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Semiconductor Nanowires: What's Next?

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## **Author**

Yang, Peidong

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## Semiconductor nanowires, what's next?

Peidong Yang, Ruoxue Yan, Melissa Fardy

Department of Chemistry, University of California, Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA.

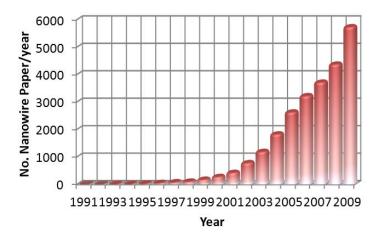
Email: p\_yang@berkeley.edu

When R. S. Wagner wrote down the following equation 
$$R_{\min} = \frac{2V_l}{RT \ln s} \sigma_{lv}$$
 for vapor-liquid-solid

whisker growth, where  $R_{min}$  is the minimum whisker radius,  $V_I$  is the molar volume of the metal droplet,  $\sigma_{IV}$  is the liquid-vapor surface energy, and s is the degree of supersaturation of the vapor<sup>1</sup>, he probably didn't expect that half a century later research into semiconductor whiskers with nanoscale dimensions would become such an active field. In the early 1990s, Hitachi scientists picked up this growth technique and applied it to the growth of III-V nanowhiskers<sup>2, 3</sup>. At the time, good positional and orientational control was achieved as well as the demonstration of the first pn junctions based on heterostructured nanowhiskers<sup>4</sup>.

This was followed by important studies in two separate research labs in the mid 1990s. A new whisker growth mechanism was proposed by William Buhro's group at Washington University, where they synthesized III-V nanowhiskers using a solution-liquid-solid process<sup>5</sup>. Meanwhile, the Charles Lieber group at Harvard initiated a research program in the area of inorganic nanorods. Carbide<sup>6</sup> and oxide nanorods<sup>7</sup> were produced through vapour phase conversion and transport processes in several of these early studies.

These early works on nanowhiskers and nanorods were popularized as semiconductor nanowires in the following decade. In the late 1990s, the field of semiconductor nanowires underwent a significant expansion and became one of the most active research areas within the nanoscience community<sup>8</sup>. Exciting developments have been made at an unusually fast pace from many research groups worldwide, including notably the Lieber group, the Yang group, the Samuelson group at Lund University and the Wang group at Georgia Tech. Initially the field went through a quite hyped period and has now developed into a relatively mature research area with ample exciting and new research opportunities. This can be seen from the vast number of papers (Figure 1) published on nanowires over the past two decades, which has increased exponentially, with most of the activity and development happening in the last ten years.



**Figure 1.** Increase in the number of publications on nanowires related topics from year 1991-2009 (Source: ISI; keyword: nanowires).

Just like any other emerging research frontier, people working in the nanowire field are constantly pushing the envelope to develop new fundamental science as well as potential applications. Several important sub-fields have emerged and each represents an exciting direction for both discovery-based and hypothesis-driven research. These sub-fields include nanowire electronics, nanowire photonics, nanowires for energy conversion and storage, and interfacing nanowires with living cells. One can get a quick idea of some of these exciting research topics by taking a glimpse at the top 10 most cited papers in this field (Figure 2), where some of the original ideas and concepts were first proposed or reported and were followed with overwhelming research activities worldwide.

Authorship	Paper title Journal , Issue, Page no., Year of publication	No. of times citated
Huang, M.H., et al.	Room-temperature ultraviolet nanowire nanolasers Science, 292, 1897 (2001)	3,567
Xia, Y.N., et al.	One-dimensional nanostructures: Synthesis, characterization, and applications Advanced Materials, 15, 353 (2003)	2,989
Pan, Z.W., et.al.	Nanobelts of semiconducting oxides Science, 291, 1947 (2001)	2,886
Morales, A.M., et.al.	A laser ablation method for the synthesis of crystalline semiconductor nanowires Science, 279, 208 (1998)	2,287
Cui, Y., et.al.	Nanowire nanosensors for highly sensitive and selective detection of biological and chemical species Science, 293, 1289 (2001)	1,793
Hu, J.T.,et.al.	Chemistry and physics in one dimension: Synthesis and properties of nanowires and nanotubes Accounts of Chemical Research, 32, 434 (1999)	1,765
Duan, X.F., et.al.	Indium phosphide nanowires as building blocks for nanoscale electronic and optoelectronic devices Nature, 409, 66 (2001)	1,531
Cui, Y., et.al.	Functional nanoscale electronic devices assembled using silicon nanowire building blocks Science, 291, 851 (2001)	1,324
Huang, M.H., et al.	Catalytic growth of zinc oxide nanowires by vapor transport Advanced Materials, 13, 113 (2001)	1,261
Gudiksen, M.S., et.al.	Growth of nanowire superlattice structures for nanoscale photonics and electronics Nature, 415, 617 (2002)	1,041

Figure 2. Top 10 most cited papers in the field of nanowire research (Source: ISI, Feb 2010).

It is not our intention to do a comprehensive research survey within this short perspective article. There are now many excellent review articles on this topic where readers can get a complete picture of nanowire research along various directions<sup>8-11</sup>. Instead we would like to provide some of our personal views on nanowire research by examining the latest research trends and activities. Some of the writing is meant to be forward-looking, speculative or even controversial, but hopefully it can stimulate more creative thinking and even more innovative ideas about nanowire research itself.

## What is fundamentally different?

What is fundamentally different here? This is a question we often ask ourselves when looking to embark on a new research direction or invest our efforts in a new type of material. Similarly, when starting to work with semiconductor nanowires, we would like to know to what extent are they different from nanocrystals, nanotubes. Will this research lead to new science or discovery of new pheonomena? Will it lead to new applications? The answer is clearly yes based on the past decade's research.

The unique one-dimensionality inherent to nanowires has already solved some of the long-standing technical problems that have plagued the thin film community. For example, integration

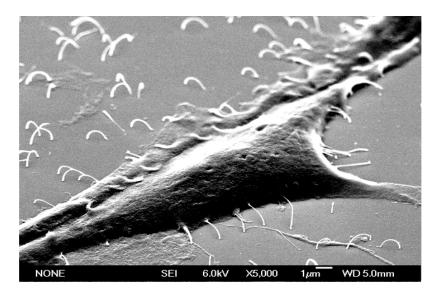
of optically active semiconductors (e.g. III-V's) onto silicon is critical for the next generation of computing tools that will merge photonics with electronics on a single platform. The conventional thin film technologies have run into interfacial lattice mismatch issues which often result in highly defective optical materials. In this regard, nanowire growth provides a natural mechanism for relaxing the lattice strain at the interface and enables dislocation-free semiconductor growth on lattice mismatched substrates, e.g. GaAs on silicon and germanium <sup>12,</sup>

The traditional semiconductor industry is unquestionably very advanced. For many decades, it has produced the devices and systems that are part of our daily lives, including transistors, sensors, lasers, light emitting diodes, and solar panels. By changing the material morphology from bulk to nanowire form, one might wonder how much fundamental difference there is. There have been a few good surprises, many of which are the result of strong photon, phonon and electron confinement within the semiconductor nanowires.

About 10 years ago, we first introduced the idea of semiconductor nanowire nanolasers<sup>14</sup>. Using ZnO nanowires as a model system, we were able to clearly demonstrate that lasing is possible for nanostructures with sub-wavelength cross-sections<sup>15</sup>. Later the idea was applied to various semiconductors with different emission wavelengths covering from UV all the way to IR<sup>16</sup>. Developing a nanoscopic, coherent light source with an extremely small footprint has many important implications. It can be used in integrated photonic circuits, in miniaturised sensor platforms with low-power consumption, and as imaging probes with high spatial resolution. These lasing studies on one-dimensional nanoscale cavities have led to recent efforts on plasmonic assisted nanowire<sup>17</sup> and nanopillar<sup>18</sup> lasing where optical modes can be further compressed at the metal-semiconductor interface, and nanoscopic lasers with all three dimensions less than one wavelength are well on the horizon.

Another good example of a fundamental difference in nanowires is the recent demonstration of silicon nanowire thermoelectrics. Using vapour-liquid-solid grown silicon nanowires, it was established early in this lab that their thermal conductivity can be significantly reduced from the bulk value of 150 W/m K (at 300 K) to ~8 W/m K<sup>19</sup>. This size-dependent reduction in thermal conductivity is a direct result of strong phonon boundary scattering at the nanowire surface. Only recently it has been demonstrated that the thermal conductivity in silicon nanowires can be further reduced down to almost the amorphous limit through a surface defect engineering process<sup>20</sup>. As a result, these rough silicon nanowires behave totally differently from their bulk counterparts. At room temperature, bulk silicon is considered to be both a good thermal conductor and electron conductor, while rough silicon nanowires are essentially thermal insulators and at the same time good electron conductors, making them good thermoelectric materials for waste heat recovery and power generation at a relevant temperature range.

Another emerging area of great interest is the interfacing of semiconductor nanowires with living cells. After years of nanowire research, we now have a good understanding of their electrical and optical functionalities. They can be used as transistors<sup>21</sup> and sub-wavelength optical wavequides<sup>22, 23</sup>. Their cross-sections are much smaller than the typical cell dimensions, which means minimal invasiveness, while their high surface area ensures proper cell-nanowire communication(Figure 3). All of these considerations make the nanowire a powerful platform to interface with living cells for various purposes<sup>24-26</sup>. This includes interfacing with stem cells for precise delivery of small molecules, DNA and proteins, and their potential use as a universal platform for guided stem cell differentiation. In another tour-de-force demonstration, the Lieber group has successfully integrated high density silicon nanowire transistor arrays for the detection, stimulation and inhibition of neuronal signal propagation<sup>27</sup>. In addition, the multiplexed signal recording capability of entire nanowire transistor arrays has enabled temporal shifts and signal propagation to be determined with very good spatial and temporal resolution. This research direction of interfacing nanowires and living cells is certainly one of the most exciting topics at the moment, and is quickly unfolding. While it is true that the nanowire in this case is serving as a versatile technological tool or platform, many new discoveries are expected when such platforms are used to tackle real biological problems.



**Figure 3** SEM image of human neural stem cells (NSCs) interfaced to silicon nanowires. The cells appear to be reorganizing themselves without experiencing great amount of stress around the bent nanowires compared to straight Si nanowires.

#### The issue of performance benchmarking

If we dive into the vast amount of nanowire literature, or even the more broadly defined nanoscience literature, we find that many of the papers claim novelty by demonstrating certain new nanostructure syntheses and/or their applications. These applications are often related to the structure's optical, electrical, and magnetic properties, where one can find related reports and discussion for their bulk counterparts in a separate research community. The infrequent comparison between nanostructured and bulk materials partly reflects the undisputed reality that there is indeed some disconnection between those who are working on semiconductor nanostructures and those who are working on more traditional bulk semiconductors. This also points out the fact that in the nanowire community we are often addressing the "yes-or-no" question due to novelty claim and priority issues, and we tend to pay less attention to the "better-or-worse" question, which is typically considered as an incremental, less-challenging, engineering optimization issue. In reality, both questions are equally important if we want to have the biggest impact from nanowire technology.

The high-efficiency and long-durability of semiconductor light-emitting diodes (LED) based on thin-film technology renders them ideal for displays and solid-state lighting<sup>28</sup>. However, further miniaturization of electrically driven multicolor light sources is crucial to a variety of fields including integrated nanophotonic and optoelectronic systems, high-resolution microdisplays, ultrahigh density optical information storage, and multiplexed chemical/biological analysis. This is where nanoscale LEDs come into play and semiconductor nanowires (III-V and nitrides) have been widely considered as good candidates for such applications. Since the first demonstration of a nanowire LED using vertical GaAs pn-junction arrays by the Hitachi team<sup>4</sup>, nanowire-based LEDs have been successfully realized in a variety of cross-nanowire junctions<sup>29-31</sup>, longitudinal<sup>32</sup> and co-axial heterostructures<sup>33</sup> with electroluminescence (EL) emission spanning the entire visible spectrum, as well as the near infra-red and ultraviolet. In particular, multicolor LEDs have been fabricated on a single substrate by contacting different n-type nanowires, including GaN (UV), CdS (green), and CdSe (near infrared), with Si nanowires as a common p-type material<sup>30</sup>, enabling easy interfacing with conventional silicon microelectronics. However, in most of these demonstrations, quantum efficiency of the light emitting devices was not reported, making it difficult to quantitatively compare with the existing thin film technologies. The highest external quantum efficiency (EQE) reported for nanowire-LEDs is in core/multishell nanowires that consist of n-GaN core and In<sub>x</sub>Ga<sub>1-x</sub>N/GaN/p-AlGaN/p-GaN shells. The estimated EQE for these nanowire LEDs was 5.8% at 440 nm and 3.9% at 540 nm<sup>33</sup>. This result is already comparable to InGaN-based single quantum-well thin film LEDs in the blue and green wavelength range<sup>34</sup>. And obviously there is still plenty of room for improvement by optimizing collection efficiency and interface control to minimize undesired non-radiative recombination.

A similar comparison can be made between nanowire and conventional thin-film solar cells. Solar cells are being pursued as environmentally friendly, renewable power sources to ease the energy crisis currently confronting human society. However, it remains a challenge to make inexpensive, high efficiency photovoltaic devices for large scale energy conversion. Semiconductor nanowires have been proposed to be fundamentally advantageous for photovoltaic applications due to their unique properties. Some of the many advantages that nanowires offer include long absorption path lengths while maintaining short distances for carrier collection/transport; interpenetrating heterojunction interfaces, allowing efficient carrier extraction following light absorption; strong light trapping in high density nanowire arrays; and modification of material properties and cell efficiencies through size and composition variation of the nanostructures. Dye-sensitized solar cells using dense arrays of oriented, crystalline ZnO nanowires as the anode have been designed to improve charge collection efficiency<sup>35</sup>. The direct electrical pathways provided by the nanowires ensure the rapid collection of carriers generated throughout the device, and an efficiency of 2.5%36 under AM 1.5 illumination has been demonstrated, limited primarily by the need to improve dye-loading by increasing the surface area of the nanowire array. Coaxial silicon nanowires (p-type/intrinsic/ n-type (p-i-n)) have achieved an apparent energy conversion efficiency of up to 3.4% under AM 1.5 illumination and are able to drive functional nanoelectronic sensors and logic devices<sup>37</sup>. And more recently, strong light trapping effects were observed in high density silicon core-shell nanowire array solar cells with efficiencies up to 6%38. Integrated with ultra-low power nanosystems, such as remote and mobile chemical and environmental sensors, nano-electronic and nano-photonic circuitry, these nanowire-based photovoltaic devices may serve as clean and sustainable miniature power sources. However, it remains a scientific challenge to design and synthesize nanowires and their heterostructures with performances exceeding that of the existing silicon photovoltaic technology, which has a commercial efficiency larger than 20% and is being pushed to it's theoretical limiting efficiency of 29%<sup>39</sup>. Issues to be considered include surface recombination problems associated with the high surface area of the nanowires.

A couple of years ago, a nanogenerator based on ZnO nanowires<sup>40</sup> was developed to power battery-free wireless nanodevices by converting ambient vibrations, hydraulic energy or mechanical movement to electricity. These devices with their varying configurations<sup>41-44</sup> demonstrate the capability of harvesting energy from ambient vibrations in different media<sup>41, 45</sup>, even from body and muscle movements<sup>46</sup>, and under a variety of frequencies (< 10 Hz to 41 kHz)<sup>41, 42</sup>. However, the major bottleneck to the application of these nanogenerators is their low output power, which is usually on the order of nW (areal power density < 1  $\mu$ W/cm<sup>2</sup>)<sup>43, 47</sup> and low output voltage, which is dictated by individual nanowires and is typically < 100 mV<sup>44, 46, 48, 49</sup>. In comparison, a commercial piezo generator based on piezoceramic thin films operating in the same frequency range can be 3-4 orders of magnitude higher in these parameters (e.g. piezoelectric heel-strike generators<sup>50</sup>). Although different strategies to improve the output power and voltage have been proposed<sup>51</sup>, these nanogenerators may never be able to power our homes or even our flash lights. However, ZnO nanowire-based nanogenerators possess unique features that make them promising solutions for independent, sustainable, maintenance-free nanosystems that have low power consumption, such as implantable biosensors, nanorobotics, and possibly portable/wearable personal electronics.

While the previous section focused on the scientific breakthroughs achieved by constantly pushing the fundamental limits of nanowires, here we would like to make the case that a technological breakthrough will come only after we address both "yes-or-no" and "better-orworse" issues with all of our undivided attention. Long term stability will also be a common problem for many of the nanowire-based devices and systems. It is true for the LEDs, solar cells, and piezoelectric generators we discussed here, as well as sensors, batteries and transistors. We need to keep in mind that all of these areas have existing mature industrial technologies (largely technologies based on thin film and bulk semiconductors). Unless there are significant cost and/or performance benefits from using nanowires, it will be difficult to displace the existing technologies.

## Bottom-up vs. top-down

There are now many different methods for making semiconductor nanowires. They are commonly placed into two categories, namely, the bottom-up and top-down approaches. The bottom-up approach starts with individual atoms and molecules and builds up the desired nanostructures. For nanowire synthesis, this includes vapour-liquid-solid (VLS) chemical vapour deposition, the solid-liquid-solid process, nanopore templating, and various hydrothermal methods. The top-down approach relies on dimensional reduction through selective etching and various nanoimprinting techniques. Similarly, for the integration of nanowire building blocks, there are also two such general approaches, the first being chemical assembly such as Langmuir-Blodgett techniques, the other being lithographical processes. So, which one is better?

The answer as of now is a bit of both. It is clear at this point that we need both approaches for many of the applications related to semiconductor nanowires. Synthesis-based bottom-up approaches can be used to generate structures with dimensions ranging from Å to hundreds of nm. On the other hand, while the fabrication based top-down processes still have difficulty creating structures below 10 nm, they have a great advantage when integration and addressability are concerned.

There are couple of good examples that illustrate the value of both strategies. The thermoelectric performance of silicon nanowires has been examined in both synthetic and fabricated nanowires. The Yang group has focused on VLS grown and chemically etched nanowires<sup>20</sup> while the Heath group has had great success with their Superlattice Nanowire Pattern Transfer (SNAP) process to produce very thin silicon nanowires<sup>52</sup>. In both cases, similar thermoelectric performance was observed.

The concept of nanowire based solar cells has attracted significant attention because of their potential benefits in carrier transport, charge separation and light absorption. The Lieber group has developed a fairly sophiscated core-sheath growth and contact strategy for their silicon p-i-n nanowire solar cells, with efficiencies up to  $3.5\%^{37}$ . On the other hand, etching and overgrowth processes have also been developed to fabricate high density silicon core-shell solar cells. Efficiencies up to 6% have been demonstrated in this type of top-down fabricated nanowire core-shell arrays<sup>38</sup>. Here, both synthetic and fabricated nanowires offer similar core-shell solar cell designs, and therefore the same operational principle, but with differences in interface sharpness and carrier recombination kinetics.

We can find a similar situation when it comes to sensor and laser research. Based on chemically synthesized nanowires, chemical/biological sensors and nanolasers and nanolasers have been developed in the Lieber and Yang groups. On the other hand, fully integrated nanowire chemical sensors and nanopillar lasers have been fabricated and tested using all top-down processes. The top-down approach typically has the advantage of being high throughput and more amenable for large scale integration.

As for the integration of ultrahigh density nanowire circuitry, this has been one of the major challenges for nanowires prepared by either method. We have many different methods to assemble high density nanowire arrays in either two or three dimensions. However, when one wants to carry out large scale integration, the choices are fairly limited, especially for addressability at the single nanowire level. In this regard, the SNAP method proposed by the Heath group is quite promising<sup>59</sup>. They have proposed a demultiplexer architecture for bridging the sub-micrometer dimensions of lithographic patterning to the nanometer-scale dimensions for ultrahigh-density nanowire circuits. This concept has been experimentally demonstrated on sub-micrometer wires and on an array of 150 silicon nanowires patterned at nanowire widths of 13 nm and a pitch of 34 nm<sup>60</sup>.

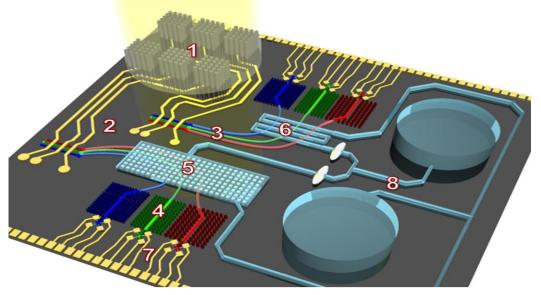
#### Where is the killer application?

So where is the killer application after all these years? Or is there one?

Optimistically the field has made great progress in advancing the fundamental science related to semiconductor nanowires. There are also many startups trying to commercialize some of the important applications, including Nanosys, Alphabet Energy, Vista Therapeutics, and QuNano. Below are three areas, in our opinion, that will see great research activity and progress in the coming years.

**Integrated nanophotonics.** Imagine what you can do if you can have a nanoscopic light source that is as small as a semiconductor transistor.

The ability to manipulate pulses of light within sub-micron volumes is vital for highly integrated light-based devices, such as optical computers, to be realized. Chemically synthesized nanowires have several unique features that make them good photonic building blocks, including inherent one-dimensionality, a variety of optical and electrical properties, good size control, low surface roughness and, in principle, the ability to operate both above and below the diffraction limit. While state-of-art lithography techniques are capable of fabricating nanostructured features with dimensions discussed in this article, chemically grown nanowires still possess unique advantages such as single crystallinity, atomically smooth surfaces and low defect density. Using a combination of nanolithographic tools, it is highly feasible to assemble photonic circuits (Fig 4) from a collection of nanowire elements that assume various functions, such as light creation, routing and detection. Since the range of nanowire materials now includes active, passive, nonlinear and semiconducting inorganic crystals9, synthesizing from the bottom-up offers novel design-by-choice schemes to facilitate the assembly of multi-function components on the same substrate. Such systems can be used in parallel with existing sensing technologies such as surface enhanced Raman spectroscopy and microfluidic systems, and could be used in many potential areas such as chemical/biological sensing, environmental monitoring, imaging and information processing. Because of their small footprint and low power consumption, they can be self-powered, and readily embedded in cell phones or wrist-watches.



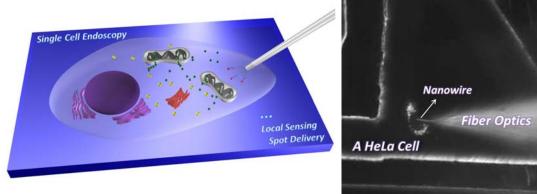
**Figure 4.** Future nano-photonic circuits for chemical analysis will require the integration of nanowire-based devices that assume different functions, such as nanowire solar cells as on-chip power supplies (1), laser diodes/LEDs as light sources(2), nanoribbons (3) and 2D photonic bandgap (PBG) nanowire arrays (4) as filters and waveguides to select and route input and output signals; (6), sample analysis chambers, such as silver nanocube arrays for SERS (5) or nanoribbon/sample intersection for absorption analysis; nanowire based photodectectors (7) and a microfluidic system for liquid sample transport (8).

**Nanowire-based single cell endoscopy.** The development of a nanoscopic coherent light source could also lead to a new type of nanowire probe for *in-situ* single cell imaging, essentially a nanowire-based single cell endoscopy.

Development of such nanowire probes would enable us to carry out intracellular imaging and probing with high spatial resolution (Figure 5), monitor in-vivo biological processes within single

living cells and greatly improve our fundamental understanding of cell functions, intracellular physiological processes, and cellular signal pathways. Nanowires have several key features that make them promising for applications in cell endoscopy including minimal invasiveness, high flexibility, high refractive index, evanescent wave optical sensing, and nonlinear optical conversion capabilities. The nanowires used for these probes will generally have diameters below 100 nm and high aspect ratios, ensuring the non-invasiveness of the nanowire probes. The nanowires are also highly flexible and yet mechanically robust. The twisting and bending in these nanowires will not cause significant optical propagation losses<sup>22</sup>, and will greatly facilitate the application of such probes in single cell imaging. Due to their high refractive index, nanowires also function as efficient sub-wavelength optical waveguides, even in high-index physiological liquids and/or living cell environments<sup>61</sup>. Waveguiding also enables highly localized excitation and detection, limiting the probe volume to the very tip of the nanowire (i.e. down to pico- and femtoliter). Additionally, the application of nonlinear optical nanowires into the probe platforms will introduce two important features<sup>62</sup>: subwavelength waveguiding and frequency conversion capabilities. This will enable the input of an IR beam at one end of the nanowire and the use of visible or UV output on the other end for the cell imaging/probing. The use of IR as an input beam would greatly benefit the entire imaging process in realistic physiological environments.

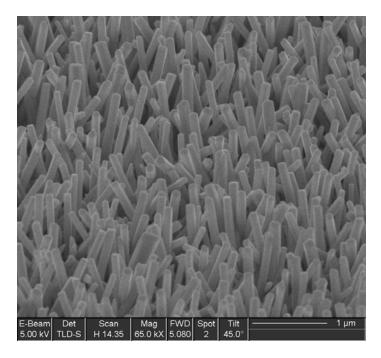
Such novel nanowire probes promise intracellular imaging with greatly enhanced three-dimensional spatial resolution as well as temporal resolution. In addition, these nanowire probes could be used for spot-delivery or extraction of chemicals (proteins/DNAs) from single living cells with much improved spatial resolution as compared to conventional delivery/extraction methods.



**Figure 5** Nanowire-based Biological probe for endoscopy, spot delivery and sensing within a single living cell. The image on the right shows a single heLa cell probed by an oxide nanowire attached onto an optical fiber tip.

**Nanowires for direct solar to fuel conversion.** Nanowires, with their unique capability to bridge the nanoscopic and macroscopic worlds, have already been demonstrated as important materials for different energy conversion purpose, some of which have been discussed earlier in this article.

One emerging and exciting direction is their application for solar to fuel conversion. The generation of fuels by the direct conversion of solar energy in a fully integrated system is an attractive goal, but no such system has been demonstrated that shows the required efficiency, is sufficiently durable, or can be manufactured at reasonable cost. In this regard, one can learn a great deal from the nature's photosynthetic organisms that routinely carry out the conversion of carbon dioxide and water to carbohydrates. There are several key features in these photosynthetic systems: spatial and directional arrangement of the light-harvesting components, charge separation and transport, and the desired chemical conversion at catalytic sites in compartmentalized spaces.



**Figure 6.** SEM image of a InGaN nanowire array, a potential light absorbing nanostructure for solar-to-fuel conversion purpose.

In order to design an efficient artificial photosynthetic materials system, whether it is for water splitting or  $CO_2$  reduction, we should try to use and optimize the same principle as much as possible. Semiconductor nanowires can be readily designed and synthesized to deterministically incorporate heterojunctions with improved light absorption, charge separation and directional transport. Meantime, it is also possible to selectively decorate different oxidation or reduction catalysts onto specific segments of the nanowires to mimic the compartmentalized reactions in Nature.

More importantly, semiconductor nanowires can now be synthesized in large quantities using both gas phase and solution phase methods. The material compositions of interest include silicon, oxides (WO<sub>3</sub>, TiO<sub>2</sub>), nitrides (InGaN, Figure 6<sup>63</sup>), phosphides (GaP), chalcogenides (CdSe) and maybe others made of earth-abundant elements. Because of their large aspect ratio and flexibility, nanowires can be readily processed (e.g. roll printing, casting, automated drawdown) into interconnecting meshes or membranes that are mechanically robust. In addition, the high surface-area nature of the nanowires often leads to a flexible mesh having a porous and open framework, which could greatly benefit the surface catalytic reaction as well as gas evolution. Having large surface-area and tunable electronic structures, these semiconductor nanowires could be used as effective photo electrodes and are expected to play an important role in the overall solar-to-fuel system design.

As a result of the numerous fundamental breakthroughs made in the past decade, we now have a good understanding of the pros and cons of using semiconductor nanowires for various applications. We can also peer into the future with reasonable confidence. We can be confident that we will continue to see many more fundamental new discoveries and science based on this unique class of nanoscale building blocks. Meantime, the future of nanowire technology will be largely dependent on how well we can balance the issues of cost, performance and stability of the nanowire-based devices and systems.

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