Development of Dip-Pen Nanolithography (DPN) and Its Derivatives

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Dip-pen nanolithography (DPN) is a unique nanofabrication tool that can directly write a variety of molecular patterns on a surface with high resolution and excellent registration. Over the past 20 years, DPN has experienced a tremendous evolution in terms of applicable inks, a remarkable improvement in fabrication throughput, and the development of various derivative technologies. Among these developments, polymer pen lithography (PPL) is the most prominent one that provides a large-scale, high-throughput, low-cost tool for nanofabrication, which significantly extends DPN and beyond. These developments not only expand the scope of the wide field of scanning probe lithography, but also enable DPN and PPL as general approaches for the fabrication or study of nanostructures and nanomaterials. In this review, a focused summary and historical perspective of the technological development of DPN and its derivatives, with a focus on PPL, in one timeline, are provided and future opportunities for technological exploration in this field are proposed.

1. Introduction

Downsizing of materials to the 1–100 nm length scale can lead to the emergence of new phenomena and unique functionalities that the bulk does not exhibit.[1–4] In the past decades, a wide variety of nanofabrication techniques have been developed to realize the nanoscale patterning of materials on a surface. The scanning probe lithography (SPL) based techniques, which make use of one or an array of sharp scanning tips to induce

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materials patterning, are particularly interesting because of their simple fabrication mechanism and the versatility to many biological and chemical materials that are difficult to fabricate with conventional fabrication techniques such as photolithography or electron-beam lithography.[5–9]

These SPL techniques can be classified into either a destructive process or a constructive one. The former usually subtracts from the underlying structure through oxidation, etching, shaving, grafting, or nanowelding through a hard tip,[10–20] delivering energy to a surface (mechanical, thermal, electrostatic, etc.). Very differently, the latter directly delivers materials to a surface from the tip in a way similar to writing letters with a quill pen. During the mid-1990s, researchers observed that tip "contaminations" in the form of molecules capable of building self-assembled monolayers (SAMs) could deposit SAMs on clean parts of the substrate when the contaminated tip was scanned over these areas.[21,22] This was then developed into a charming nanofabrication tool in Mirkin's group in 1999, coining the term dip-pen nanolithography (DPN) (**Figure 1**).[23] DPN can directly transfer a wide variety of "inks" (small molecules, polymers, DNA, proteins, peptides, colloidal nanoparticles, metal ions, sols, etc.) to various substrates at a sub-50 nm length scale. Also, those DPN-generated patterns of organic molecules and catalysts can be used for further controlled assembly of other nanomaterials, such as peptide arrays, carbon nanotubes, gold nanoparticles, and graphene oxide sheets.[24–27] In general, a meniscus formed between the scanning tip and the substrate (either by condensation of ambient humidity or the used ink itself) serves as a conduit for ink transport. With the computer-aided control of the tip movement, complex and arbitrary structures can be easily made. Over the past twenty years, DPN has experienced a tremendous development in terms of applicable inks, a remarkable improvement of the fabrication throughput, and the development of various derivative technologies. Compared with conventional nanofabrication technologies, DPN is combining many desirable attributes, including high resolution, good registration, in situ imaging capability, masklessness, low cost, flexible material compatibility and the capability to operate at ambient conditions.

In the literature, there are several review articles on DPN, which focus on the detailed discussion of certain parts of the DPN development.[28–33] In this paper, we aim for providing a

Figure 1. Mechanism and ink transport in DPN. A) Schematic representation of DPN. Reproduced with permission.[23] Copyright 2008, American Association for the Advancement of Science. B) Time-dependent feature size increase in DPN with copolymer ink as an example. Reproduced with permission.[40] Copyright 2010, National Academy of Sciences. C,D) Schematic diagrams of the ink transport processes for diffusive molecular inks and liquid materials, respectively. Reproduced with permission.[41] Copyright 2013, Higher Education Press and Springer-Verlag Berlin Heidelberg.

focus review of the entire technological development of DPN and its derivative techniques over the past two decades in an historical context. We will first discuss the mechanism of DPN, and then review the key milestones in the timeline of the development of DPN and its derivative technologies. For details on the applications of each technique, readers are suggested to look into the other topic-focused review articles in the literature.[34–39]

2. Ink Transport Models of DPN

In DPN, molecular inks are first inked on to a sharp tip, which is then loaded on a scanning probe microscope. The scanning probe setup controls the vertical contact between the tip and the underlying substrate as well as the lateral movement of the tip over the surface. The ink-coated tip delivers materials onto the substrate through a meniscus (either condensed from ambient humidity or built up by the ink itself) that connects the tip and the substrate surface (Figure 1A). It is noteworthy that DPN shows a unique characteristic of time-dependent feature size increase (Figure 1B). Many approaches have been developed to model the ink transfer process.[42] The parameters influencing the transport process include the chemical and physical characteristics of the ink, the surface tension, the tip structure, the ink coverage on the tip, the Laplace pressure at the meniscus, the operation parameters (dwell time, contact force, lifting speed, etc.), and the ambient humidity and temperature.[41] Among them, the ink materials play the most important role and are generally classified into diffusive inks and liquid inks. As the name suggests, the molecular diffusion dominates the transport of diffusive inks while the fluid flow dominates the transport of liquid inks. Here, we summarize these two different transport manners individually.

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Diffusive inks are typically water-soluble small molecules that can build self-assembled monolayers (SAM) for surface modification (Figure 1C).[43–47] Many physical models have been built to analyze the theoretical transport process of small molecule inks and focus on understanding the formation and function

of the water meniscus acting as transfer route. In general, the physical transport process is divided into three steps: 1) dissolution: the ink molecules on the tip dissolve in the water meniscus; 2) diffusion: the water meniscus serves as a transport channel that enables ink molecules to diffuse from the tip to the substrate; 3) assembly: ink molecules self-assemble onto the substrate through a thermally activated process or chemical reaction.

Liquid inks are viscoelastic liquids, in which the transport is dominated by the surface tension rather than by aid of a meniscus (Figure 1D). Liquid inks are not only good at directly constructing desired nanostructures, but also can be used as carriers to transport or synthesize other nanostructures. Therefore, liquid inks, especially viscous polymer inks, have become a new research hotspot in the development of DPN.[48,49] Up to now, only a few complete models have been set up to study this transport process, and a detailed understanding is not yet available. However, some important problems have been identified. Different from diffusive inks, the transport process of liquid inks belongs to the category of fluid dynamics, which is manipulated by the mass fluid flow through a pressure gradient.[48] The pressure gradient is attributed to the capillary pressure in a classical DPN process[50] and is influenced by many factors including liquid viscosity, tip structure, Laplace pressure at the meniscus, surface energy, humidity, temperature and operation parameters. Besides, the transport mass and rate of liquid inks are strongly related to the contact time, resting time, and ink viscosity.[51] Longer contact time or resting time enables a larger ink transport, while the transport can be slowed down by viscous force. In the future, there is a great opportunity for modeling and experimental study to enable a full understanding of liquid ink transport processes from tip to substrate.

Interestingly, there are also inks falling somewhat between the clear lines of diffusive and liquid inks. One well-known example of this kind is phospholipids.[52] In the DPN of phospholipids, also known as lipid-DPN (L-DPN), amphiphilic lipid molecules are written and self-assemble into ordered stacks of membranes.[53–56] By virtue of the layered self-assembly of the molecules which also includes surface diffusion in the process, yet a more liquid ink like bulk transition of material at the same time, this ink combines aspects of both ink regimes discussed above.[57]

Thorough understanding and prediction of material transfer in DPN would be highly beneficial in regard to the homogeneity of the lithography outcome.[58–60] This would be crucial in the context of using DPN in industrial fabrication applications, but—as detailed above—is still not fully achieved (especially in regard to the liquid inks for their even more complicated transfer theory). As an alternative, a more practical approach is the direct monitoring of mass transfer, which is, however, limited by the minute mass of transferred material in a single written feature.[61,62]

3. Development of DPN and Its Derivatives

In 1999, Piner et al. first reported the invention of DPN, where an atomic force microscope (AFM) tip was used to directly deliver alkanethiols onto a gold thin film in a manner analogous to that of a dip pen.[23] From then on, DPN has gone through a remarkable journey in its technological development

from a very low-throughput and materials-limited tool, to a versatile and powerful platform to pattern and functionalize a surface. **Figure 2** outlines the milestones in the development of DPN over the past two decades. In general, the development follows the rationale of making DPN higher-throughput, lower-cost, more versatile by increasing the number of operating tips, the design of cheaper tips, and the use of external energy such as heat, electricity, and photons. Technically, it can be separated into cantilever-based development and cantilever-free development as discussed in the following.

3.1. Parallelization of DPN

In the original report of DPN it was performed in a "single-pen" fashion. Although it provides great patterning flexibility and high resolution, it was criticized to be extremely low-throughput. To address the challenge, parallel DPN (p-DPN) using an array of cantilever tips was developed. In the array operation, only one of the parallel tips is employed to monitor the lithography process with a feedback system, while the other tips carry out the parallel writing in a passive manner. As such, the throughput of DPN scales by the number of the tip operated simultaneously in an array. The p-DPN idea was first demonstrated with eight tips in an array in 2000[63] and then 250 tips in 2005.[64] In 2006, a real large-area DPN parallelization was achieved with the use of a 55000-tip array over one square centimeter area.[65] The density in this massive tip array is so high that this lays the foundation of high-throughput DPN patterning, which is particularly useful for fabricating combinatorial libraries of features that systematically vary in size, spacing, and shape.[76]

Additionally, by introducing arrays of cantilevers, DPN gained the ability to write multiplexed patterns (i.e., intertwined patterns consisting of more than one chemical component) by coating neighboring tips of the array with different inks. In single tip DPN, this can be achieved by carefully realignment upon tip exchange,[77] but multitip arrays offer a much easier implementation, as their relative position to each other is exactly known.[78–81]

3.2. Cantilever-Based Derivatives of DPN

Apart from the parallelization, another dimension of development in DPN is to expand its versatility with the additional input of electrical, thermal, and mechanical energy. In 2001, a DPN derivative, named electrochemical dip-pen nanolithography (E-DPN) was introduced to directly fabricate metal and semiconductor nanostructures with nanometer dimension.[66] For E-DPN, the critical development is that the water meniscus formed between the tip and the substrate not only transported metal salts as a channel, but also electrochemically reduced these precursors to metals as a nanometer-sized electrochemical cell. This modification significantly extends the applied range of DPN from patterning organic small molecules to fabricating conductive nanostructures. For example, Maynor et al. used E-DPN to direct-write poly(thiophene) nanowires on semiconducting and insulating surfaces in the sub-100 nm
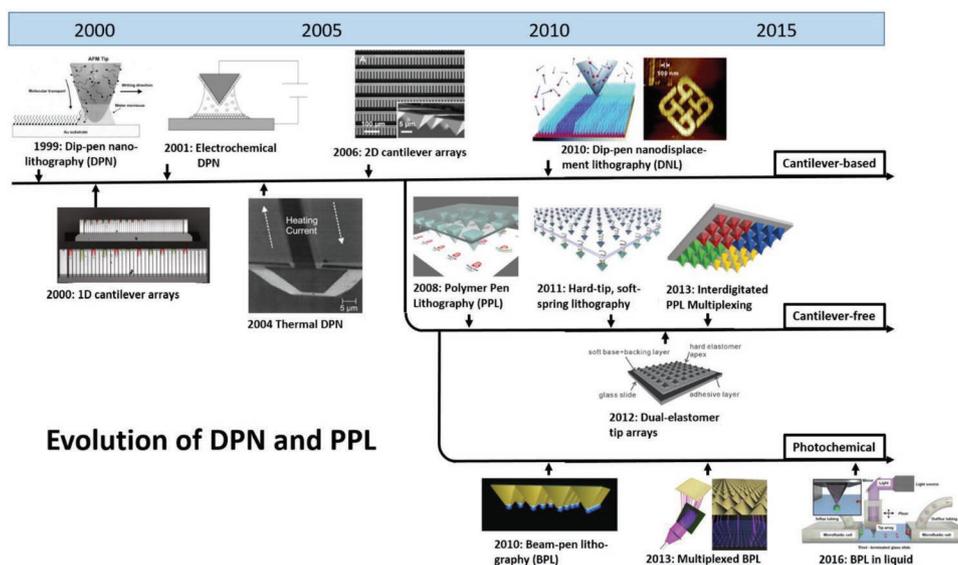
Figure 2. Timeline of major milestones in DPN research. DPN has gone through a remarkable evolution from a single tip[23] to parallel tip array[63–65] and also extended several cantilever-based (E-DPN,[66] tDPN,[67] and DNL[68]) and cantilever-free DPN derivatives (PPL,[69–71] HSL,[72] and BPL[73–75]). As a sub-branch of the cantilever-free category, BPL opened up the way for photochemistry as additional lithographic option for PPL. Reproduced with permission.[23] Copyright 2008, American Association for the Advancement of Science. Reproduced with permission.[63] Copyright 2000, American Association for the Advancement of Science. Reproduced with permission.[64] Copyright 2005, Wiley-VCH. Reproduced with permission.[65] Copyright 2006, Wiley-VCH. Reproduced with permission.[66] Copyright 2001, American Chemical Society. Reproduced with permission.[67] Copyright 2004, AIP Publishing. Reproduced with permission.[68] Copyright 2010, The Royal Society of Chemistry. Reproduced with permission.[69] Copyright 2008, American Association for the Advancement of Science. Reproduced with permission.[70] Copyright 2012, Wiley-VCH. Reproduced with permission.[71] Copyright 2018, Wiley-VCH. Reproduced with permission.[72] Copyright 2011, Springer Nature. Reproduced with permission.[73] Copyright 2010, Springer Nature. Reproduced with permission.[74] Copyright 2013, Springer Nature. Reproduced with permission.[75] Copyright 2016, The Royal Society of Chemistry.

scale,[82] and to fabricate nanoscale gallium nitride/gallium oxide heterostructures via local chemical modification of GaN nanowires by applying a voltage.[83] Agarwal et al. also demonstrated E-DPN for the immobilization of biological molecules (Histidine-tagged proteins) on a metallic nickel surface by the tip-induced metal chelation (Ni-His bond).[84]

In 2004, thermal DPN (tDPN) was developed, which utilizes a heated cantilever tip to melt and deposit solid organic inks on a surface.[67] This refinement of DPN allows one to deposit a variety of solid inks with an appropriate melting temperature that cannot be used in conventional DPN. For example, octadecylphosphonic acid is immobile at room temperature, but it could be transported onto mica surfaces by tDPN when the tip was heated above the ink's melting temperature near 100 °C. In 2006, Nelson et al. used tDPN to perform nanoscale deposition of continuous indium metal lines with a width less than 80 nm.[85] Also, tDPN allows controlling the ink transport and feature size by changing the tip temperature.[86] In 2008, Lee et al. directly deposited surface-aligned functional polymer nanostructures (PNIPAAm) on epoxy-silane SAM-functionalized silicon oxide with the use of tDPN.[87] Felts et al. investigated the nanometer-scale flow of molten polyethylene from a heated tip during tDPN.[88] They claim that the polymer flow depends on surface capillary forces and not on shear between tip and substrate and the rate of polymer mass flow can be tuned by changing the polymer viscosity as a function of temperature.

Another interesting approach of using tip-based lithography is the catalytic scanning probe lithography (cSPL).[89] Here, either heat (similar to tDPN) or tip-anchored catalysts are used

to induce highly localized chemical reactions on a surface. This was first demonstrated for metalized tips as catalyst (e.g., Pt,[90] Pd,[91] or Cu[92]), but quickly expanded to (bio-)catalyst attached to tips (e.g., enzymes like *Staphylococcal* serine V8 protease,[93] alkaline phosphatase,[94] or horseradish peroxidase (HRP)[95]). Recently, the technique was also combined with polymer pen lithography (PPL) stamps instead of DPN tips, allowing for even further massive parallelization.[96]

In 2010, a mechanical DPN derivative namely dip-pen nanodisplacement lithography (DNL), was introduced to program the 2D and 3D nanostructures of polymer brushes.[68] The core of DNL is that a homogeneous SAM preassembled on a substrate is displaced with surface-initiated atom transfer radical polymerization (SI-ATRP) initiators through tip-induced mechanical scratching at the nanometer scale. Subsequently, functional polymer brushes can be grown from the initiated areas. With precise control of the position and density of the initiators, 2D and 3D arrays of polymer brushes can be made. DNL combines the advantages of destructive nanografting[97,98] and constructive DPN. Because the preassembled SAM significantly limits the lateral diffusion of the initiator ink, DNL ensures that the feature resolution is largely determined by the radius curvature of the AFM tip. In addition, the grafting density of the displaced initiators can be adjusted by the lithography force, which is a major difference from the ink transportation in classical DPN.[99]

In 2011, DNL was employed to fabricate arbitrary 3D polymer structures by rational control of the lateral spacing between arrays of nanosized polymer brushes.[100,101] Based on the confinement

effects between neighboring polymer brushes, the surface morphology evolved from collapsed to stretched structures as a function of lateral spacing. In this case, this spacing-control strategy combined with DNL can be employed to construct 3D structures composed of polymer brushes (Figure 4A).

Importantly, DNL can also be operated with cantilever tip arrays. Similar to p-DPN, parallel (p-DNL) using tip arrays also significantly improves the throughput while maintaining the feature deviation over a larger area to be less than 5%. The cm-size DNL-generated polymer brushes could serve as an etching resist to construct and pattern metal structures for optical applications,[102,103] and were employed as an extra-cellular matrix to study the cell adhesion.[104]

3.3. Cantilever-Free Derivatives of DPN

After an eventful decade of development of DPN mentioned above, it was found that the cantilever arrays, especially those high-density ones, were too costly in the long run. This is due to the fact that these cantilever tips are fabricated with tedious lithography and etching processes and comparably costly raw materials. Therefore, it has been deemed highly desirable to make tips in a much more cost-effective manner over a large area. With this direction, scientists have developed several types of cantilever-free derivative technologies as follows.

3.3.1. Polymer Pen Lithography

A critical milestone of the DPN technical evolution is the development of PPL in 2008 (**Figure 3**).[69] Instead of the conventional cantilever-based tips utilized in all the previous SPL approaches, PPL makes use of cantilever-free, transparent elastomeric tips for the patterning. The tips, typically made

of silicone rubber known as poly (dimethylsiloxane) (PDMS), are easily made through a well-known molding process, which allows rapid and low-cost fabrication of the tips over a large area (Figure 3A). For example, Huo et al. demonstrated the fabrication of a PPL array with as many as 11 million pyramid-shaped tips from a premade silicone mold (Figure 3B,C). The elastomeric tip array is attached to a glass backing layer so that it can be readily mounted onto a conventional DPN nanofabrication system, and the lithography is otherwise operated like a p-DPN process. PPL merges concepts of cantilever-based DPN and microcontact printing.[87,88] Here, PPL not only acquires the high-resolution patterning attributes of DPN, but also adds in the massive replication capability of contact printing for large areas. In general, the development of scanning probe lithography is often attributed to the result of novel tip designs,[105,106] and here PPL was the first example of cantilever-free scanning probe lithography. For the first time researchers truly saw the potential of scanning probe lithography for large-scale practical applications due to low materials and fabrication cost of the tips and the easy handling of the PPL process.

PPL can pattern features ranging in size from sub-100 nm to over 10 μm by changing the contact force and contact time.[107] Here, the 2008 Beijing Olympic logo was made by PPL as an example (Figure 3D). As a novel molecular printing tool, PPL can transport various materials ranging from small molecules to biological molecules[108] to polymers[40] in a high-throughput fashion with excellent registration and high resolution. Especially, based on DPN and PPL, scanning probe block copolymer lithography (SPBCL) was developed to transfer phase-separating block copolymer inks in the nanometer features on a surface (**Figure 4**B).[40]

Importantly, when the pyramidal tip of PPL contacts the surface, the contact area changes as a function of contact force because of the elastomeric nature of the tips. This feature-size dependence on force enabled by the compression of the
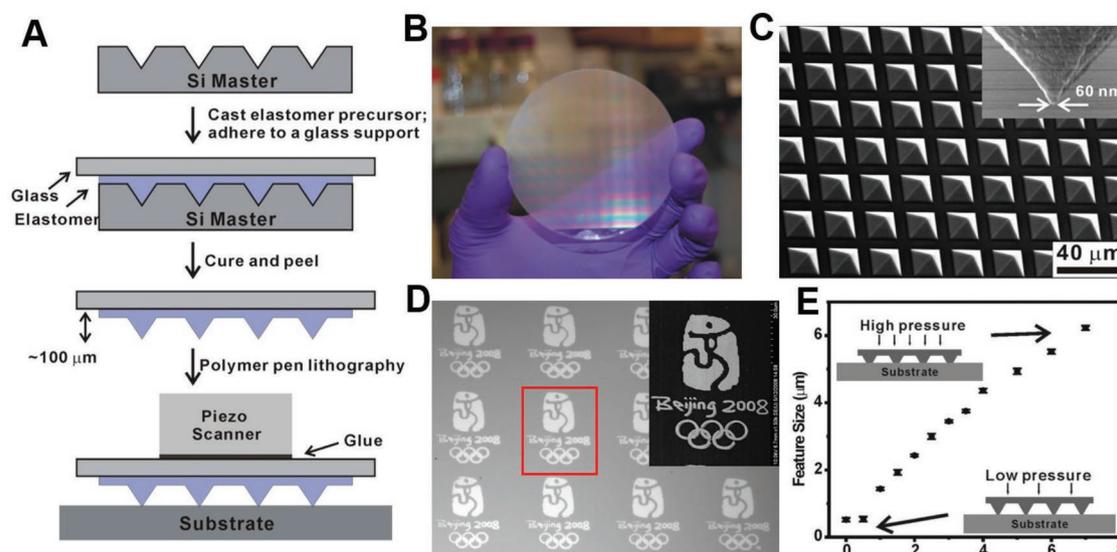
Figure 3. Polymer pen lithography. A) Schematic illustration of PPL setup. B) Optical image of an 11 million pen array. C) SEM image of the pen array. D) Force-dependent feature size increase in PPL. E) A zoom-in optical image of the 2008 Beijing Olympic logo made by PPL (inset, magnified SEM image of a single logo). Reproduced with permission.[69] Copyright 2008, American Association for the Advancement of Science.
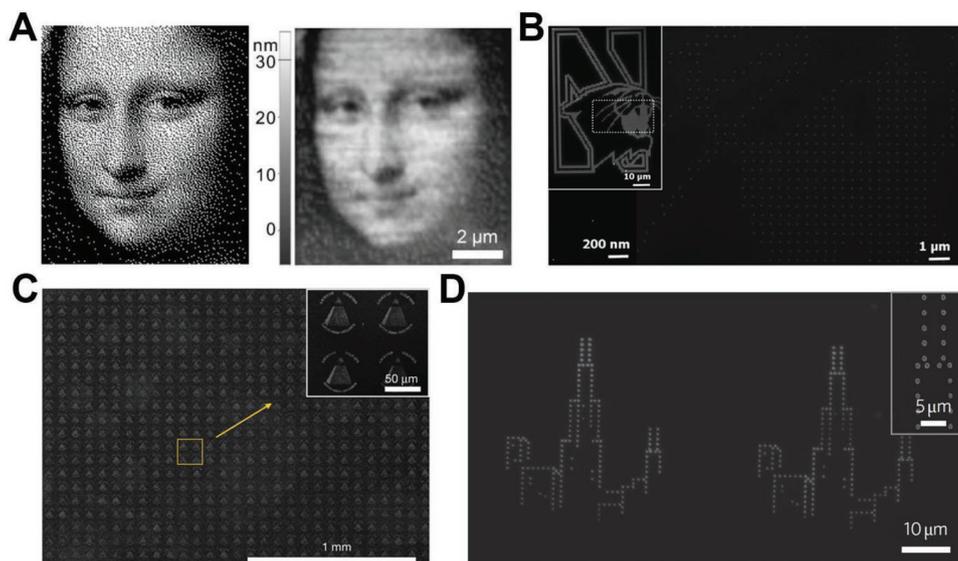
Figure 4. Representative patterns made by DPN derivatives. A) Bitmap image of Monalisa and corresponding AFM topographical image of DNL-patterned Monalisa. Reproduced with permission.[100] Copyright 2011, Wiley-VCH. B) SEM image of the magnified portion of Northwestern University Wildcat logo made by SPBCL (inset, dark field optical microscopy image of this logo). Reproduced with permission.[40] Copyright 2010, National Academy of Sciences. C) SEM image of a representative region of HSL-patterned ≈19 000 pyramid duplicates from the US $1 bank-note (inset, magnified SEM image of four pyramid replicas). Reproduced with permission.[72] Copyright 2011, Springer Nature. D) Magnified optical image of the gold Chicago skyline pattern made by BPL (inset, magnified SEM image of the gold features). Reproduced with permission.[73] Copyright 2010, Springer Nature.

polymeric tips is a distinguishing controllable parameter that is not realized in a classical DPN (Figure 3E). Utilizing this force-dependent property, PPL can pattern combinatorial library of features from nanoscale to microscale over large areas by simply tilting the tip array.[109,110] In recent years, Chen et al. used PPL to create combinatorial libraries consisting of every combination of metallic elements (Au, Ag,Co, Cu, and Ni) through polymer nanoreactor-mediated synthesis.[111–113] Furthermore, the large area elastomeric tip array significantly increases the amount of ink adsorbed and enables multiple printing tasks without re-inking. For operation, the leveling of the massively parallel tip arrays can be performed simply and straightforward by eye observing the tip deformation in-situ or—slower but of utmost accuracy—in a force-feedback way by measuring the forces of the stamp pressing onto the substrate.[114–117] To further improve the leveling accuracy and patterning uniformity, Xie et al. developed new dual-elastomer tip arrays in 2012, in which the pyramidal tip of a PPL array is made of a harder polymer apex and the rest is made of softer elastomer.[70] When contacting the substrate, the softer elastomer absorbs the deformation first, thus lowering the pressure on the tip apex. As such, nonuniformity caused by, e.g., bowing of the large-area tip array can be minimized.

Another new challenge arising from the massive parallelization was to preserve the DPN multiplexing capabilities in PPL. When switching from the single tip to high-density massive tip array in cantilever-based DPN, multiplexed ink delivery to particular tips via microfluidic networks becomes either prohibitively complex or only groups of tips can be addressed.[118] Alternatives put forward so far includes the use of ink-jet filled PPL stamp molds as ink pad[108] or altering the printing strategy to the use of segmented stamps carrying the different desired inks.[71] Another strategy for multiplexing of PPL is to individually actuate

each pen of a PPL pen array. Han et al. developed a novel strategy to realize individual tip control, termed pneumatically actuated active polymer pen lithography, where the individual probe is pneumatically actuated via a computer control interface.[119] The inflatable tip array was fabricated by the combining a PDMS block with micro chambers and channels with a conventional PPL tip array, so the vertical tip displacement can be controlled by the amount of the pneumatic pressure, resulting in an independent tip-substrate contact. Brown et al. reported an active PPL pen array in which a resistive heater was positioned below each pen.[120] Local heating was employed to actuate a single probe by thermal expansion of the PDMS beneath this tip, so each tip of the PPL pen array can be independently brought into contact the patterning area. This cantilever-free SPL architecture can pattern dot-matrix style, whit features sizes tuned across the nano- and macroscales. Huang et al. developed a photoactuated PPL strategy to individually actuate each pen.[121] The critical development is the fabrication of photoactuated pen arrays made of PDMS-CNT composites, which can locally expand under light irradiation.[122] The local expansion enables the pen to contact the substrate, resulting in local material transport by individual pens. Besides, the expansion is reversible with light on and off, enabling a reversible out-of-plane motion of individual pens of the array for locally molecular printing. The independent tip control further enhances the multiplexing capability of PPL.

3.3.2. Hard-Tip, Soft-Spring Lithography (HSL)

PPL is a significant step forward in that it combines most of the advantages of DPN and microcontact printing. However, the ultrahigh resolution of SPL, especially in the sub-50 nm scale, is difficult to achieve because of the easy deformation of

the soft elastomeric tips. In 2011, another cantilever-free version, named HSL, was developed to overcome the resolution limit while keeping the high-throughput patterning attribute.[72] The key innovation of HSL is the fabrication of ultrasharp and hard Si tip arrays on an elastomer layer, in which the soft elastomeric layer acts as the deformable spring to support the incompressible tips. Since the Si-tip array has an average tip apex of 22 nm, HSL can easily pattern nanoscale features smaller than 50 nm (Figure 4C). Because the hard Si tips eliminate the deformation under pressure, HSL only exhibits contact time-dependent feature size control without the force-dependent one in PPL caused by the compressive tips. However, also because of the hard tips, HSL can also transfer energy to a surface rather than materials, which cannot be realized by classic PPL. The invention of HSL is the first time to integrate a hard tip to the cantilever-free system. Compared with the other lithographic techniques,[6,123] HSL integrates several advantages in terms of ultrahigh resolution, scalability, maskless writing, materials flexibility, easy operation, low cost, and good reproducibility.

3.3.3. Beam Pen Lithography (BPL)

Taking advantage of the transparent pyramidal structure of the PPL tips, incident light from the glass side of the tip array can readily pass through and concentrate at the apex of the tips.[124] To further improve the contrast of optical transmittance at the tip, a normal PPL tip array can be coated with a thin layer of Au while a hole is opened at the tip apex. When this tip array is brought close enough to the substrate, the tips can function as an array of massively parallel near-field scanning optical microscope (NSOM) probes, which lead to the invention of BPL in 2010,[73] as cantilever free alternative to NSOM based lithography.[125] Huo et al. demonstrated concentration of UV light at the BPL tip apex and used that to perform near-field photolithography at the nanoscale. Flexible patterning is enabled by programming the scanning path and controlling the UV light irradiation on the photoresist (Figure 4D). In 2013, BPL was transformed into a true desktop nanofabrication tool by introducing a digital micro-mirror device and developing a novel approach for coordinating the UV light with the movement of tip array.[74] This actuated BPL approach is the first time to allow rapid production of multiscale structures ranging from macro- to nanoscale in one experiment.

Early works of BPL only delivered energy to pattern the underlying materials. In 2015, Xie et al. demonstrated the simultaneous delivery of energy and photocurable materials by BPL.[126] Here, the on-tip photomodulation of ink allows tuning of the molecular printing process. The key innovation is to use light to dynamically control either the viscosity of the ink via photopolymerization, or the composition of the ink via photoisomerization. By introducing the BPL setup in solution in a microfluidic setup, even more advanced photochemistry and multiplexing capabilities via solvent exchange were introduced.[75] In 2017, a high-refractive-index array was developed to carry out the BPL process in solution with a high resolution.[127] When exposed to light, a total internal reflection was achieved by matching of the high-refractive-index SU-8 pyramidal tips with suitable solvents. Combined with conventional photolithography, BPL has evolved to a simple, flexible, high-yield and low-cost tool to generate various surface patterns relevant to optics, electronics and biology,[128–130] opening up diverse strategies for photochemical patterning.[39,131]

4. Summary

To the present day, DPN has gone through 20 years of rapid development, and evolved into a flexible, affordable, and reliable tool for molecular printing. Based on the ultrahigh precision of AFM, DPN can directly write a wide range of materials on a variety of substrates with the smallest features at the sub-50 nm scale. To circumvent the limitations in throughput, p-DPN and PPL and some other parallel-tip derivatives were developed. In particular, PPL combines the advantages of DPN and microcontact printing, and achieves high-resolution, high-throughput, large-scale, material flexible, and low-cost molecular printing. In addition, DPN and PPL have spawned many types of more specialized derivatives, such as E-DPN, tDPN, DNL, BPL, and HSL. These developments expand the scope of DPN and PPL and enable these techniques for even more widespread use in the fields of electronics, optics, biology, and medicine.

It is certain that the advance of DPN will not stop anyway soon, and many issues will continue to challenge researchers. Looking beyond, one can find remarkable research opportunities for DPN and its derivatives in four aspects, including the multiple-ink delivery (multiplexing), the control of individual tip over a large area, 3D DPN, and the application for combinational materials and molecular screening. For the multiplexing, it is critical to understand different inks' transportation mechanism and dynamics so as to allow a high precision of delivery. This is important in particular when printing two or more kinds of inks that are vastly different in material properties. In this area, one good route may be to use viscous polymer as a carrier ink for a cargo compound to minimize the difference in ink behavior when varying cargo, allowing for good uniformity and reproducibility of printing. In the area of independent control of individual tips, it is necessary to find new solutions to enable high frequency actuation of the tips with minimum degrees of crosstalk among the neighboring tips. At the same time, cost effectiveness in the form of inexpensive tip arrays should be preserved, ideally. Current strategies based on heat expansion of the tip have inherent drawbacks in the slow thermal relaxation of the materials and crosstalk between tips because of thermal radiation. It is more appealing to use electrical and magnetic fields to actuate the tips. 3D DPN will be one critical area of development in the near future. Being able to precisely deliver nanoscale materials with high precision, DPN certainly has a huge potential to create 3D structures similar to 3D printing, but in much smaller length scales. This will address the remarkable challenge of current 3D printing technology at the sub-micrometer size. Finally, it is expected that DPN and PPL will make a huge impact in combinatorial materials synthesis and screening, by taking advantage of the tiny use of the materials, the multiplexing capability, and the remarkable feature control ability of the technology. We believe that further development of DPN and PPL methods will finally converge on a controllable, reproducible, easy-handling and universal technology for researchers studying surface/interface science, material science and as flexible tool in nanofabrication.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

dip-pen nanolithography, nanofabrication, nanopatterning, polymer pen lithography, scanning probe lithography

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