CHEMICAL REVIEWS

Editorial

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Introduction: 1D Nanomaterials/Nanowires

Wires of different forms have been an integral part of human society for centuries. Electricity is being delivered through powerlines to every household; information is routinely transmitted through optical fibers, and bridge-building requires the use of mechanically robust cables. In the past 25 years, scientists have discovered a fundamentally new process for making nanoscopic wires, 1000 times thinner than human hairs, enabling a new generation of computing, integrated photonics, energy and biomedical technologies.

Semiconductor nanowires are a new class of semiconductors with typical cross-sectional dimensions that can be tuned from 1−100 nm and lengths spanning from hundreds of nanometers to millimeters.[1] Much of today's nanowire research relies on the powerful method developed by Dr. R. S. Wagner at Bell Laboratories, known as the "vapor−liquid−solid process".[2] Wagner, in 1964, discussed the growth of silicon microwires or whiskers, and he pointed out that one of the catalysts that can be used in this vapor−liquid−solid process is gold. Gold is often being used today to grow silicon nanowires, as well as copper, titanium, nickel, and aluminum. Wagner's work in the 1960s set the foundation for much of today's nanowire research.

In the early 1990s, while many groups were researching heavily on carbon nanotubes, several groups started to explore the synthesis and characterization of semiconductor nanowires or nanowhiskers, including oxides, III−V compounds, and elemental semiconductors.[3−7] The growth methods were very much inspired by Wagner's vapor−liquid−solid crystal methods with the introduction of metal nanoparticles in order to define the diameter of the resulting nanowires.

The first direct *in situ* observation of vapor−liquid−solid nanowire growth was made back in 2001 using an *in situ* high temperature transmission electron microscope.[8] The creation of the solid−liquid interface is the starting point for one-dimensional crystal growth; this underpins the fundamental nucleation step at the nanometer scale for all of the vapor−liquid−solid processes. This nanowire growth mechanism demonstrated that a general concept of nanoparticle-catalyzed growth could be used to synthesize single crystal semiconductor nanowires in a predictable manner for the first time. These early studies provided the intellectual underpinnings for the predictable growth of nanowires with many different compositions.

In the following two decades, this nanowire research direction 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. The field has witnessed the rational syntheses of a large number of group III−V and II−VI binary and ternary nanowires, the growth of nanowires with controllable doping, and the synthesis of molecular-scale nanowires. Many nanoscale axial and radial nanowire heterostructures have also been designed and researched for their novel photonic and electronic properties.[9−12] This capability of rational design and synthesis of semiconductor nanowires quickly led to a host of nanowire electronic and photonic, biomedical, as well as energy conversion and storage devices within the past two decades. This special issue aims to comprehensively review these active research frontiers, the progress, opportunities, and challenges. To start, L. Güniat, P. Caroff, and A. Fontcuberta i Morral provide a review on key developments for vapor phase nanowire growth, and D. Huo, M. J. Kim, Z. Lyu, Y. Shi, B. J. Wiley, and Y. Xia review the nanowire synthesis based on colloidal approaches.

Several groups, notably the Lieber group from Harvard University, have shown unambiguously that semiconductor nanowires with predictable and controlled electrical properties can be rationally designed and synthesized, thus providing electronically tunable nanoscale building blocks for device assembly. For example, the Harvard team 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; they have assembled active bipolar transistors showing emitter current gains and used the p- and n-type nanowires to assemble complementary inverters, which represent a key element for logic.[13] These nanowires have been used as fundamental building blocks for the bottom-up assembly of vertically interconnected three-dimensional "CMOS" circuits and nanoprocessors. C. Jia, Z. Lin, Y. Huang, and X. Duan review the progress and challenges for nanowire based electronics.

Nanowires can also be used to directly interface with mammalian cells for electrical and optical stimulation purposes.[14] For example, the Lieber group has pushed the interface between nanowire devices and cells with their pioneering work on using nanowire transistors to probe the action potential of a single neuron cell with nanometer resolution.[15] They have continued to pioneer this exciting field by recording electrical activity from cultured cardiac cells, and fresh brain tissue, demonstrating unprecedented spatial and temporal resolution. This emerging frontier at the nanowire bioelectric interface will be covered in a brief focus review by B. Tian and C. M. Lieber.

Similar to nanowire electronics, the field of nanowire photonics has also experienced significant growth in the early 2000s. Since the discovery of the first room-temperature ultraviolet nanowire laser,[16] many other optical processes have been studied for these semiconductor nanowire building blocks including, for example, subwavelength waveguiding and nonlinear optical mixing.[17−20] These studies laid the foundation for nanowire based subwavelength photonic integration, novel nanowire scanning probe imaging, and spectroscopy as well as solar energy conversion. It has now led into a new area of exciting fundamental research—*nanowire photonics*.[21] The ability to manipulate pulses of light within submicron volumes is vital for highly integrated light-based devices, such as optical computers, to be realized. Chemically

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synthesized nanowires represent an important class of photonic building blocks that exhibit subwavelength optical functionalities. In this thematic issue, L. N. Quan, J. Kang, C. Z. Ning, and P. D. Yang briefly survey the current status of the nanowire photonics overall, and E. Barrigón, M. Heurlin, Z. Bi, B. Monemar, and L. Samuelson comprehensively review the progress made in the synthesis and photonic applications of III−V and III-nitride nanowires.

The development of nanowire photonics laid a solid foundation for the use of semiconductor nanowires in solar energy conversion, notably nanowire based photovoltaics. Various nanowire heterostructure designs were introduced for the purpose of solar energy harvesting.[22−24] This concept of using nanowires for photovoltaic applications represents a solar cell design model system by optimizing the light absorption/trapping, charge separation, and charge collection, and it should have great impact in the field of renewable energy.

More recently, many groups have devoted significant efforts to systematically examine the photoelectrochemical properties of high surface-area semiconductor nanowire arrays.[25] Semiconductor nanostructures with complex compositions and heterojunctions[26] have been extensively examined in the search for better materials for artificial photosynthesis, a process of directly converting water and carbon dioxide into liquid fuels using sunlight. Semiconductor nanowires represent an important class of nanostructure building block 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. Early in 2013, the Yang group announced the first fully integrated nanowire-based system for direct solar water splitting.[27] In 2015, the same team created a synthetic "leaf" that is a hybrid system of semiconducting nanowires and bacteria *S. Ovata*.[28] The nanowires gather sunlight, and the bacteria trigger the use of carbon dioxide and water to complete the photosynthetic process and produce a targeted carbon-based chemical such as butanol. This is 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. A comprehensive review of this exciting direction can be found in this issue by J. Deng, Y. Su, D. Liu, P. D. Yang, B. Liu, and C. Liu.

In addition to the solar energy conversion and storage, nanowires have also played a significant role in the development of battery materials, thermoelectrics, and piezoelectrics.[29] It is well documented that materials in confined dimensions could have very different ion diffusion kinetics and strain/stress response. As a result, nanowires have great capability for realizing a variety of applications in the fields of energy storage, since they could maintain electron transport along the long axis and have confinement effects across the diameter.

Nanowires have also been demonstrated to exhibit fundamentally different phonon transport properties from their bulk counterparts. For example, the Yang group has demonstrated for the first time silicon nanowires have size-dependent thermal conductivities. Thin nanowires display significantly lower thermal conductivity because of strong boundary phonon scattering. This fundamental observation led to a new way of designing efficient thermoelectric materials. Later, the same team 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.[30] R. Chen, J. Lee, W. Lee, and D. Li review the progress made in this particular area.

Finally, semiconductor ZnO and GaN possess relatively large spontaneous polarization along the longitudinal direction of the nanowires due to the asymmetry structure in the direction of the *c*-axis. The couplings of the piezoelectricity, photoexcitation, and optical/electrical properties in these nanowires have generated new research areas such as piezotronics and piezo-phototronics. C. F. Pan, J. Zhai, and Z. L. Wang provide an in-depth discussion of the mechanism and applications of nanowire based piezotronics and piezo-phototronics.

Nanowires can now be synthesized and assembled with specific compositions, heterojunctions, and architectures. This has already led to a host of nanowire applications in electronic and photonic, biomedical, as well as energy conversion and storage devices. Each of these applications has been developed based on years of research into the synthesis, characterization, manipulation, and assembly of nanowires. The path from fundamental understanding to practical applications has led to numerous benefits for the entire materials, chemistry, physics, and engineering research community. The interdisciplinary nature of the research presented in this thematic issue represents the future of scientific discovery, where scientific boundaries are no longer relevant.[31,32]

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