust to mechanical deformation, can record solution pH changes with high-resolution, and, when modified with phospholipid bilayers, can record the intracellular potential of single cells. Significantly, electrical recordings of spontaneously beating cardiomyocytes demonstrate that our 3D NW probes can continuously monitor extra- to intracellular signals during cellular uptake. The nanometer size, biomimetic surface coating, and flexible 3D device geometry render these active semiconductor nanoprobes a new and powerful tool for intracellular measurements\textsuperscript{14}.
References:


