Nanofabrication beyond Electronics

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ABSTRACT This Nano Focus article reviews recent developments in nanofabrication based on invited talks given at the "Chemical Methods of Nanofabrication" symposium, which was organized by the authors and presented at the 237th ACS National Meeting and Exhibition as one of seven symposia within the meeting theme, "Nanoscience: Challenges for the Future". The three-day symposium included 25 experts from academia, national laboratories, and industry from around the world, to discuss current progress and future directions in nanofabrication. We highlight several of the key results discussed and future directions and challenges in this rapidly changing field.

The ability to fabricate materials with dimensions at the nanometer scale is the foundation of nanoscience and nanotechnology and enables progress in this area. Many nanofabrication tools and methods can be traced to centuries-old lithography concepts, including molding, printing, and writing. The past decade has witnessed tremendous growth in the field of nanofabrication, in part due to pressure from the electronics industry to keep pace with Moore's Law,[1] which forecasts the doubling of device density on integrated circuits every 18 months. While the production of increasingly smaller electronic components remains a strong driving force for nanofabrication, the latest developments have provided researchers with powerful new tools and nanostructured materials to address a wide variety of problems in diverse areas, including materials science and engineering, the life sciences, energy, and medicine.

Nanofabrication, as the name implies, differs from microfabrication and conventional fabrication technologies with its objective and capability to make structures with at least one dimension less than 100 nm. Structures with dimensions on this length scale exhibit a host of new physical and chemical properties. The International Technology Roadmap for Semiconductors (ITRS) is an aggressive plan for increasing resolution and developing fine lithographic features for the coming decades.[2] Depending on the intended application, additional attributes may be desirable, including complexity of structures, feature density, and materials generality. Fidelity and scalability (parallel, simple, and cost-effective processing) are all keys to developing new and useful technologies. The "Chemical Methods of Nanofabrication" symposium at the 237th ACS National Meeting and Exhibition demonstrated remarkable progress in nearly every aforementioned category, with highlights presented below.

Working around the Diffraction Limit. For the last few decades, the electronics industry has been surprisingly successful in using shorter wavelength light and circumventing the diffraction limit in photolithography, which restricts resolution to approximately one-quarter to one-half of the wavelength of the light used, or $\sim\lambda/4$ to $\lambda/2$. However, as feature sizes continue to decrease, the technical challenge and expensive capital cost associated with deep ultraviolet optics have raised major concerns regarding the sustainability of photolithography. These challenges have motivated the development of new lithography processes and a complementary focus on nonoptical technologies as alternative resolutions.[3] John Fourkas of the University of Maryland reported a new technique called resolution augmentation through photoinduced deactivation (RAPID).[4] The RAPID technique circumvents the $\lambda/4$ diffraction limit, allowing for fabrication of polymer nanostructures at a resolution of $\sim\lambda/20$. Unlike conventional photolithography, RAPID is based on multiphoton absorption polymerization (MAP)[5] and stimulated emission depletion (STED) of a radical photoinitiator (such as malachite green carbinol base).[4] In experiments described by Fourkas, a 200 fs pulse of 800 nm light is used to initiate photopolymerization of a negative-tone photoresist in the focal volume of the beam, while a continuous-wave laser beam of the same color deactivates the photopolymerization except at a small region at the center of the

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focal volume of the first laser beam (Figure 1A). This small region defines the smallest volume element, or voxel, that can be created by RAPID; for an 800 nm laser, it was determined to be 40 nm (Figure 1B).[4] Because RAPID relies on multiphoton absorption, which requires high laser power, it is still unclear whether this technique can achieve the high throughput of conventional photolithography. However, as initial experiments have shown,[2] this new technique will significantly improve the resolution of MAP-based three-dimensional (3D) nanofabrication (Figure 1C).[5]

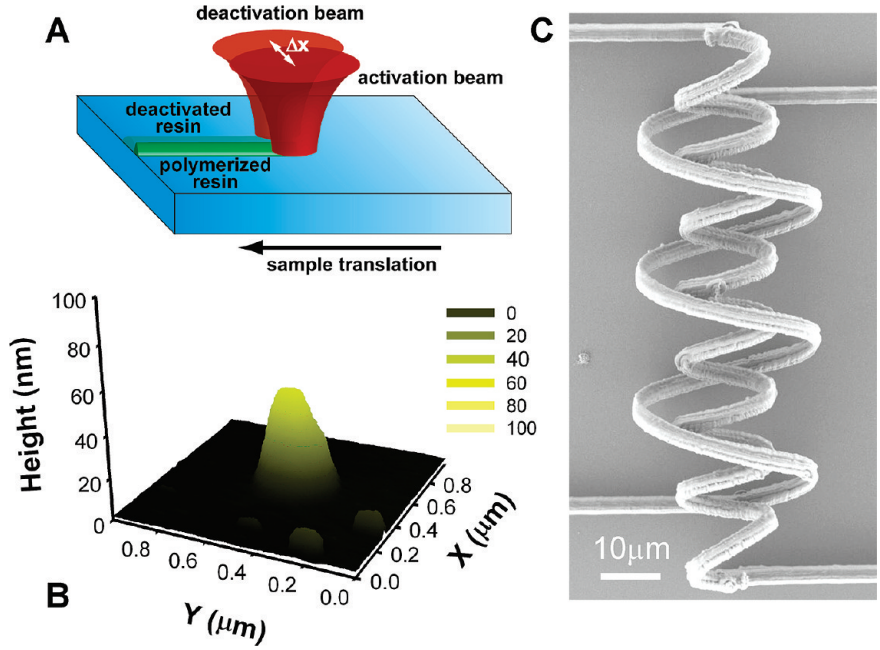

Figure 1. Working around the diffraction limits in photolithography. (A) Schematic illustration of RAPID. (B) Atomic force microscopy (AFM) topography image of a 40 nm voxel created by RAPID using 800 nm light. Panels A and B reproduced with permission from ref 4. Copyright 2009 AAAS (http://www.sciencemag.org/). (C) Double-spring polymer structure generated by MAP. Reproduced with permission from ref 5. Copyright 2007 Wiley-VCH Verlag GmbH & Co.

Unconventional Lithography. The diffraction limit in photolithography has motivated the development of a number of unconventional lithography techniques over the last few decades including microcontact printing,[6,7] imprint lithography, [8,9] direct-write dip-pen nanolithography,[10,11] a variety of indirect scanning probe lithographies,[10,12] self-assembly,[6] and inkjet printing technologies.[13] Many of these techniques are reminiscent of conventional macroscopic molding, printing, and writing technologies. Unlike photolithography, these nanofabrication methods operate on entirely different principles, some of which allow the construction of objects at sub-100 nanometer dimensions or below. For example, microcontact printing[6,7] and nanoimprint lithography[8] are essentially the miniaturization of molding technologies, with their resolution limits defined by van der Waals contact of two materials, separations of ~0.4 nm. Dip-pen nanolithography (DPN)[10,11] is a scanning-probe-based lithography technique that typically uses the meniscus resulting from capillary condensation between an atomic force microscope (AFM) tip and a substrate in ambient environments to control the delivery of molecules onto a surface. The resolution of DPN is limited mainly by the radius of curvature of the AFM tip and the size of the meniscus, which is theoretically predicted to be as narrow as five molecules across, or 2 nm for an atomically sharp tip.[14] Thus far, line width resolution as small as 15 nm and spatial resolution as small as 5 nm have been achieved.[15]

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Despite the impressive resolution, many of these unconventional lithography techniques rely on photolithography or electron-beam lithography techniques to fabricate the molds, the pens, or the nozzles. Therefore, the replicated structures indirectly inherit the resolution limits and defects imposed by these other lithography techniques. Another limitation is that, as resolution of a technique increases, the throughput and fidelity of the nanostructures fabricated often deteriorate. Notably, a number of reports in this symposium demonstrated how one can improve resolution, control defects, and increase throughput for these unconventional methods.

Controlling Defects. As structures become smaller and smaller, fabrication defects can become significant. Stephen Chou of Princeton University reported a self-perfection by liquefaction (SPEL) technique, which removes nanostructure fabrication defects, line-edge roughness as well as significantly improves line width resolution.[16] The SPEL technique works by selectively melting nanostructures using a 20 ns pulse of an excimer laser ($\lambda = 308$ nm) while applying a set of boundary conditions to reshape the molten material before solidification. For example, if a flat plate is placed above silicon nanostructures with a fixed gap between the plate and the nanostructure, a taller and narrower structure can be formed (Figure 2A). SPEL has been demonstrated with chromium, silicon, and polymers, and in principle, it should work well for many other metals, semiconductors, and polymers. Strikingly, this postfabrication self-perfection technique can reduce the line-edge roughness by more than 300%.[16] It is anticipated that a combination of SPEL and nanoimprint lithography,[8] also pioneered by Chou, can meet

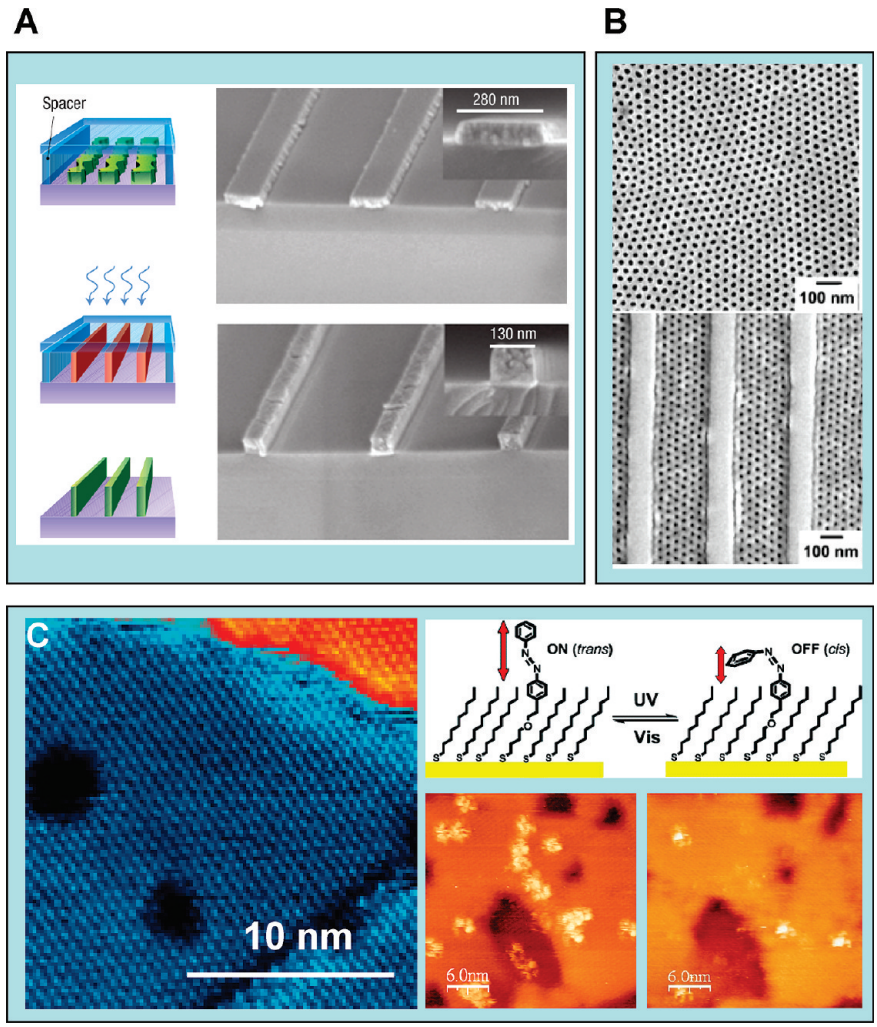

Figure 2. Remove, direct, and use nanofabrication defects. (A) Guided SPEL narrows the width and increases the height of silicon nanowires. Reproduced with permission from ref 16. Copyright 2008 Nature Publishing Group (http://www.nature.com/nnano). (B) Block copolymer self-assembly is registered with lithographically defined trenches. Images courtesy of Charles T. Black. (C) Defects in a decanethiol SAM on Au{111} and use of SAMs to control the chemical environment for single-molecule optical switches. Panel C (left) reproduced from ref 19 and (right) reproduced from ref 22. Copyright 2008 American Chemical Society.

a number of the stringent requirements set by the ITRS for lithography.[2]

In another case, Chuck Black of Brookhaven National Laboratory showed that diblock copolymers composed of 70% polystyrene and 30% poly(methyl methacrylate) (70:30 PS/PMMA) can form hexagonal lattices of 20 nm diameter cylindrical PMMA domains in a matrix of PS.[17,18] The pitch of the cylindrical domains can be delicately controlled by adjusting the polymer length. The hexagonal lattices can be generated over large areas, but the PMMA domains do not exhibit long-range interactions necessary to fabricate high-density electronic circuits. By using lithography to create trenches for the polymer to self-assemble, Black and co-workers can control the registry of the polymer self-assembly process while introducing local ordering within each trench (Figure 2B). Since the polymer self-assembly process is compatible with photolithography, this technique (coupled with standard lithographic methods) could become a powerful new approach to fabrication of high-density devices.

Making Use of Defects and Self-Assembled Monolayers. The remarkable ordering and properties of self-assembled monolayers (SAMs)[6,19] is the basis for a number of unconventional lithography methods such as microcontact printing,[6,7] DPN,[10,11] nanografting,[12] microdisplacement printing, and contact electrochemical replication.[21] Furthermore, the molecular ordering and defects in SAMs can also be useful for controlling the chemical environment of a molecule, as Paul Weiss (Penn State University) and others have demonstrated.[19,22,23] As revealed by molecularly resolved scanning tunneling microscopy (STM) images, different types of defects, including vacancy and domain boundaries, are incorporated into an alkanethiolate SAM formed on Au(111).[19] In collaboration with Jim Tour's group at Rice University, Weiss and co-workers make use of these defects as anchor points for placement of single azobenzene-functionalized molecules (*i.e.*, 4-[2-(4-phenylazophenyl)ethoxy]-butane-1-thiol) in the matrix of a decanethiolate SAM.[22] The azobenzene moiety could be reversibly photoisomerized between *trans* and *cis* conformations when illuminated by UV and visible light, respectively (Figure 2C). This experiment illustrates an elegant use of SAMs for the fabrication of single-molecule switches.

Defects can be created intentionally in SAMs and used for subsequent modification purposes. For example, Gang-yu Liu of University of California, Davis, used an AFM probe to create regular arrays of defects within a SAM in a process called nanografting.[12] Simultaneous introduction of protein molecules during this process allowed Liu and co-workers to investigate biological activity of a small number of proteins within well-controlled chemical environments.[24]

Template-Driven Syntheses and Self-Assembly. Synthetic chemistry is one of the most powerful tools for making and manipulating nanostructures. Scalability of certain chemical methods makes them attractive approaches for nanofabrication. This is particularly exciting when a template (*e.g.*, a mold, confined space, micelles, or seed crystals) can be used to direct nanofabrication over large areas and produce nanostructures in large quantities with excellent

control over nanostructure size, shape, composition, structure, and surface chemistry.

Younan Xia of Washington University in St. Louis reported a wet chemistry method for synthesizing silver cubes with an edge length of 97 ± 6 nm.[25] The excellent control over size and shape makes it possible to functionalize selected faces of a silver nanocube using shadow deposition or plasma etching and assemble them into a range of higher order structures, including dimers and ordered solids (Figure 3A).[25,26] In another case, So-Jung Park utilized a cooperative self-assembly of block copolymers and nanoparticles to form ordered arrays of nanoparticles. Figure 3B shows one such example where CdSe nanoparticles spontaneously form cavity-like structures inside discrete block copolymer assemblies.[27] This process opens a new route to fabricating hierarchical nanoparticle assemblies with controllable structural parameters. By applying the concept of reticular chemistry, which links molecular building blocks into ordered 3D structures, Omar Yaghi and coworkers at University of California, Los Angeles, prepared a series of highly porous crystalline materials called zeolitic imidazolate frameworks (ZIFs).[28] These ZIFs exhibit excellent selectivity toward carbon dioxide compared to nitrogen, methane, and carbon monoxide, making them potential candidates for natural gas purification.[28] To generate large numbers of monodispersed submicrometer structures, Joseph DeSimone at the University of North Carolina introduced a nanostructure replication process called particle [or pattern] replication in nonwetting templates (PRINT) (Figure 3C). The PRINT method works well because the low viscosity and nonwetting characteristic of perfluoropolyether enables accurate molding and replication of nanoscale features.[29]

For any nanofabrication method to be useful, simplicity and scalability must be considered. Chad Mirkin emphasized the simplicity of the method of on-

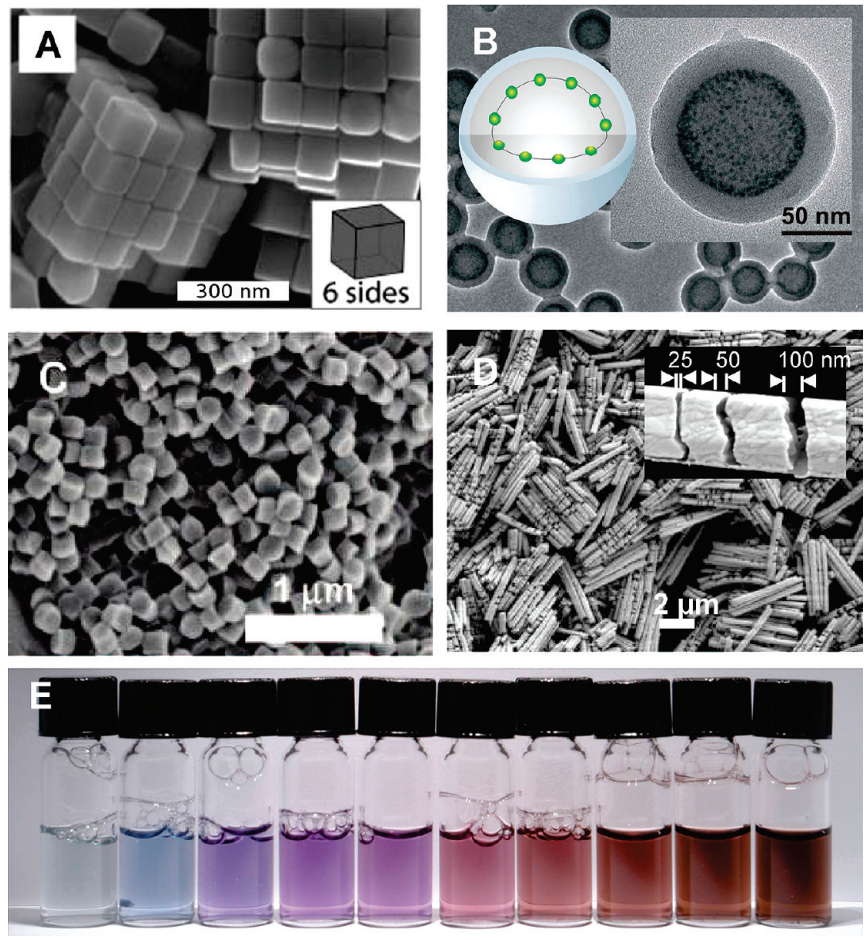

Figure 3. Nanostructures enabled by precision nanofabrication technologies. (A) Monodispersed Ag nanocubes (edge length 97 ± 6 nm) with six faces functionalized with hydrophobic thiolate SAMs self-assemble in water. Reproduced with permission from ref 25. Copyright 2008 Wiley-VCH Verlag GmbH & Co. (B) Radial arrangement of CdSe quantum dots formed by cooperative self-assembly of quantum dots and block copolymers. (C) Scanning electron micrograph of poly(ethylene glycol)-based cylindrical nanoparticles (200 nm in both diameter and height) made by particle replication in nonwetting templates (PRINT). Reproduced from ref 29. Copyright 2008 American Chemical Society. (D) Gold nanorods with controlled nanoscale gaps made by on-wire lithography (OWL). Reproduced with permission from ref 30. Copyright 2005 AAAS (http://www.sciencemag.org/). (E) Optically pure single-walled carbon nanotubes sorted according to their buoyant density. Image courtesy of Mark Hersam.

wire lithography (OWL) developed in his group (Figure 3D).[30] In OWL, gold and silver are electrochemically deposited in an alternating fashion within nanoscale pores defined by an anodized aluminum oxide template. After removing the template, the rods are deposited on a glass slide and coated with a layer of support material such as silicon nitride before removing the sacrificial silver by wet chemical etching. This method enables the synthesis of large numbers of rods with controlled nanoscale gaps and has been used to generate a variety of materials with challenging geometries, including surface-enhanced Raman-active disk arrays, molecular transport junctions, nanoscopic motors, and structures with unusual plasmonic properties.

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The synthesis and purification of nanomaterials, including carbon nanotubes, continues to be a rich area of study, more than one decade after they were first reported in the literature. Mark Hersam of Northwestern Univer-

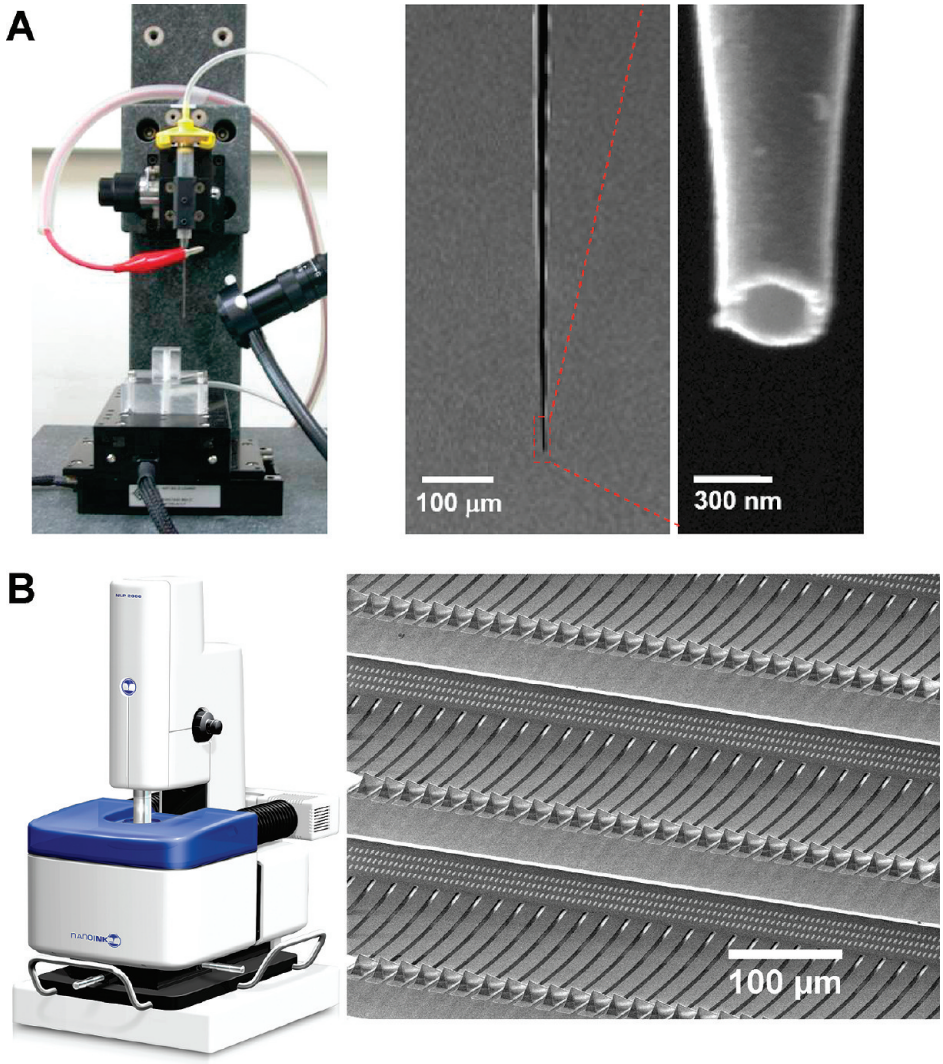

Figure 4. New nanofabrication tools. (A) High-resolution electrohydrodynamic (e-jet) printer (with a nanoscale glass capillary nozzle) invented by John Rogers and co-workers at the NSEC Center for Nanoscale Chemical−Electrical−Mechanical Manufacturing Systems at the University of Illinois Urbana—Champaign. Images courtesy of John Rogers. (B) Tip-array based nanofabrication tool (NLP2000) developed by NanoInk, Inc. and scanning electron micrograph showing part of a 55 000 pen array. Images courtesy of Jason Haaheim.

sity reported a postsynthesis method to sort single-walled carbon nanotubes (SWNTs) according to their buoyant density.[31−33] Fine tuning of this technique has led to separation of optically pure nanotubes as isolated vials of solutions (Figure 3E). These optically pure nanotubes, previously unattainable in milligram quantities, have enabled the Northwestern team and collaborators to address a host of fundamental problems ranging from exciton dynamics[34] to transparent conductive thin films.[35]

As purer nanotube samples become available, researchers are revisiting an ambitious project that aims to amplify a specific nanotube structure into large quantities by a process called continued growth or "cloning".[36,37] This method uses a pre-existing nanotube as a seed to template the continued growth in an epitaxial manner. Short nanotube seeds can result in the growth of longer nanotubes, which may be cut into a number of short nanotube segments. This method is the only synthetic method known that allows growth of a specific SWNT structure and helicity. The initial proof-of-concept for cloning was demonstrated with a neat fiber (containing no surfactants) made of SWNTs by Wang and co-workers,[36] and further, the cloning conditions for individual SWNTs on a surface have been identified.[37,38] With the advent of separations that afford seed nanotubes of identical structure and with increased understanding of nanotube growth kinetics, large-scale syntheses of electronically pure nanotube materials may become possible.

New Nanofabrication Tools. New nanofabrication methods and tools that provide unique capabilities can enable major scientific advances. In this regard, John Rogers and co-workers of the University of Illinois at Urbana—Champaign reported a new high-resolution electrohydrodynamic jet (e-jet) printer technique.[13,39] The e-jet method is based on electrohydrodynamically induced fluid flow of liquid "inks" through fine gold-coated glass microcapillary nozzles when an electrical field is applied between the nozzle and a conducting support substrate. The nozzle can be made as small as 300 nm (Figure 4A).[13,39] Because e-jet printingcan work in drop-on-demand mode, arbitrary geometries and patterns can be created in a way similar to an office inkjet printer. However, unlike an office printer, the e-jet printer has feature resolution on the sub-100 nm length scale and enables printing of a variety of inks including sol−gels and DNA.[13,40] The

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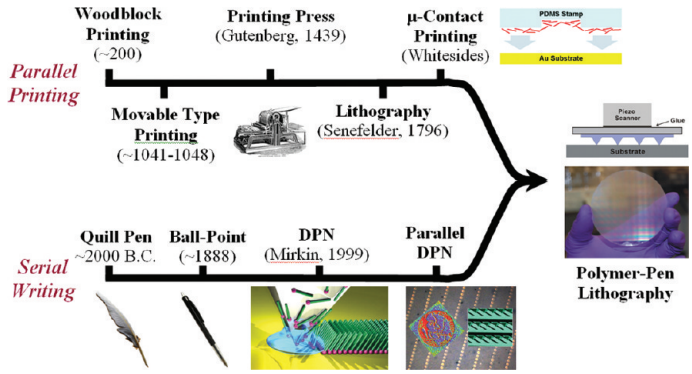

Figure 5. The development of polymer-pen lithography—a tool combining advantages of printing and writing technologies—in a historic perspective. DPN image reproduced from ref 10. Copyright 2007 Nature Publishing Group. Polymer-pen lithography images reproduced with permission from ref 41. Copyright 2008 AAAS. Parallel DPN and μ-contact image reproduced from refs 43 and 59, respectively. Copyright 2007 ACS.

printer requires conductive substrates, and only a single nozzle has been demonstrated; however, it is worth noting that Rogers and co-workers have generously made the design of the e-jet printer available to the research community, allowing refinement and expansion of its current capabilities.

In another presentation, Mirkin introduced a new technology, called polymer pen lithography (PPL).[41] This scanning probe contact printing method merges the attributes of microcontact printing and DPN to create a massively parallel nanoprinting tool which can be scaled to include millions of pens (elastomeric arrays of pyramids) over areas of many square centimeters.[41]

NanoInk Incorporated also released its third-generation desktop fabrication tool based on DPN, the NPL2000, which integrates both high-resolution mechanical motion and an optical microscope (Figure 4B). This simplified tool, according to Jason Haaheim of NanoInk, provides an integrated solution to massively parallel DPN using two-dimensional cantilever arrays consisting of as many as 55 000 pens (Figure 4B).[42,43] The use of large pen arrays overcomes the throughput limitations of conventional single pen DPN. Furthermore, the recent development of multiplexed inking methods has further provided the capability of multiplexed molecular patterning at the nanometer scale.[44] Because most scanning probe lithographies work by moving a "pen" or similar tool with delicate computer-driven piezoelectric control, the NPL2000 has the potential to become a general working platform for DPN,[10,11] PPL,[41] as well as other scanning probe lithographies[10,21] that are based on moving pen arrays over a surface.

A common feature of e-jet printing, PPL, and DPN is that they enable direct patterning of soft matter. This capability enables opportunities to create nanoarrays of proteins, nucleic acids, and small molecules, allowing researchers to address important problems in molecular biology, cell biology, and materials science. Such structures can be used to study cell−surface interactions, as scaffolds for controlling materials assembly, and as arrays for multiplexed molecular diagnostics.[45−47] Thus, these new tools have the potential for addressing niche applications that may not have been the intention when first developed. An interesting example is the development of PPL.[41] Using concepts from both microcontact printing and DPN, PPL emerged as an extremely simple nanofabrication tool that combines flexibility of serial writing and high throughput of parallel printing (Figure 5). This combination enables the use of PPL for pursuing biological applications of chemically tailored surfaces.[45−47]

OUTLOOK AND CHALLENGES AHEAD

The exciting progress reported at the "Chemical Methods of Nanofabrication" symposium suggests that the field of nanofabrication will not only continue to advance its current frontiers and respond to the needs of the electronics industry but is also uniquely positioned to take on new challenges facing the development of new biomedical and energy-related technologies.

In the area of biomedicine, developments in nanofabrication tools will allow production of ever smaller and more sensitive diagnostic and therapeutic probes, to delineate the enormous numbers of biological structures and functions. The ability to construct sophisticated surfaces with multiplexed chemicals and in controlled chemical environments will enable understanding and mimicking of complex biological systems. For example, nanostructures and devices are emerging as sensitive bioanalysis platforms based on remarkable optical and electrical properties arising from nanofabrication. Examples reported include dual optical switches for DNA sequence analysis based on fluorescence quenching and simultaneous Ra-

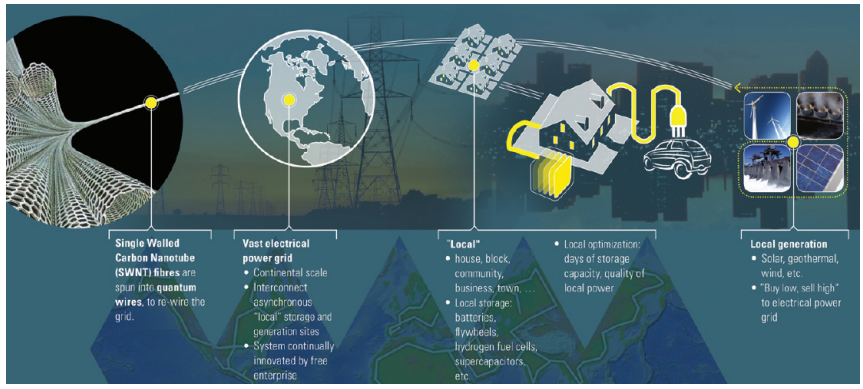

Figure 6. One-world energy scheme through a distributed storage-generation grid: the vision of the late Richard Smalley illuminates a range of new challenges facing nanofabrication in the areas of nanomaterials synthesis, assembly, catalysis, and energy harvest, storage and transportation. Image courtesy of Wade Adams of the Richard E. Smalley Institute for Nanoscale Science and Technology at Rice University.

The ability to construct sophisticated surfaces with multiplexed chemicals and in controlled chemical environments will enable understanding and mimicking of complex biological systems.

man scattering of gold nanoparticle aggregates,[48] Raman "hot spots" within synthesized dimers of silver cubes or spheres leading to enhanced sensitivity by factors of 2×10^7,[49] and bioelectrical "noses" based on human olfactory receptor-coated SWNT-FET (field effect transistor) that afford detection of odorant molecules with single carbon mismatches.[50] Likewise, nanofabrication has allowed opportunities to address a variety of complex problems in biological systems, ranging from drug delivery,[29] to eye tissue regeneration,[51] to self-organization and responsive behavior.[52,53] As new materials and nanofabrication tools become available, exciting applications in the area of biomedicine will continue to emerge.

In the area of energy, nanofabrication can provide new capabilities to understand and to control how basic energy carriers such as photons, electrons, holes, and phonons convert and transport energy, and how to fabricate the structures to direct conversion and transport at length scales spanning nanometer to macroscopic length scales. As perhaps a tip of the iceberg, the symposium contained examples of how new nanofabrication tools and processes can be used to probe carrier dynamics,[54] to structure organic solar cells,[55,56] and to make electrically conductive carbon nanotube wires over hundreds of meters long.[57] In an integrated picture, the late Richard Smalley envisioned our energy system evolve to the point where energy is transported as electricity over a distributed storage-generation grid rather than the primary energy sources used today: coal and oil (Figure 6).[58] Much like broadband Internet is to information, this distributed energy grid would enable energy inputs from both plants and local energy generation through solar cells on rooftops. An integrated solution such as this requires meeting a series of scientific and technical challenges. For example: how can we store energy at 10−100× the capacity of current batteries? How can we produce energy in a greener and more cost-effective process at a scale large enough to sustain reasonable conditions for 10 billion people? How can we transport electricity over thousands of miles at a capacity 1000× greater than that what is currently possible with copper wires? Discovering solutions to questions like these is motivating researchers to explore new ways to understand and to control matter at the nanoscale. With the capability to control matter with increasingly high precision and sophistication, nanofabrication is positioned to play a more significant role in addressing a large number of fundamental problems associated with our energy challenges.

In short, the future of nanofabrication is bright. As Stephen Chou remarked at the conclusion of his talk, "Nanofabrication will continue to be the foundation and enabler of the entire field of nanotechnology and nanoscience. We already have developed many powerful nanobfabrication methods such as nanoimprint lithography, nanoprint, and self-assembly. Yet this is just a beginning: a variety of new nanofabrication technologies based on new principles will continue to emerge."

Conflict of Interest: C.A.M. is the founder of NanoInk, Incorporated and is currently a member of its Scientific Advisory Board.

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