Title

30 Years of Semiconductor Nanowire Research: A Personal Journey

Permalink

https://escholarship.org/uc/item/0q83x459

Journal

Israel Journal of Chemistry, 65(2)

ISSN

0021-2148

Author

Yang, Peidong

Publication Date

2025-02-01

DOI

10.1002/ijch.202300127

Peer reviewed

30 years of semiconductor nanowire research: A Personal Journey

Peidong Yang
Department of Chemistry, Materials Science and Engineering
Kavli Energy Nanoscience Institute, University of California, Berkeley
Materials and Chemical Science Division, Lawrence Berkeley National Laboratory
Berkeley, California 94720, USA
Email: p_yang@berkeley.edu

In 1993, I joined Prof. Charles Lieber's lab at Harvard University to pursue my Ph.D. in solid state and materials chemistry. At the time, I could barely speak English as a first-year graduate student just finishing my undergraduate training at the University of Science and Technology of China. Meantime the solid-state research community was experiencing some significant transition. The wild gold rush in high-temperature (T_c) cuprate superconductors (HTSC) started to taper down, while the superconductivity based on C_{60} started to overtake a big part of the research community as well as in major scientific journals. As my undergraduate research was on high-temperature cuprate-based superconductors, my first project at Harvard was a continuation of this line of research,[1] which was about the infinite layered cuprate compound based on pulsed laser deposition. It was expected that this infinite layered cuprate holds the promise of being a room-temperature superconductor, however, it was never materialized. It was my second project at Harvard that eventually led to the birth of inorganic nanowires.

This second project is about flux line pinning in high T_c superconductors using columnar defects as the pinning centers. The basic idea is that linear structural defects can pin the flux lines within HTSCs so that their critical current density (the maximal current density that these HTSCs can carry with zero resistance) can be enhanced. The question is how to create such linear structural defects within crystalline cuprate thin films. Scientists have already successfully demonstrated the concept by irradiating HTSC crystals with high-energy ions at synchrotron beamline facilities. However, such heavy ion irradiation is practically not viable for large-scale processes. We reasoned that maybe we could introduce some sort of linear nanoscopic objects into HTSC to form a composite, and then these linear nanoscopic objects would serve as the magnetic flux line pinning centers.

The Beginning

So what will these "linear nanoscopic objects" look like? At the time, Sumio Ijima had just published his carbon nanotube papers. Carbon nanotubes are certainly linear, and nanoscopic, however, they will be readily oxidized in the high-temperature oxidative process conditions for HTSC growth. This left us with not much choice, we need to create some sort of linear nanoscopic stable oxide structures for this purpose. That was the beginning of the concept of inorganic nanowires (Figure 1).[2,3]

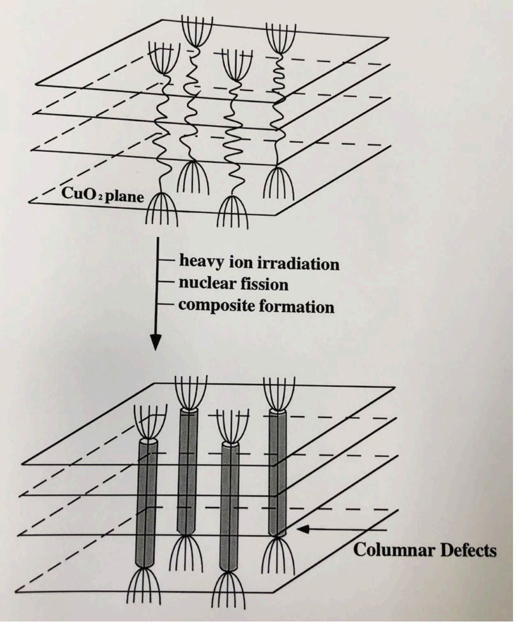


Figure 1: Flux line pinning in high-temperature cuprate superconductor with linear nanoscopic objects, the beginning of the concept for inorganic nanowires (Ph.D. thesis, P. Yang, Harvard University, 1997).[4]

Now the next question came, how to produce such "linear nanoscopic oxide structures"? Note in the early 1990s, quantum-confined colloidal nanoparticle research was starting to pick up speed. Many research groups were also busy with exciting research on C_{60} and its associated doping and superconductivity. There were simply no established methods to produce such a one-dimensional (1D) nanostructure of inorganic materials. Through literature, we were aware of Wager's early work back in the 1970s at Bell Lab using the vapor-liquid-solid (VLS) process to grow large semiconductor whiskers (Figure 2).[5] This VLS method clearly established an effective way to produce one-dimensional crystals. In order to produce 1D nanoscopic crystals, we will need to introduce metal nanoparticles as the catalysts. This immediately led to the production of a collection of oxide nanowires (MgO, Al_2O_3, TiO_2, and ZnO), eventually, MgO nanowires were successfully incorporated into HTSC $Bi_2Sr_2CaCu_2O_x$ thin films, leading to significantly enhanced flux line pinning and critical current density (Figure 3).[2,3]

This collection of oxide nanowires grown via solid-vapor and vapor-liquid-solid processes formed the first fundamental patent for inorganic nanowires. At the time of patent filing (1995-1996), we called them "nanorods".[6] Meantime, Hitachi scientists have also picked up this growth technique and applied it to the growth of III-V nanowhiskers.[7] At the same timeframe, 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.[8] And in 1998, my graduate colleague Alfredo Morales reported his first attempt to produce silicon nanowires using a laser-based VLS method.[9] At a similar time, S. T. Lee group also reported their silicon nanowire growth using pulsed laser deposition.[10] These early studies on nanowhiskers and nanorods were eventually popularized as semiconductor nanowires, and that started an era of very active research on these exciting one-dimensional nanostructures.

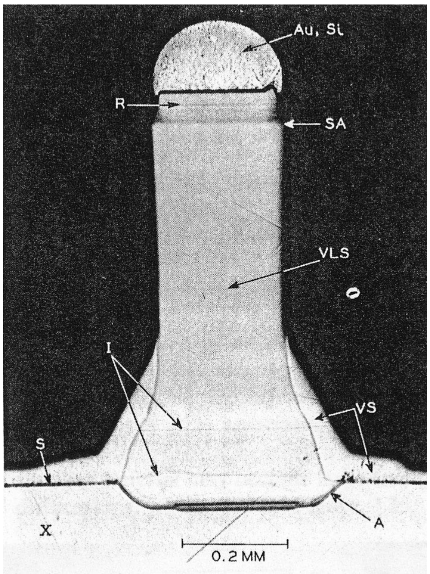


Figure 2: Wagner's Si whiskers, Bell lab, 1970s [Ref. 5. Reproduced with permission, American Institute of Physics].

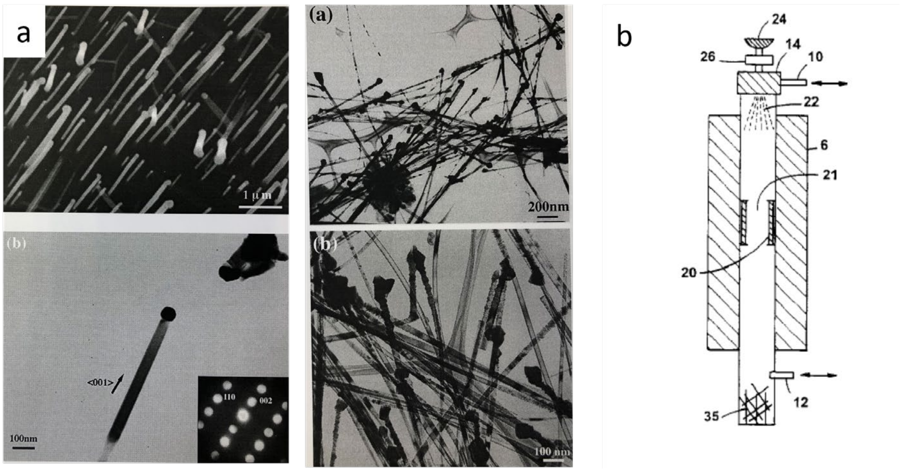


Figure 3: [a] Collection of oxide nanowires grown at Harvard Chemistry (ca. 1995), from the Ph.D. thesis, P. Yang, Harvard University, 1997. [b] An illustration for the production of oxide nanowires, from patent "Metal oxide nanorods"; Filed in 1996; US Patent 5,897,945, April 27, 1999. In this original patent, nanowires were defined as "*have diameters between 1 and 200 nm and aspect ratios between 5 and 2000*".

In 1997, I graduated from Harvard Chemistry and started a brief 18-month postdoc stint at UCSB working on self-assembly and mesoporous materials. In 1999, I started my independent career at the University of California, Berkeley with the entire program focusing on semiconductor nanowires.

The first thing we did at Berkeley was the direct observation of VLS nanowire growth. For the first time, the nucleation and growth of nanowires were directly observed within a high-temperature in-situ transmission-electron-microscope (TEM, Figure 4). This direct in-situ observation of vapor-liquid-solid nanowire growth was made by my first graduate student Yiying Wu (now at Ohio State University) in 2001.[11] The creation of a solid-liquid interface is the starting point for one-dimensional crystal growth; this observation underpins the fundamental nucleation step at the nanometer scale for all of the vapor-liquid-solid processes. These early studies of the nanowire growth mechanism demonstrated that a general concept of nanoparticle-catalyzed growth could be used to synthesize single-crystalline semiconductor nanowires predictably for the first time. Significantly, these early studies provided the intellectual underpinnings for the predictable growth of nanowires of virtually any semiconductor material in the periodic table.

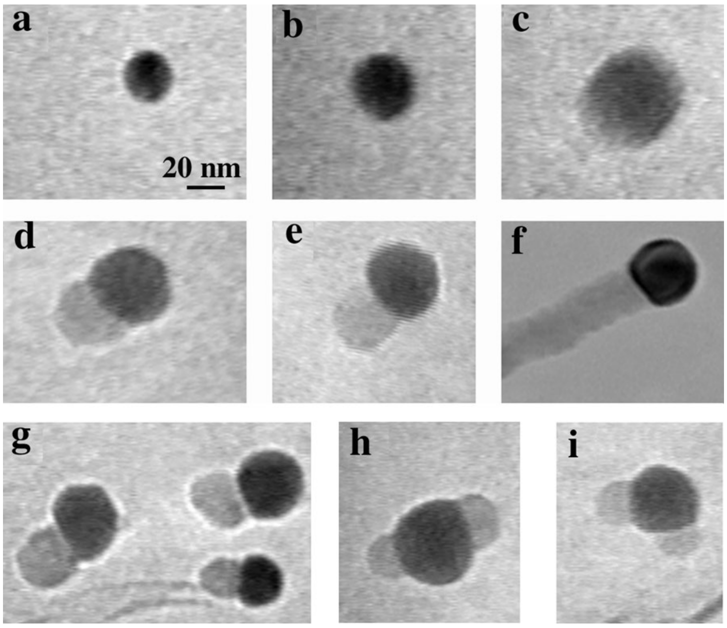


Figure 4: Seeing is believing. In-situ high-temperature TEM observation of VLS growth of Ge nanowires [Ref 11, *Reproduced with permission, American Chemical Society*].

The Invention of Nanolasers

At the transition of the centuries, the world was in its own transition. We witnessed the tragic falling of the World Trade Center in the Sept 11 attack. Meantime we have also witnessed several very important breakthroughs in the nanowire research community. This was a time when we had a good fundamental understanding of the vapor-liquid-solid nanowire growth mechanism and started to explore precisely controlled nanowire growth. Several groups (Lieber, Yang, Samuelson) have demonstrated general concepts for the growth of nanoscale axial and core-shell heterostructures based on our fundamental understanding of the vapor-liquid-solid growth mechanism.[12], [13], [14] With this capability of making heterostructured nanowires, it opened up an entirely new world of exploring the electrical, optical, and optoelectronic properties of semiconductor nanowires.[15] For example, the Lieber group created the first diode structures using crossed p-type and n-type nanowires, showing that they exhibit rectifying transport similar to planar p-n junctions. Active bipolar transistors and complementary inverters were also assembled and demonstrated at the time.

In parallel with the exciting nanowire electronics research, my group started to move into an unexplored territory: Nanowire photonics. In retrospect, all of this happened as a natural evolution of the creative research itself since the entire optoelectronic and information industry relies on semiconductors, and both sectors were aggressively scaling down the device sizes in order to improve the device performance while reducing the device footprint and energy consumption. In this regard, semiconductor nanowires offer a perfect structural platform to address these scientific and technological needs.

In 2001, we introduced the first idea of semiconductor nanowire nanolasers.[16] This was accomplished with my first postdoc fellow Michael Huang (now at National Tsinghua University). Using ZnO nanowires as a model system, we were able to clearly demonstrate that lasing is possible for nanostructures with sub-wavelength cross-sections. Later the idea was applied to various semiconductor nanowires with different emission wavelengths covering from UV to IR.[17] A semiconductor nanowire can fulfill two fundamental requirements for traditional lasers: they act as both the optical gain medium and the optical cavity (Figure 5). These high-quality single-crystalline structures were grown bottom-up without any extended defects that would otherwise lower the luminescent efficiency, a critical parameter for reaching the laser threshold. By building the cavity up atom by atom, the crystal planes were used to define the side facets of the waveguide and the mirrors of the resonator. At the time, it was unclear if mirror facets could be so small because they could induce enough scattering loss that the optical cavity would be too inefficient for laser oscillation. In this case, these nanowire nanolasers shattered expectations by lasing at room temperature.

It is now understood that these well-faceted nanowires with cross-sectional dimensions on the order of the (sub)wavelength of light support Fabry-Perót cavity modes. This understanding has allowed the exploration of numerous new materials, new applications, and nanoscale optical phenomena. The library of nanowire laser materials has expanded enormously, resulting in lasers that emit light in the UV, visible, and near-IR. Optically pumped laser oscillation has been demonstrated for ZnO, GaN, InGaN, CdS, CdSe, GaAs, InGaAs, AlGaAs, ZnS, GaSb, and a collection of halide perovskites with different compositions.[18] By introducing novel photonic complexities, researchers have modified the lasing modes of nanowires to achieve single-mode lasing and nanowire ring resonator lasers. The compact form factor of one-dimensional nanoscale lasers has enabled the development of new photonic applications such as nanoscale optical routing, nanoscale electro-optic modulators, and single-cell probes.[17, 18] This field has enjoyed tremendous progress in the past 20 years. Low-cost lasers offer the prospect of sensors and point-of-care diagnostics that are disposable and produced on a large scale.

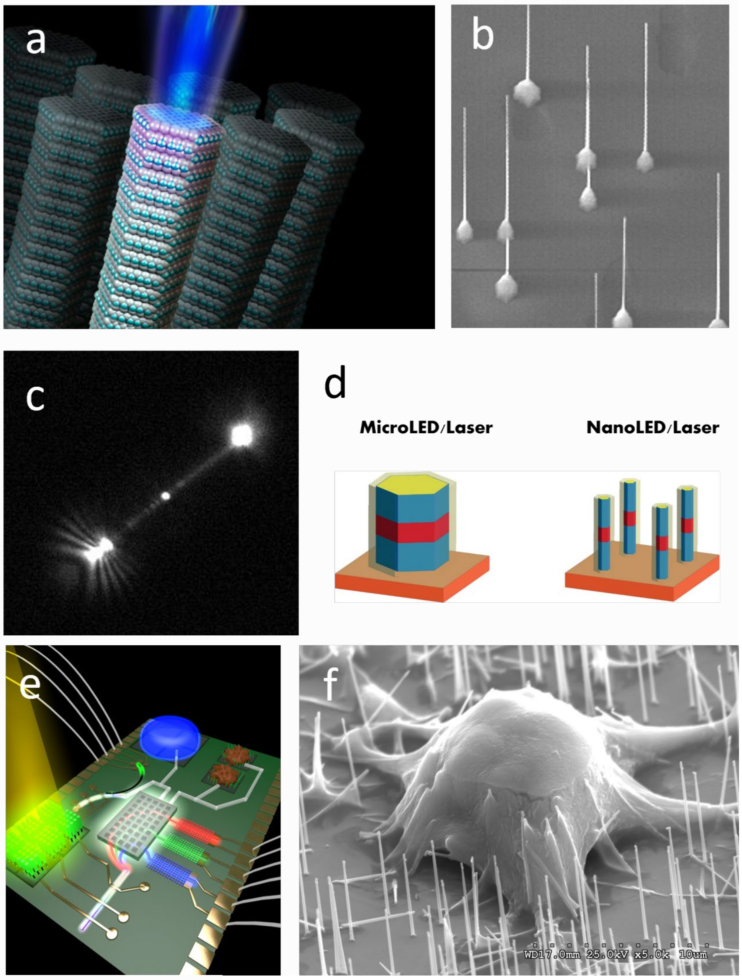


Figure 5: Nanowire nanolasers. (a). Schematic illustration for nanowire nanolasers; (b). SEM image of vertical UV nanowire emitters; (c). Optical image of an optically-pumped nanowire laser; (d). Schematic for microLED/LD and nanoLED/LD based on nanowire heterostructures; (e). Schematic illustration for a nano-photonic circuitry for chemical analysis based on nanowire building blocks; (f). SEM image of mouse embryonic stem (mES) cells interfaced to silicon nanowires [Ref 26, Reproduced with permission, American Chemical Society].

Research in miniaturized lasers and their applications is paramount for the continued growth of photonic technologies because they can enable new applications and discoveries unattainable by traditional photonics. Developing a nanoscopic, coherent light source with an extremely small footprint has many important implications. It can be used in integrated photonic circuits, in miniaturized sensor platforms with low power consumption, and as imaging probes with high spatial resolution (Figure 5). The development of highly stable, wavelength-tunable coherent light sources on the nanoscale can unlock the potential for commercial applications in optical communications, sensing, imaging, and data storage, among many others. The ability to manipulate pulses of light within sub-micron volumes is vital for highly integrated photon-based devices, such as optical computers, to be realized.

Given that the fabrication of silicon-based integrated circuits is beginning to reach its physical limits, large-scale integration of electrically driven nanolaser arrays will represent a significant step toward the realization of a nanoscale photonic integrated circuit that processes information at rates that are orders of magnitude faster than their electrical counterparts. In this regard, an electrically pumped nanowire laser will enable the compact integration of nanoscale optical components. Lasing from electrical injection in a single nanowire level device, however, is sufficiently different from the bulk semiconductor devices, and requires unique and creative electrical injection configurations. One of the first electrically driven semiconductor nanowire lasers was developed based on a CdS nanowire.[19] Later on, electrical injection in *p-n* junction core-shell nanowires and *p-i-n* longitudinal nanowires was investigated using numerical simulation.[20]

Back in 2010, I led an electrical injection nanolaser research team with C. Z. Ning, C. Chang, M. Wu, and S. L. Chuang. This was a very intense and focused research effort within the DARPA NACHOS program with a central mission to demonstrate an electrical injection nanowire laser. The overarching goal of the NACHOS program is to demonstrate semiconductor lasers that have volume sizes no larger than the cubic of the wavelength in vacuum and can operate at room temperature under electrical injection in continuous-wave mode. It was during this time we demonstrated electrically driven metallic cavity nanolasers, based on the structure with InP/InGaAs/InP nano-pillar and SiN layer overcoating.[21] These metallic cavity nanolasers can be used as azimuthally polarized beams, driven by electrical injection. Such plasmonic-based nanolasers, by themselves, belong to a new class of nanolasers due to their different light-matter interaction. Our early lasing studies on one-dimensional nanoscale cavities have led to research on plasmonic assisted nanowire and nanopillar 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.

Other than nanolasers, these nanowires, and their heterostructures also serve as excellent platforms as nanoscopic vertical light-emitting diodes (LEDs) for active display purposes. Specifically, gallium nitride and gallium arsenide-based materials have been used to construct core-shell nanowire LEDs and potentially laser diodes (LDs, Figure 5). The Samulseon group at Lund University has devoted more than a decade of their work to this class of important optoelectronic nanostructures.[22] There is already a hint of nanowire-based nanoLED potentially being integrated into high-definition display devices.

Our discovery of the first room-temperature ultraviolet nanowire nanolaser (the world's smallest laser, 2001) has led to a new area of exciting fundamental research --- *nanowire photonics.*[23] These studies laid the foundation for nanowire-based sub-wavelength photonic integration, novel nanowire scanning probe imaging and spectroscopy as well as solar energy conversion. Later my group also discovered that these semiconductor nanowires, having high refractive index, can function as low-loss optical waveguides for UV and visible lights both in air or liquid medium.[24] Using a $KNbO_3$ nanowire as a key component, my team has created an optical probe that potentially combines fluorescence microscopy and force microscopy.[25]

Nanowires, with their unique dimensionality, can also be used to directly interface with living cells for electrical and optical stimulation purposes.[26,27] Developing such flexible nanowire probes would enable the researchers to monitor in-vivo biological processes within single living cells and will greatly improve our fundamental understanding of cell functions, intracellular physiological processes, and cellular signal pathways. In 2007, we showed that silicon nanowires can be directly interfaced with Mammalian cells (Figure 5).[26] 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 successfully integrated high-density silicon nanowire transistor arrays for the detection, stimulation, and inhibition of neuronal signal propagation.[28] 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 discoveries are expected when such platforms are used to tackle real biological problems.

The Foundational Nanowire IP

In 2001, together with a couple of my colleagues at Berkeley, we filed several important patents claiming the foundational rights for this class of semiconductor nanostructures, which were eventually granted years later[29] (Figure 6). At a similar time window, the Lieber group at Harvard has also filed their foundational nanowire IPs. Our early foundational IP portfolio was built on our ongoing research efforts at the time, and it also led to a series of fundamental and interesting observations in several areas, e.g. quantum wire laser based on core-shell GaN/AlGaN nanowires (2005);[30] the first dye-sensitized nanowire solar cell (2007);[31] nanowire-Mammalian cell interface (2007);[26] and size-dependent thermal conductivity within nanowires (2000-2008).[32,33]

In 2001, together with my colleagues Paul Alivisatos and Charles Lieber, we became the scientific co-founders of Nanosys Inc. with an initial intention to commercialize the quantum dot and nanowire technologies from three research groups. Nanosys, at the time, licensed all the foundational nanowires IPs from both Berkeley and Harvard teams. In 2013, OneD Material (now dba OneD Battery Sciences) acquired from Nanosys its nanowire-related intellectual property assets, R&D team, and facilities (including exclusive rights to commercialize nanowire inventions from Berkeley). Silicon nanowires are now being produced in large industrial quantities (in multi-tons of silicon nanowires grown on EV-grade graphite powders) using state-of-the-art CVD systems at a competitive cost as battery anodes to meet market requirements for world-leading EV battery makers (Figure 7). Using nanoparticles as catalysts for highly efficient silicon nanowire growth by decomposing silane gas in commercial CVD equipment has resulted in lowering costs dramatically to help EV makers decrease battery costs for affordable EVs with longer ranges with smaller batteries. The use of nanowire anodes in batteries leads to significantly higher energy and power densities, faster charging at lower temperatures, and better performance for a wide range of applications, from power tools to consumer electronics and electrical vehicles.

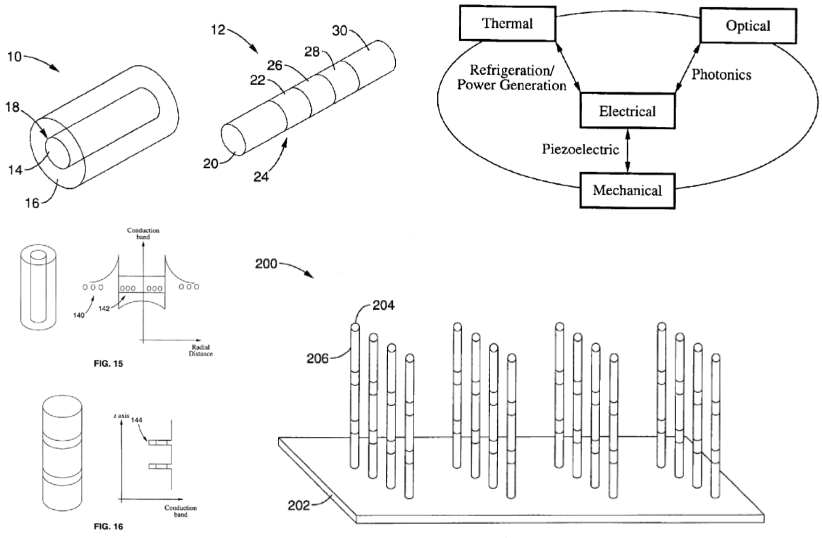


Figure 6: Schematics drawings for various nanowire heterojunctions covered in several fundamental nanowire IPs from Berkeley (*US Patent No. 9,881,999, US 7,569,941, US 7,569,847, US 6,996,147, US 6,882,051, US 5,897,945, US 7,834,264)*. This collection of foundational nanowire IPs was later licensed and commercialized at several companies.

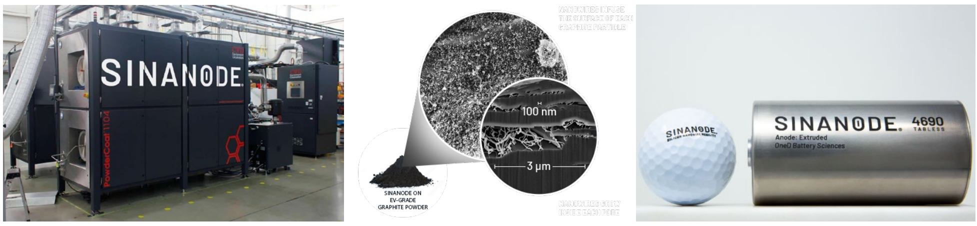


Figure 7. Large-scale production of silicon nanowires at OneD for silicon-based battery anode applications (Credit: Y. Zhu, OneD).

OneD's SiNANOde® materials add silicon nanowires' unique electrochemical and electronic properties to commercial graphite powders commonly used in coating anode electrodes for lithium-ion batteries. This silicon nanowire anode technology is compatible with the entire EV supply chain, from materials suppliers to EV cell factories. With the scaled-up nanowire CVD production system, it is now possible to process up to 100 tons per year of nanowire-based composite material, for a total anode active material capacity of 340 MWh in a CVD machine costing less than $2M. An even larger commercial CVD machine enables the anode material production for a very large scale of up to 1000 Tons/year or 3 GWh capacity. Several other companies are also aggressively commercializing silicon nanowire anode technology, notably Amprius Inc. with the original technology coming out of Stanford University. [34]

Other than the significant impact silicon nanowires already had in the lithium battery industry, these semiconductor nanowires were also demonstrated to exhibit fundamentally different phonon transport properties from their bulk counterparts. Phonon transport is expected to be greatly impeded in thin (i.e., $d<\Lambda$, where d is the diameter and Λ is the phonon mean free path) one-dimensional nanostructures as a result of increased boundary scattering and reduced phonon group velocities stemming from phonon confinement. Size-dependent thermal conductivity in nanostructures presents a major hurdle in the drive toward miniaturization in the semiconductor industry. Yet poor heat transport is advantageous for thermoelectric materials, which are characterized by a figure of merit ($ZT = \alpha^2T/[\rho(\varkappa_p + \varkappa_e)]$, with α, T, ρ, $\varkappa_p$, and $\varkappa_e$ the Seebeck coefficient, absolute temperature, electronic resistivity, lattice thermal conductivity, and electronic thermal conductivity, respectively) that improves as phonon transport worsens. In the 1990s, Dr. Millie Dresselhaus predicted that ZT can be increased above bulk values in thin nanowires by carefully tailoring their diameters, compositions, and carrier concentrations.[35] In 2003, my team (with my colleague Arun Majumdar) demonstrated for the first time silicon nanowires indeed have size-dependent thermal conductivities and verified this early prediction experimentally.[32,33]

In 2008, This fundamental observation led to a new way of designing efficient thermoelectric material. We discovered that silicon nanowires with rough surfaces and diameters of about 50 nm exhibit a 100-fold reduction in thermal conductivity, yielding ZT~0.6 at room temperature.[36] Based on this particular set of IP portfolios, in 2009, I co-founded Alphabet Energy with Matthew L. Scullin, another Berkeley graduate. In 2014, Alphabet Energy introduced the world's first industrial-scale thermoelectric generator, the E1. The E1 takes exhaust heat from large industrial engines and turns it into electricity. The result is an engine that needs less fuel to deliver the same power. The E1 is optimized for engines up to 1,400 kW, and works on any engine or exhaust source, generating up to 25 kWe on a standard 1,000 kW engine (Figure 8).

Figure 8. Silicon nanowire exhibits size-dependent thermal conductivities, leading to silicon-based thermoelectric modules for waste heat recovery at *Alphabet Energy*.

It is important to note that the engines that generate most of the world's power typically operate at only 30–40 percent efficiency, releasing roughly 15 terawatts of heat to the environment. These silicon nanowire arrays show great promise as high-performance, scalable thermoelectric materials for waste heat recovery in power plants, refineries, and automobiles. This nanowire thermoelectric technology could have a global impact on the waste heat recovery and power co-generation industry, and make a significant contribution to the global efforts of curbing greenhouse gas emissions.

Nanowire Photochemical Diodes

Besides their tremendous potential in nanolasers, nanophotonics, energy storage, and thermoelectric energy conversion, semiconductor nanowires also represent a powerful platform for solar energy conversion including photovoltaics and artificial photosynthesis due to their strong light absorption and large surface area. Artificial photosynthesis is an integrated system that combines multiple processes, from light absorption, and charge separation, to surface molecular activation and transformation.[37,38,39] Back in the early 2000s, my team started to explore the photovoltaic direction by introducing for the first time the idea of a nanowire solar cell.[31,40] At the time, we have also devoted a significant amount of effort to systematically examine the photoelectrochemical properties of the high surface-area semiconductor nanowire arrays and have introduced the concept of using semiconductor nanowires for artificial photosynthetic purposes.[37-39,41]

Over time, my team has developed semiconductor nanowire arrays with complex compositions and heterojunctions, in searching for better materials for artificial photosynthesis, a process of directly converting water and carbon dioxide into liquid fuels using sunlight. It became clear that semiconductor nanowires represent an important class of nanostructure building blocks for direct solar-to-fuel applications because of their high surface area, tunable bandgap, and efficient charge transport and collection. Nanowires can be readily designed and synthesized to deterministically incorporate heterojunctions with improved light absorption, charge separation, and vectorial transport. Meanwhile, it is also possible to selectively decorate different oxidation or reduction catalysts onto specific segments of the nanowires to mimic the compartmentalized reactions in natural photosynthesis. These one-dimensional nanostructures offer an important experimental platform for the first-time demonstration of single optical-path photochemical diodes that was originally proposed by Dr. Art Nozik back in the 1970s.[42]

This original photoelectrochemical diode concept can be seen as a predecessor to the modern artificial leaf. In this case, a pair of semiconductors can be directly combined through an ohmic contact, resulting in a design coupling of both oxidative and reductive half-reactions for overall fuel production. The resulting device structure mimics the operating principle of natural photosynthesis, in which two complementary light absorbers are necessary to couple carbohydrate synthesis to O_2 evolution.

In the original design, two semiconductors were used, one is a p-type semiconductor serving as a photocathode, and the other side is an n-type semiconductor serving as a photoanode. When these electrodes are in contact with the electrolyte, effectively two liquid junction solar cells are established. Each of these two liquid junction solar cells will generate its own photovoltage. The combined photovoltages will provide a sufficient driving force to carry out the water/CO2 reduction and water oxidation. One should note the original concept was based on bulk semiconductors, and naturally, this original design was not a single optical-path device. While the original proposal suits overall water splitting, CO_2 reduction poses additional challenges including higher catalytic overpotentials or a control of the selectivity.

In the early 2000s, an ambitious effort called the Helios Program was launched at Lawrence Berkeley National Laboratory.[43,44] Part of its mission is to develop a functional artificial photosynthetic system that can carry out solar water splitting or fix CO2 using solar energy without external bias. It was at this time that we modified the original photochemical diodes by introducing semiconductor nanowires as the key photoelectrode components within the design (Figure 9).

Replacing the original bulk semiconductor with semiconductor nanowires has several major advantages and eliminates some of the major scientific bottlenecks in the original bulk design. These single-crystalline semiconductor nanowires typically have great minority carrier mobility, so that the photo-generated minority carriers can be effectively transferred to the nanowire/electrolyte interface over a relatively short distance to participate in the oxidation/reduction half-reactions. Nanowire arrays also naturally have a large surface area and enable the stacking of the surface catalysts along the third dimension, and this effectively removed the solar photon flux mismatching issue in the original bulk design. Lastly, these nanowire electrodes can be designed to be a single optical path device considering their own bandgap and absorption coefficient.

In 2013, using Si and TiO_2 nanowires as building blocks, a proof-of-concept solar-to-fuel conversion nanowire-based photochemical diode was demonstrated for direct solar water splitting.[45] As the photochemical diodes are essentially photocathode and photoanode linked in series, the output current from the two electrodes needs to match, otherwise, the overall performance will be limited by the electrode producing a lower photocurrent. So far, photochemical diode performance is largely limited by the low current output from the photoanodes, typically large bandgap oxides. So it was not surprising that the first nanowire photochemical diode only delivered solar-to-fuel efficiency at 0.12%. Fundamentally, one can use semiconductors with better photocurrent output in order to increase the overall solar-to-hydrogen conversion efficiency. For example, by using InP and BiVO4 photoelectrode couple, it is expected that the overall efficiency can reach 3%. And more recently some efforts on running the water splitting at a higher temperature using nitride nanowires have already pushed the efficiency to 10%.[46]

The concept of nanowire-based photochemical diodes from the Helios Program was later propagated into the Energy Hub, Joint Center of Artificial Photosynthesis (JCAP), in 2010, but with a clear focus on running the CO2 reduction on the photocathode. While the overall thermodynamic energy needs for CO2RR/OER and HER/OER are quite similar, the overpotential to drive CO2 reduction towards C2+ products is significantly larger than that for HER. This introduced another significant scientific challenge: the photovoltage gap. Going back to the fundamental physics of the photochemical diode itself, the photovoltage outputs from the two electrodes are limited considering their bandgap as well as the overall solar spectrum. Yet this photovoltage must be large enough to cover the overall thermodynamic voltage needs for the two half-reactions (e.g. CO2RR/OER), the additional overpotential needs to drive these two separate half-reactions, and IR drops and ohmic loss if any (Figure 9).

This led us to the introduction of bio-photochemical diodes back in the early 2010s.[47] The overpotential issue can be largely circumvented by using biological systems operating with very low overpotentials, close to the standard thermodynamic potentials. Taking advantage of an overpotential <200 mV of the bacterium *Sporomusa ovata*, a Si – TiO_2 nanowire biophotochemical diode was able to perform unassisted acetate production at a 0.38% solar-to-chemical efficiency and faradaic efficiency up to 90%. By feeding this CO2-derived acetate to a genetically engineered *Escherichia coli*., one can produce many other value-added chemicals such as *n*-butanol, polyhydroxybutyrate (PHB) polymer, and different isoprenoid natural products. This was the first time that a fully integrated system was assembled to produce value-added chemicals directly and solely from CO_2, H_2O, and sunlight, and is widely considered one of the major breakthroughs in the field of artificial photosynthesis. Similarly, the acetate produced by *S. Ovata* can be passed onto other microorganisms such as *C. basilensis* and *R. Pal* for the purpose of PHB production and N2 fixation at ambient conditions.[48,49] More recently, close packing of *Sporomusa ovata* bacteria onto conductive Si nanowire arrays resulted in a solar-to-chemical conversion efficiency of 3.6% for acetate production, when driving the process by an externally wired, multi-junction Si solar cell. For these biophotochemical diodes, the next step remains to be enhancing the CO2 turnover rates by using adaptive laboratory evolution techniques and/or genetic modification of reaction pathways. By increasing the turnover rates for these microorganisms, one can achieve better overall solar-to-chemical conversion efficiency under bias-free conditions. The other research frontier would be the genetic modification of reaction pathways to produce different chemical products, all from CO2 and sunlight.[50,51,52]

Along the way, I have also coined the name "Liquid Sunlight" based on the photosynthetic biohybrid work.[53] This term is now trademarked to my research group at Berkeley. Liquid sunlight can be considered as a new form of chemical energy converted and stored in chemical bonds from solar energy. Efficient capture and storage of solar energy can provide unlimited renewable power sources and drive the capture and conversion of greenhouse gases such as CO_2 into valuable chemicals. Such an artificial photosynthetic process presents one of the most important solutions, if not the only one, towards net-zero carbon emission or even negative emission society in the near future. This name "Liquid sunlight" has now been used in several large national research initiatives in Europe and Asia, as well as in phase III of DOE energy hub: Liquid Sunlight Alliance (LiSA).

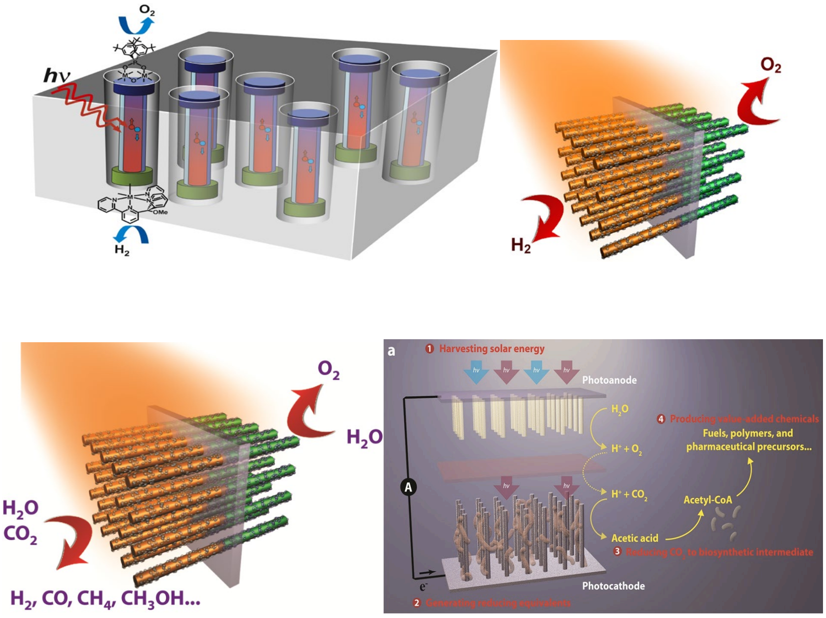


Fig. 9. The evolution of nanowire photochemical diode design from the Helios program to JCAP. Schematic illustrations of nanowire photochemical diode from 2003 to 2015, initially for solar water splitting, and later for coupling CO_2 reduction reaction (CO_2RR) with water oxidation.

With a modular design for photochemical diodes, these proof-of-concept devices leave much room for improvement and welcome performance enhancements by updating individual components with the latest improvements (Figure 10).

Specifically, the balance between solar-generated electron flux and the turnover frequency of the electrocatalyst demands the development of better electrocatalysts, especially for OER and CO_2 reduction. Ideally, an overpotential of less than 200 mV at 10 mA/cm^2 is desired. This is however currently non-existent for CO2RR electrocatalysts. In this regard, any new development in discovering new CO2RR electrocatalysts with very low overpotential will advance the field of the nanowire photochemical diode significantly.

Alternatively, one can further expand the definition of photochemical diode by including other types of oxidations that are not that sluggish and require much lower overpotential. For example, the thermodynamically energy-demanding O_2 evolution ($E_{H2O/O2}$ = 1.23 V vs. RHE) can be replaced by organic oxidations, e.g. glycerol oxidation, which readily occurs at lower applied potentials of 0.3-0.6 V vs. RHE. This induces a negative shift in the oxidation curve which improves the overlap operation current of the photocathode and photoanode, resulting in lower overall photovoltage requirement and higher operating photocurrents under no applied bias voltage.[54] It is also interesting to point out that certain microorganisms can obtain chemical energy through oxidation (chemoautotrophs) of inorganic/organic sources, i.e. using inorganic/organic substances as electron sources. To this extent, this expanded version of the photochemical diodes follows the basic energy conversion principles for some of these chemoautotrophs. It offers the additional benefits of fixing CO2 into C2+ compounds at high operating current density, while simultaneously upgrading biomass into other value-added chemicals, all operating at bias-free one-sun irradiation.

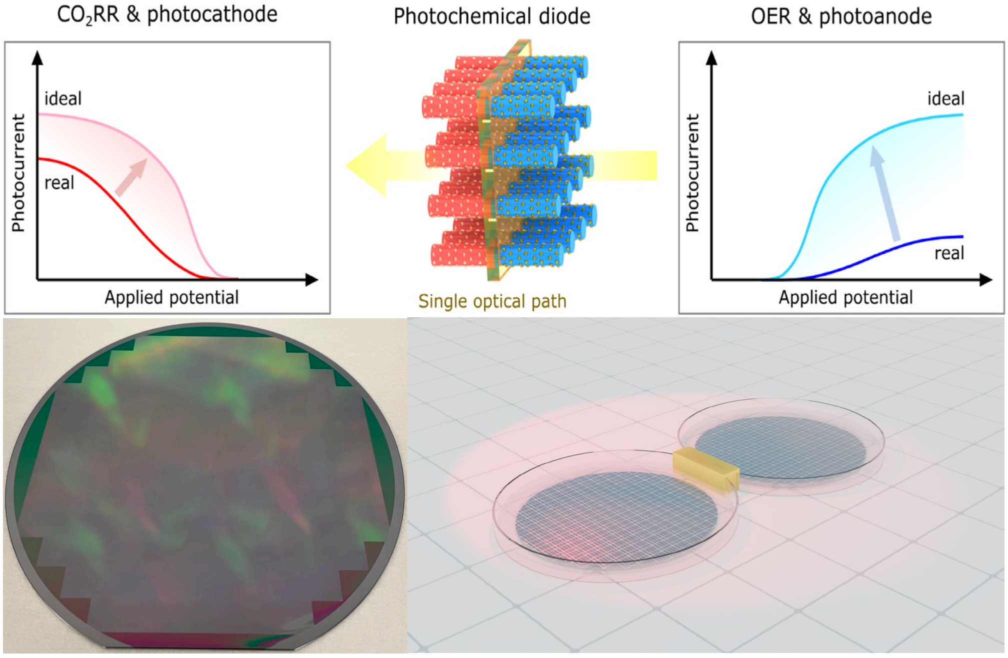


Figure 10. Nanowire photochemical diodes and their overall thermodynamic energy consideration from the photocathode and photoanode for the reduction/oxidation half-reactions. CO2RR: CO2 reduction reaction; OER: Oxygen evolution reaction [Ref 44, Reproduced with permission, The American Association for the Advancement of

Science]; A photo of a 6-inch wafer of silicon nanowire photocathode; and a schematical drawing of the coupled photocathode/photoanode for large-scale implementation.

Looking forward

Nanoscience research has been centered around three classes of nanostructures for their unique physical behavior defined by their structural dimensionalities: C_{60} & quantum dot (0-dimensional, 0D), carbon nanotube and semiconductor nanowire (1D), graphene and 2D materials (2D). The term 'nanowire' is generally used to describe a large aspect ratio nanostructure with a diameter between 1-100 nm. Both descriptors are pertinent to the physical and technological significance of nanowires.[55,56] Firstly, the diameter puts the radial dimension of these structures at or below the characteristic length scale of various interesting and fundamental phenomena: the exciton Bohr radius, wavelength of light, phonon mean free path, exciton diffusion length, and others. As a result, this two-dimensional confinement endows nanowires with unique size-dependent properties that stray from those of their corresponding bulk material, including many being discussed above, for example, sub-wavelength nanowire lasing; enhancement of electronic density of states;[57] size-dependent phonon transport.[55] Secondly, the one unconstrained dimension can direct the conduction of quantum particles such as electrons, phonons, and photons. Hence, nanowires provide a convenient platform through which researchers may study confined charge separation and transport phenomena.[58, 59, 60] This control over various forms of energy transport makes nanowires ideal materials for advanced solid-state applications that were discussed in this personal account. Nanowire research has quickly evolved into a large, dynamic, interdisciplinary research frontier with scientists and engineers from many different communities including chemistry, physics, materials science, and electrical engineering. Several important sub-fields have emerged, and each represents an exciting direction for both discovery-based and hypothesis-driven research. These flourishing sub-fields include nanowire electronics,[61] nanowire photonics,[17,18,23,62] nanowires for energy conversion and storage,[58] and interfacing nanowires with living cells.[63]

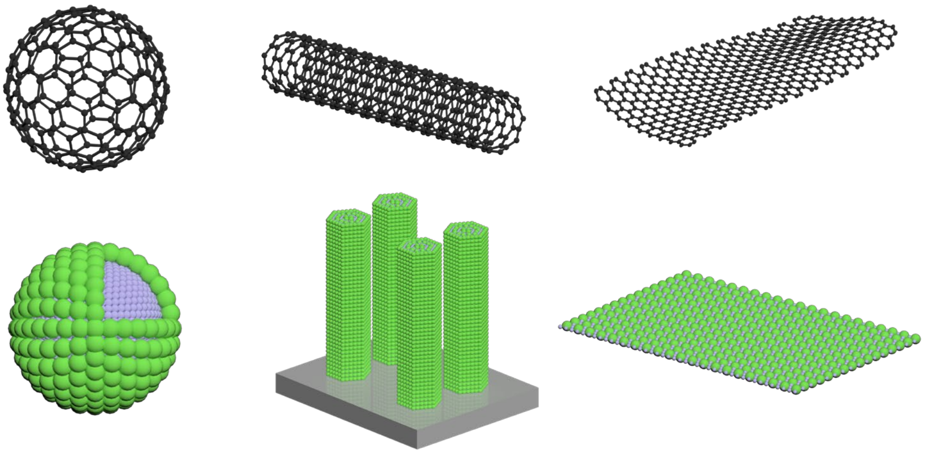


Figure 11. Historically nanoscience research has been centered around three classes of nanostructures for their unique physical behavior defined by their structural dimensionalities: C_{60} & quantum dot (0-dimensional, 0D), carbon nanotube and semiconductor nanowire (1D), graphene and 2D materials (2D).

After I received the invitation to put together an article for this special issue of *Rosarium Philosophorum* on Nanoscience and Nanotechnology, I decided to put together something that is quite personal, a chronicle collection of events for nanowire research as I saw it over the last 30 years. The field itself certainly has been progressing with amazing accomplishments from many top research groups.[55] I apologize if I missed important contributions from particular research groups. Many important nanowire studies are not covered here including for example nanowire electronics, piezoelectrics, quantum transport, and batteries. The purpose of this *Rosarium Philosophorum* article, however, is not to be comprehensive, but rather a personal reflection of my own journal over the past 30 years, with many joys and sorrows. For more comprehensive coverage of this topic, one can find it in the special issue I edited back in 2019 for *Chemical Review*.

References

---

[1] A. M. Morales, P. Yang, C. M. Lieber, *J. Am. Chem. Soc.* **1994**, 116, 8360.
[2] *Chemistry on the Nanometer Scale, The Robert A. Welch Foundation 40th Conference on Chemical Research,* **1996**, 110.
[3] P. Yang, C. M. Lieber, *Science*, **1996**, 273, 1836.
[4] Ph.D. thesis, P. Yang Harvard University, **1997.**
[5] R. S. Wagner, W. C. Ellis, *Appl. Phys. Lett.* **1964**, 4, 89.
[6] "Metal oxide nanorods"; US Patent 5,897,945, April 27, 1999; Filed Feb 26, 1996.
[7] K. Hiruma, M. Yazawa, T. Katsuyama, K. Ogawa, K. Haraguchi, M. Koguchi, and H. Kakibayashi, *J. Appl. Phys.*, **1995**, 77, 447.

---

[8] T. J. Trentler; K. M. Hickman; S. C. Goel; A. M. Viano; P. C. Gibbons; W. E. Buhro, *Science*, **1995** 270,1791.

[9] A. M. Morales, C. M. Lieber, *Science*, **1998**, 279. 208.

[10] Y. F. Zhang, Y. H. Tang, N. Wang, D. P. Yu, C. S. Lee, I. Bello, S. T. Lee, Appl. Phys. Lett. **1998**, 72, 1835.

[11] Y. Wu, P. Yang; *J. Am. Chem. Soc.* ***2001,*** 123 (13), 3165.

[12] L. J. Lauhon, M. S. Gudiksen, C. L. Wang, C. M. Lieber, *Nature* **2002,** *420*, 57.

[13] Y. Wu, R. Fan, P. Yang, *Nano Lett,* **2002***, 2, 83.*

[14] M. T. Bjork, B. J. Ohlsson, T. Sass, A. I. Persson, C. Thelander, M. H. Magnusson, K. Deppert, L. R. Wallenberg, L. Samuelson, *Nano Lett.* **2002,** 2, 87.

[15] Y. Huang, X. F. Duan, Y. Cui, L. J. Lauhon, K. H. Kim, C. M. Lieber, *Science* **2001,** *294*, 1313.

[16] M. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, *Science*, **2001**, 292, 1897.

[17] S. W. Eaton, A. Fu, A. B. Wong, C. Z. Ning, P. Yang, *Nature Mater. Rev*, **2016**,1, 16028.

[18] L. Quan, J. Kang, C. Z. Ning, P. Yang. *Chem. Rev*. **2019**, 119, 15, 9153.

[19] X. Duan; Y. Huang; R. Agarwal; C. M. Lieber, *Nature* **2003,** *421* (6920), 241.

[20] D. Li, C. Z. Ning, *Nano Lett.* **2008**, *8* (12), 4234.

[21] K. Ding, L. J. Yin, M. T. Hill, Z. C. Liu, P. J. van Veldhoven, C. Z. Ning, *Appl. Phys. Lett.* **2013**, *102* (4) 041110.

[22] C. P. T. Svensson, T. Mårtensson, J. Trägårdh, C. Larsson, M. Rask, D. Hessman, L. Samuelson, J. Ohlsson, *Nanotechnology* **2008**, 19 (30), 305201

[23] R. Yan, D. Gargas, P. Yang, *Nature Photonics*, **2009**, 3, 569.

[24] M. Law, D. Sirbuly, J. Johnson, J. Goldberger, R. Saykally, P. Yang, *Science*, **2004**, 305, 1269.

[25] Y. Nakayama, P. J. Pauzauskie, A. Radenovic, R. M. Onorato, R. J. Saykally, J. Liphardt, P. Yang, *Nature*, **2007**, 447, 1908.

[26] W. Kim, J. K. Ng, M. E. Kunitake, B. R. Conklin, P. Yang, *J. Am. Chem. Soc.* **2007**, 129, 7228.

[27] R. Yan, J. Park, Y. Choi, C. Heo, S. Yang, L. P. Lee, P. Yang, *Nature Nano.* **2012**, 7, 191.

[28] F. Patolsky, B. P. Timko, G. Yu, Y. Fang, A. B. Greytak, G. F. Zheng, C. M. Lieber, *Science* **2006,** *313*, 1100.

[29] Nanowires, nanostructures and devices fabricated therefrom; US Patent 6,882,051, April 19, 2005. Nanowire optoelectronic switching device and method; US Patent 6,882,767; April 19, 2005

[30] H. Choi, J. Johnson, R. He, S. Lee, F. Kim, P. Pauzauskie, J. Goldberger, R. Saykally, P. Yang, *J. Phys. Chem. B,* **2003**, 107, 8723.

[31] M. Law, L. E. Greene, J. C. Johnson, R. Saykally, P. Yang, Nature Materials, **2005**, 4, 455.

[32] D. Li, Y. Wu, P. Kim, L. Shi, N. Mingo, Y. Liu, P. Yang, A. Majumdar, *Appl. Phys. Lett.* **2003**, 83, 3186.

---

[33] D. Li, Y. Wu, P. Kim, L. Shi, N. Mingo, Y. Liu, P. Yang, A. Majumdar, *Appl. Phys. Lett.* **2003,** 83, 2934.

[34] C. Chan, H. Peng, G. Liu, K. Mcilwrath, X. Zhang, R. Huggins, Y. Cui, *Nature Nano.* **2008**, 3, 31.

[35] L. D. Hicks, M. S. Dresselhaus, *Physical Review. B, Condensed Matter*. 1993, 47: 16631.

[36] A. I. Hochbaum, R. Chen, R. D. Delgado, W. Liang, E. C. Garnett, M. Najarian, A. Majumdar, P. Yang, *Nature,* 2008, 451, 163.

[37] Y. Wu, H. Yan, P. Yang, *Topics in Catalysis,* 2002, 19(2), 197.

[38] P. Yang, J. Tarascon, *Nature Mater.*, 2012, 11, 560.

[39] C. Liu, N. Dasgupta, P. Yang, *Chem. Mater.*, **2014**, 1, 26.

[40] J. Tang, Z. Huo, S. Brittman, P. Yang, *Nature Nano*. **2011,** 6, 568.

[41] Y. Su, C. Liu, S. Brittman, J. Tang, A. Fu, P. Yang, *Nature Nano*. **2016,** 11, 609.

[42] Arthur J. Nozik, *Applied Physics Letters* **1997,** 30, 567-569.

[43] https://www2.lbl.gov/LBL-Programs/helios-serc/html/overview.html

[44] V. Andrei, I. Roh, P. Yang, Sci. Adv., **2023**, 9, eade904.

[45] C. Liu, J. Tang, H. Chen, B. Liu, P. Yang, *Nano Lett*, **2013**, 13, 2989.

[46] P. Zhou, I. A. Navid, Y. Ma, Y. Xiao, P. Wang, Z. Ye, B. Zhou, K. Sun, Z. Mi, Z., *Nature*, **2023**, *613*(7942), 66.

[47] C. Liu, J. J. Gallagher, K. K. Sakimoto, E. M. Nichols, C. J. Chang, M. C. Y. Chang, P. Yang, *Nano Lett.*, **2015**, 15(5), 3634.

[48] S. Cestellos-Blanco, S. Friedline, K. B. Sander, A. J Abel, J. Kim, D. S. Clark, A. P. Arkin, P. Yang. Front. Microbiol., **2021,** 12: 700010.

[49] S. Cestellos-Blanco, R. R. Chan, Y. Shen, J. Kim, T. A. Tacken, R. Ledbetter, S. Yu, L. C. Seefeldt, P. Yang, Proc. Natl. Acad. Sci. U.S.A., 2022, 119, e2122364119.

[50] K. Sakimoto, N. Kornienko, P. Yang, *Acct. Chem. Res*, **2017**, 50, 476.

[51] S. Cestellos-Blanco, H. Zhang, J. Kim, Y. Shen, P. Yang, *Nature Cata.* **2020,** 3, 245.

[52] P. Yang, *Nano Letters*, **2021**, 21, 5453.

[53] K. Bourzac, *Proc. Natl Acad. Sci. USA* **2016,** 113, 4545.

[54] J. Lin, I. Roh, P. Yang, J. Am. Chem. Soc., **2023**, 145, 12987-12991.

[55] Special Issue on 1D nanostructures and semiconductor nanowires, *Chem. Rev.* **2019**, Aug, Vol 119 (15).

[56] E. Garnett, L. Mai, and P. Yang. *Chem. Rev.* **2019**, 119, 15, 8955.

[57] R. Chen, J. Lee, W. Lee, D. Li, *Chem Rev.*, **2019**, 119, 15, 9260.

[58] A. Hochbaum and P. Yang. *Chem. Rev.* **2010**, 110, 527.

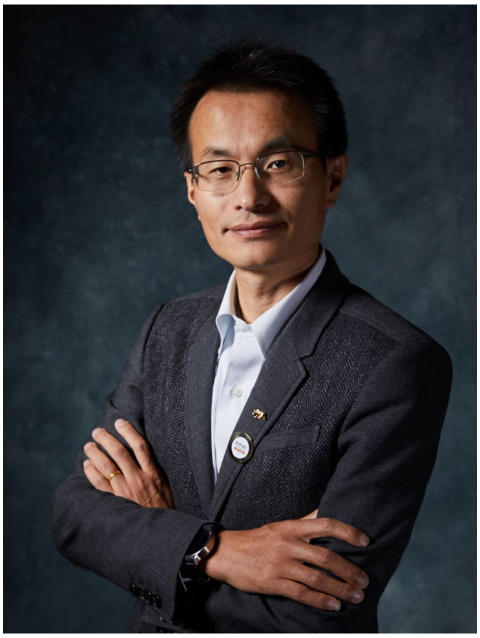
[59] M. S. Gudiksen, L. J. Lauhon, J. Wang, D. C. Smith, C. M. Lieber, *Nature* **2002,** *415*, 617.

[60] C. Pan, J. Zhai, Z. L. Wang, *Chem. Rev.* **2019**, 119, 15, 9303.

[61] C. Jia, Z. Lin, Y. Huang, X. Duan; *Chem. Rev.* **2019**, 119, 15, 9074.

[62] E. Barrigón**,** M. Heurlin, Z. Bi, B. Monemar, L. Samuelson; *Chem. Rev.* **2019**, 119, 15, 9170.

[63] B. Tian, C. M. Lieber; *Chem. Rev.* **2019**, 119, 15, 9136.



Peidong Yang is a Chemistry professor, S. K. and Angela Chan Distinguished Chair Professor in Energy at the University of California, Berkeley. He is a senior faculty scientist at the Materials and Chemical Sciences Division, Lawrence Berkeley National Laboratory. He is a member of both the National Academy of Sciences and the American Academy of Arts and Sciences. He is also a foreign member of the Chinese Academy of Sciences. Dr. Yang received his B.A. in Chemistry from the University of Science and Technology in China in 1993. He then received his Ph.D. in Chemistry from Harvard University in 1997, and did his postdoctoral fellowship at the University of California, Santa Barbara. Soon after, he joined the faculty at the University of California, Berkeley. He is the recipient of numerous awards including the Global Energy Prize, MacArthur Fellowship, E. O. Lawrence Award, Alan T. Waterman Award. He is the 2014 Thomas Reuters Citation Laureate for Physics.