THREE-DIMENSIONAL STEREOLITHOGRAPHIC NANOSCALE PRINTING AND ADDITIVE NANOMANUFACTURING

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ABSTRACT

Over the past decade, three dimension (3D) printing or additive manufacturing has been on the rise in many research institutions as well as large manufacturing industries due to its potential in automated 3D solid design production. Its initial capabilities have been constantly improved since its inception to the point where 3D printing is projected to succeed the industrial production assembly line with a fully automated line. Current technology has allowed 3D printing to produce models through the use of stereolithography, a method of printing which prints parts in a layer-by-layer approach via photopolymerization. This method however comes with its limitations in dimensioning and tolerancing as well as spatial resolution. Furthermore, the recent growth in nanotechnology has spurred a necessity for nanofabrication production, which is impossible to do with the naked human eye. Due to the fact that robotics as well as heavy industrial machinery are needed for nanoscale production and manufacturing, the ideal approach would be through a fully automated process with enough precision wherein the lack of human interaction would result in little to no human error. Nanoscale stereolithographic 3D printing allows for extremely precise detail and the approach allows for production for items and tools of nanomaterials and support scaffolds in biomedicine, tissue engineering, nanoscale as well as microscale circuit boards, nanofilters, and photonic devices. Despite the fact that the extreme miniaturization and nanoscaling of functional components found in microscale integrated circuits as well as other microbiomedical devices has driven the research and development in other 3D printed nanofabrication technologies, these technologies are still just merely in its infancy. This research aims to utilize block copolymer nanofabrication as well as electrospun polymer nanofibers to improve the existing technologies associated to commercial 3D nanoscale printing including stereolithography and layer by layer deposition, respectively. With such research and new technological advancements, the road for the improvement of more precise machining and manufacturing in the nanoscale world for applications in precision biomedical and electrical components will be paved.

OVERVIEW

Additive manufacturing, also fondly known as 3D printing is a new manufacturing technique which is projected to one day replace traditional manufacturing techniques. Conceptually, additive manufacturing differs from traditional subtractive manufacturing methods in that rather than starting with a material in its raw form and machining by shaving parts away, additive manufacturing builds its product by adding and fusing parts together. Additive manufacturing is essentially a manufacturing process that creates three dimensional parts of virtually any shapes from a 3D model. These models can be created with commercial and/or industrial Computer Aided Design (CAD) software packages such as SolidWorks, PTC Creo Parametric, AutoDesk Inventor...etc post modelling and rendering, 3D scanners with the use of multiple cameras, as well as photogrammetric software. After the virtual three dimensional model is scanned and stored electronically, the additive procedure then manufactures the model in a method which is wastes less energy, time, produces less scrap, and requires much less material processing and machining. Typically, 3D printing generates models in a Layer-by-Layer (LbL) method, meaning that in general, models are created via a bottom-up approach, generating one plane at a time while building them perpendicularly. The benefits of additive manufacturing over traditional manufacturing methods are that it reduces the amount of time and money invested to create products in the long run for large industrial purposes.

HISTORY

Additive manufacturing has only very recently been invented and developed. Early additive manufacturing equipment and materials were developed and merely first appeared in the early 1980s. In 1981, Hideo Kodama invented a technique and methodology of three dimensional polymer fabrication by the photo-hardening of a thermoset polymer at the Nagoya Municipal Industrial Research Institute. Essentially, the material properties such as the ductility and malleability of the polymers were adjusted and controlled via ultraviolet radiation exposure as shown in Figure 1. As the liquid polymer substrate in the vat is exposed to the UV beam, the exposed area, hardens up.

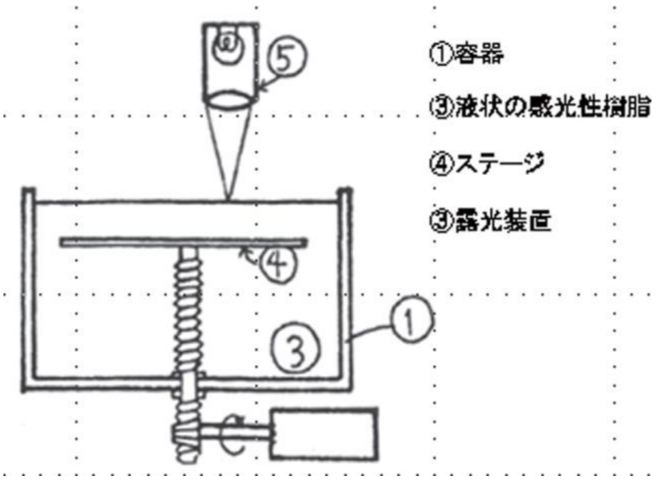

Figure 1. Kodama's schematic for the first 3D printer. UV rays (5) beam into the polymer substrate (3) in a vat (1) into the elevator platform (4). *Automatic method for fabricating a three-dimensional plastic model with photo-hardening polymer* (1981)

Since this was printed LbL, once the first layer is completed, the platform lowers analogous to an elevator. Once the model is completed, it will be fully submerged in the substrate. According to Kodama, during that time, this process to create the models can be done "in a short time, at a low cost, and without excessive manual labor."

A few years later in 1986, Charles Hull patented a method of 3D printing by which he dubbed Stereolithography (SLA) in his brainchild company, 3D Systems Inc. As shown in Figure 2, stereolithography is very similar to photolithography in that they both rely on the ability to adjust and manipulate material properties with Ultraviolet light exposure. However, stereolithography leverages the high accuracy of this technology with precision equipment combined with application of this specifically to three dimensional printing. SLA utilizes the bottom-up approach of manufacturing techniques and is considered the "Gold Standard" of mass manufacturing of products with 3D printing industrially.

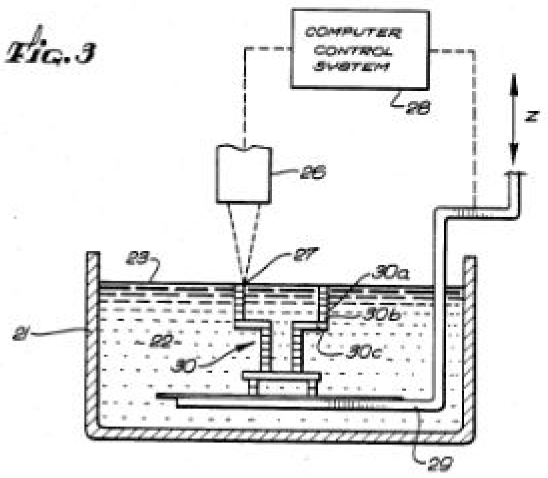

Figure 2. Hull's schematic of stereolithographic 3D printing
Apparatus for Production of Three-Dimensional Objects by Stereolithography (1986)

STEREOLITHOGRAPHY (SLA)

With the rise of interests in 3D printing and additive manufacturing, comes large industrial and economically feasible techniques of the manufacturing process. Stereolithography, now considered the gold standard of additive manufacturing uses concepts of photolithography as well as material property manipulation due to UV sensitivity. With UV light exposure in small areas, the photo polymers would harden up and would be stacked up layer-by-layer, thus making SLA a

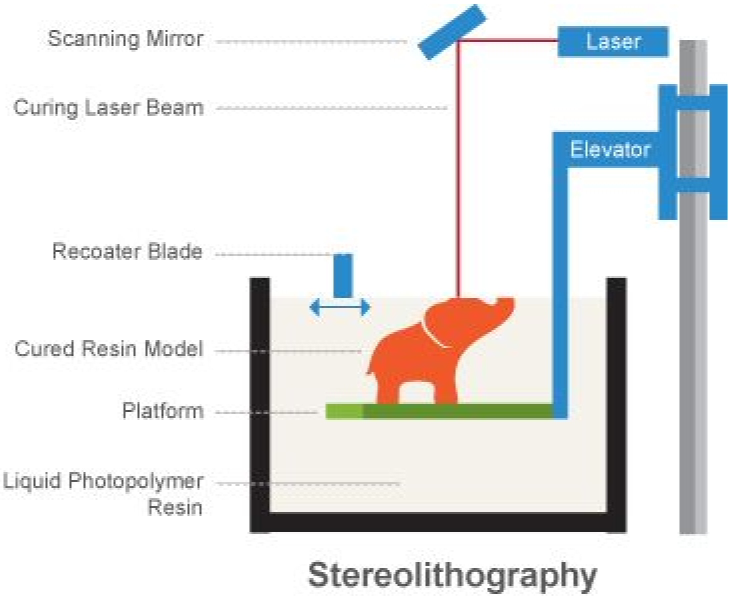

Figure 3. SLA with a more descriptive model. As the laser hardens up certain areas of the resin, the elevator lowers and allows for the product creation in a LbL fashion.

photopolymerization LbL process. SLA does not have as many mechanically intricate components as the other techniques explored later do. However, it allows for fairly rapid prototyping. The major benefits for stereolithography are that it is very convenient for most large scale industrial manufacturing plants to produces models faster than most other methods, it is cheaper than most other methods, and it is extremely accurate and produces models with a very high resolution. Since the UV light is emitted in the form of a laser, the total exposed area of the liquid substrate by the radiation has a very small surface area, therefore, the resolution is very precise and very high detail. In fact, most 3D printers that use SLA have a 0.001 inch tolerance and a layer thickness of 0.001 inch. What this means is that to print an object that is 1 inch tall, the SLA printer will print 1000 layers with the UV laser. The drawbacks to SLA printing are that only one material can be used to print the entire part since the vat can only hold one type of liquid substrate and due to the fact that the product was created with material property manipulation with UV exposure, the finished product will be UV sensitive.

FUSED DEPOSITION MODELLING (FDM)

Due to the fact that SLA is a long run investment payoff process for industry, the next most common method for additive manufacturing is Fused Deposition Modelling (FDM). This technology is prevalent in most research, consumer, and commercially owned 3D printers for rapid prototyping as well as for hobbyists. The cost and payoff comparison of Stereolithographic and Fused Deposition Modelling manufacturing is analogous to the cost and payoff comparison of LaserJet and InkJet Paper printing. FDM was patented by S. Scott Crump in 1989 at Stratasys, Ltd. Stratasys Ltd. to this date is the largest producer of FDM 3D printers such as the Makerbot series for home purposes and the uPrint for research purposes. FDM as aforementioned is the technology used most widely in the consumer level. It is commercial grade technology for hobbyists or for novelty, but also has major manufacturing impacts. Figure 4 shows how FDM works, Essentially, the filament is driven down through a heated nozzle by where the plastic, usually Acrylonitrile Butadiene Styrene

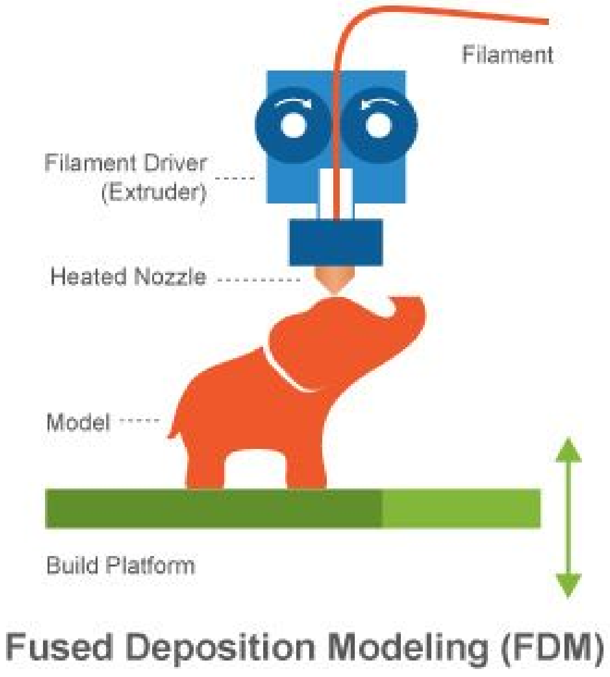

Figure 4. FDM with a more descriptive model. Thermoplastic is melted and extruded through a nozzle and solidifies not unlike a hot glue gun

(ABS) or Polylactic Acid (PLA), melts and attaches to the build platform. The nozzle has three degrees of translational freedom and thus is able to build the model layer by layer. In most FDM cases, rather than having the platform move like the SLA, the nozzle is configured in an apparatus which allows for multi degree for translational movement and thus the nozzle moves rather than the platform. The major benefits for FDM printing are that the printer itself is cheaper than most of the other printers on the market, the finished printed products are generally strong enough for functional prototypes, and it has the ability to print multiple different materials and colors in a single layer. The ability to print multiple different materials for an object proves to be incredibly useful to pretty much fully prototype plastics in one step from start to finish. Some drawbacks of FDM are are the low resolution which is typically a 0.01 in layer thickness and the anisotropic properties of the finished model. The reason for the resolution of FDM being lower than the resolution of SLA is simply due to the fact that the exposure area of the laser to the liquid substrate is much smaller and more precise than that of the FDM nozzle. Despite FDM printers mainly being a novelty, many industries are pushing to incorporate FDM additive manufacturing because it allows for rapid, cheap, in house prototyping. Traditionally, prototyping involved contacting a third party manufacturer to create custom molds and die casts to create a prototype which would then require more time and shipping. With the introduction of fast FDM additive manufacturing, there is more transparency, efficiency, and financial viability in prototyping.

INKJET STYLE PRINTING

With the advances in additive manufacturing as well as the techniques of stereolithography and fused deposition modelling, each of those popular techniques have their benefits and drawbacks. In order to combat the drawbacks and to improve the benefits of both, the technology of InkJet Style Printing emerged. InkJet Style printing is a more recently developed printing technique and was developed in 1993 in the Massachusetts Institute of

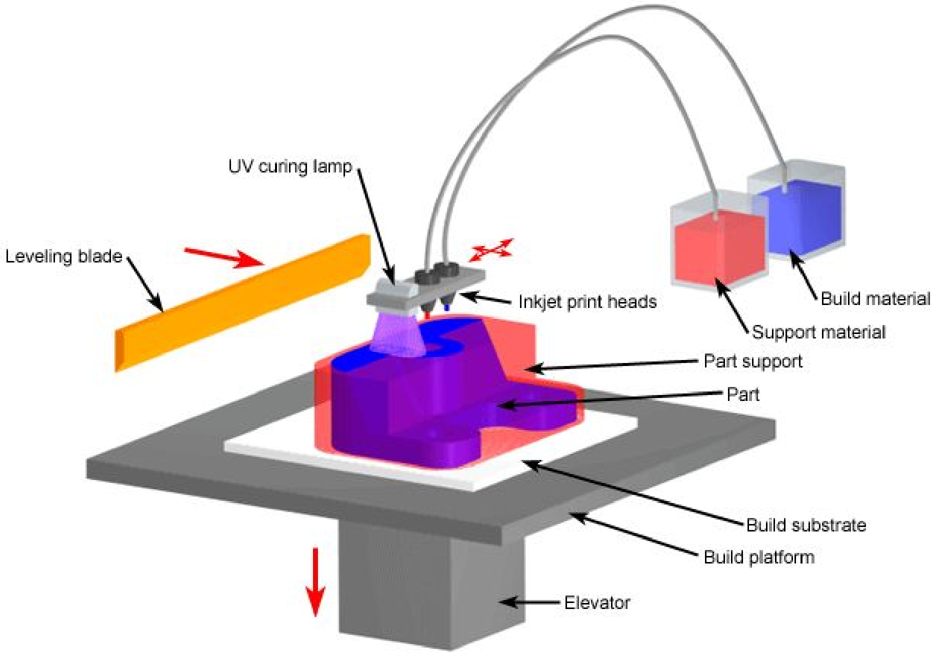

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Figure 5. InkJet Style Printing combines the techniques of FDM with its moving print heads and LbL bottom up approach with the methodology of SLA with photocuring the material

Technology and licensed in 1995 by the Z Corporation. This technology essentially bridged together the methodologies of stereolithography and fused deposition modelling. As exhibited in Figure 5, InkJet Style Printing combines the techniques of fused deposition modelling with its moving print head nozzles extruding the substrate resin with the layer-by-layer, bottom-up approach and the methodology of photolithography where the material properties of the print materials are adjusted via controlled UV exposure adjustments. In Figure 5, the print heads have multi degrees of translational movement and deposit the liquid build and support materials before being hardened up by the UV curing lamp. After the model is built, it is then submerged and incubated into a chemical bath for several hours to dissolve the support material. The benefits for InkJet Style Printing include a great surface finish, a very high resolution of 0.0006 inch for layer thickness, it is relatively fast, and like the FDM printing technique it can print out multiple materials and colors in a single layer. Some of the drawbacks to the InkJet Style Printing Technique are like the SLA method of printing, the finished product will be UV sensitive since the model was created with controlled ultraviolet exposure, and like normal inkjet printers, 3D Inkjet printers are expensive in that the build and support material are rather expensive.

SELECTIVE LASER SINTERING (SLS)

Generally speaking and for the most part, additive manufacturing mostly deals specifically with polymers due to high versatility for manufacturing and application. However, the technology for additive manufacturing for various materials aside from polymers exist. The method of Selective Laser Sintering (SLS) has applications on several types of metals, ceramics, and plastics. SLS was developed and patented by Dr. Carl Deckard and DR. Joe Beaman at the University of Texas at Austin in the mid-1980s under sponsorship of DARPA. Figure 6 shows how SLS technology is operated.

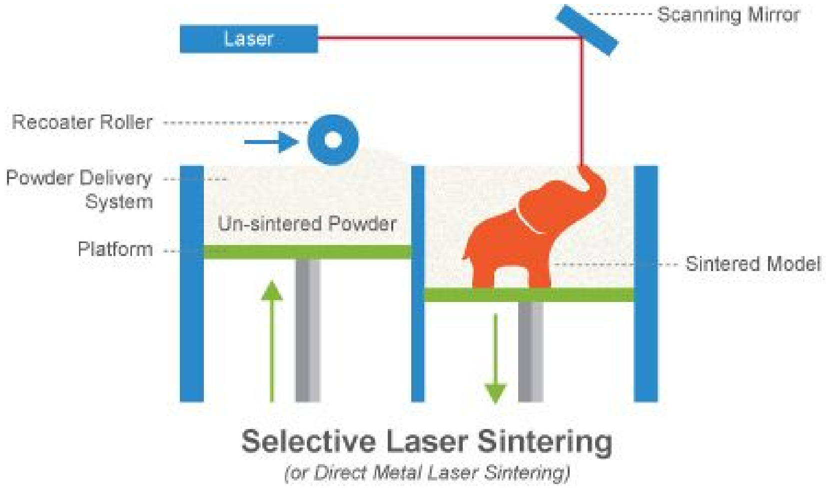


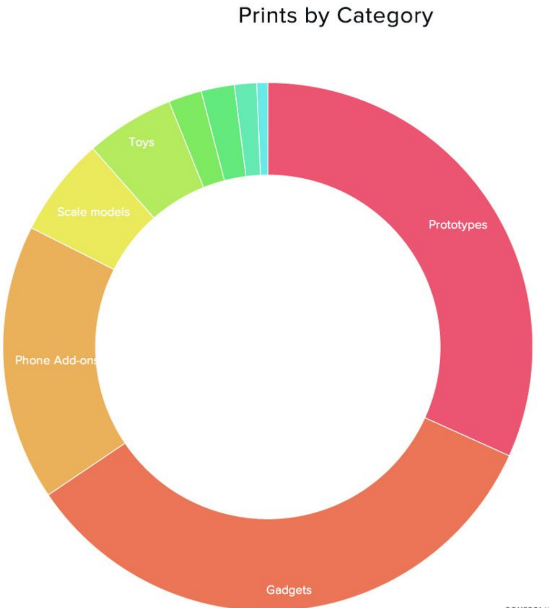
Figure 6. SLS schematic and technique. A high powered laser is beamed onto the surface of a vat of powdered sinter material wherein new coats of powder are periodically replenished

Essentially a high powered laser is beamed into a vat of powdered sinter material such as metal dust or plastic scraps. As this happens, the powdered sinter materials are melted and fused together. This procedure, like the SLA utilizes a laser to produce LbL bottom-up finished product models. As one layer is completed, a recoater roller pushes more of the sinter material into the sinter vat where the new layer can be completed once again. This technology can also be applied for ceramics as well, however that would require a lot of power. Benefits of SLS include the versatility that this process has on metals such as steel, aluminum, titanium, cobalt-chrome...etc, ceramics and glass, as well as other polymers that the other techniques use. Additionally, this process is very accurate due to the precision of the laser which produces layer thicknesses of 0.001 inch. This process does, however come with many drawbacks and downsides as well such as if the product machined was metal, additional heat treatment is still necessary to maximize mechanical properties. This process is also incredibly expensive not only due to equipment costs, but also due to the fact that this is a high energy and high power consumption apparatus. Furthermore, the surface finishing of the product is very rough and there is much residual stress within the model from the sintering.

BENEFITS AND APPLICATIONS

Despite the fact that additive manufacturing especially three-dimensional printing is merely in its infancy and acts as a novelty for hobbyists, there is a plethora of benefits as well as applications additive manufacturing has for large scale manufacturing industries and plants. Its versatility as well as ability to save time and money in the long run makes it a hot topic for many research institutions as well as private corporations with interests in product research and development. Figure 7 on the depicts the collected

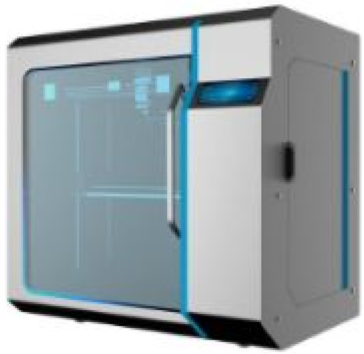
Figure 7. Collected data by 3D Hubs on 3D Printer usage. Prototypes, the largest category takes up 38% of the usage. Combined with Gadgets, these categories take up nearly 75%. More information with an interactive breakdown of the numbers can be found at https://www.3dhubs.com/trends/2013-november



data on 3D printing usage collected by 3D Hubs. This shows that primarily, the largest use of 3D printers was used for printing prototypes, which took up 38% of all collected data regarding printing usage. The reasons as to why the applications for large scale manufacturing are huge are because instead of traditional manufacturing techniques which involve subtractive manufacturing, 3D printing allows for in-house manufacturing without the need to contract production jobs to third party manufacturers to develop a potentially unsafe template for a design for mass production. 3D printing offers designers an option to develop 3D prototypes faster than that of traditional methods. It also operates pretty much as a 1 Step Procedure because there is usually no need for multiple machining to process the product, saving many companies a lot of money and time in the long run. Additive manufacturing is also projected to signal the start of the "Third Industrial Revolution" in that 3D printing may one day succeed the industrial worker assembly with a pretty much fully automated process.

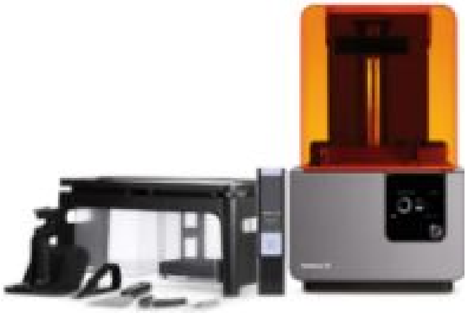
TECHNOLOGY AND THE BINGHAMTON UNIVERSITY ADDITIVE MANUFACTURING LAB FACILITY

As additive manufacturing techniques are being researched and developed exponentially, the technology has developed to a point where there are many different and diverse applications for a variety of purposes. Many of these purposes range from large scale efficient rapid prototyping purposes for manufacturing plants, to parametrically controlled precision oriented purposes for research applications for device and process improvement, to mechanically intricate aesthetically functioning devices for novelty for hobbyists. As such mentioned, these devices have a range of costs depending on the purpose and application. Figure 8 on the left shows the HK Affinity A17 used largely for industrial plants and research facilities. Its high cost is attributed to its ability to prototype large products with high resolution and precision. Figure 9 to the right exhibits the FormLabs Form 2. This is a printer which utilizes FDM to create models and can be used to rapid prototype rather quickly for small models for smaller scale product developers who want to see if they have developed a mechanically and structurally stable and



HK Affinity A17
~ 16 in x 16 in x 16 in
$13,000

Figure 8



FormLabs Form 2
~ 6 in x 6 in x 7 in
$3,500

Figure 9

aesthetically pleasing design. Aside from the higher end models of the spectrum of 3D printer Models, there are also a number of commercial and consumer grade 3D printers in the market for home usage, not unlike paper printers when inkjet printers were first invented. Figure 10 to the left shows the design of the Precision Reprap I3. This hobbyist targeted device was intended to make very basic prints most likely CAD models that are obtained from open source object libraries or user created model part files. The devices, like most novelty printers utilize FDM printing technologies for usually ABS and/or PLA polymers. Essentially such a device is a great investment for small casual prints but usually lacks the precision to make very small layer thicknesses for maximum resolution. The next devices in Figure 11 is a basically an even simpler and cheaper technology mainly marketed to kids to spur interest in additive manufacturing. This model is pretty much just the nozzle of any typical FDM 3D printer. This model works pretty much like building models with a hot glue gun, where the pen melts inserted polymer cartridges with a heating mechanism and polymer structures set and dry when cooled at room temperature. This device is a very simple one with a very basic design which can accurately show the capabilities of additive manufacturing not only to children, but also to hobbyists who wish to learn more about it. Binghamton University also has several 3D Printers in the Additive Manufacturing Laboratory in the Engineering & Science building of the Innovative Technologies Complex as displayed in Figure 12. The devices there are mostly meant for research purposes as well as for rapid prototyping for local companies as well as University-sponsored projects.

Precision Reprap I3
~ 9 in x 9 in x 8 in
$198

Figure 10

Soyan Pen 4 Kids
~ Infinite !!
$59 !!
FREE SHIPPING

Figure 11

Stratasys uPrint SE Plus
Technique: FDM
~ 8 in x 8 in x 6 in
0.01 in layer thickness
$9,400

EOS m290
Technique: Direct Metal Laser Sintering
~ 10 in x 10 in x 13 in
20 micron layer thickness
$700,000

Stratasys Objet30 Prime
Technique: Polyjet UV Curing
~ 12 in x 8 in x 6 in
0.0006 in layer thickness
$19,900

Stratasys Makerbot
Technique: FDM
~ 10 in x 8 in x 6 in
0.02 in layer thickness
$2,500

Figure 12

NANOTECHNOLOGICAL APPLICATIONS

Since its initial development, there has been much research, development, and interest in the topic of additive manufacturing. Despite the fact that additive manufacturing and three dimensional printing is still in its infancy in terms of efficient and effective industrial application, potential benefits in its incorporation for large scale investment payoffs for being widely industrially practical for large manufacturing plants are evident. To increase efficacy for the incorporation of additive manufacturing techniques, miniaturization of the processes is extremely crucial in improving resolution and capabilities. Perhaps the biggest issue of 3D printing is that problem with resolution. Typically, users and manufacturers will try and save printing time at the expense of resolution, whether it is saving the Stereolithography (.stl) file in low resolution to save computer hardware memory of by printing larger layer thicknesses to expedite the print time. This results in hasty sub-par, lower quality, and inaccurate prints as shown in Figure 13.. Traditional manufacturing processes and machining, due to its subtractive rather than additive manufacturing properties, do not have this issue. Nanoscale printing and nanotechnological developments to additive manufacturing, or additive nanomanufacturing allows for precision details and allows for production and prototyping of biomedical nanomaterials, tissue engineering tools,nanoscale circuit boards, and nanophotonic devices very feasible for single step processes.

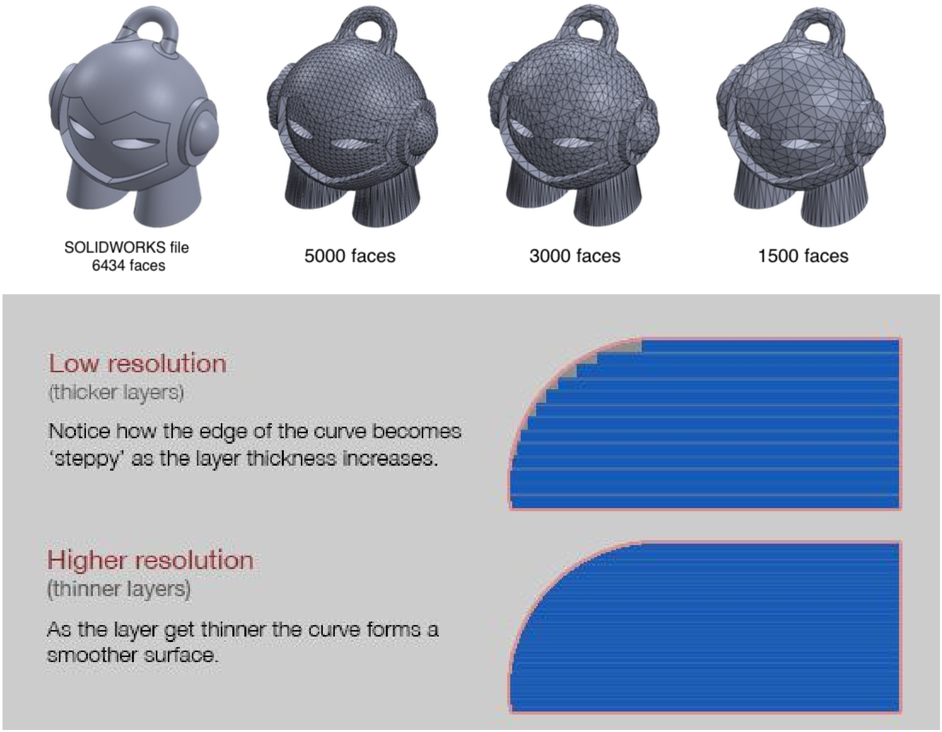


Figure 13.
Top) CAD models with various resolution save meshes. Less faces require less computing memory but do not print as precisely.
(Bottom) Different layer thicknesses. Thinner layers require more printing and time to result in more precision prints, whilst thicker ones have a shorter print time.

Generally, optimal Three-Dimensional Nanoprinting principles include:

1. True nanometer precision in positioning and material delivery.
    - Nanotechnology, by definition pertains itself for dimensions and tolerances of magnitudes in between 0 nm to 100 nm.
    - Since the technology will be applied at the molecular level, tools such as the Atomic Force Microscopy (AFM) and Scanning Tunnelling Microscopy (STM) will be utilized.
2. Accommodation of a wide range of materials.
    - As additive manufacturing techniques have versatility in different materials, miniaturization should not have a huge effect on as such
3. 3D custom design support
    - Supporting software to accurately design 3D models and Stereolithography files.
4. Ease of use and efficient throughput
5. Economical
    - 3D nanoprinting should be efficient and not produce a lot of waste such as what additive manufacturing offers when compared to traditional subtractive manufacturing techniques.

SCANNING PROBE LITHOGRAPHY

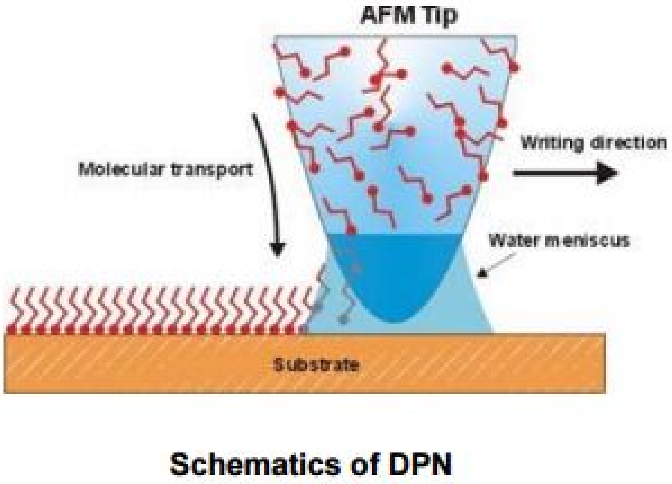


Figure 14. Schematic of DPN applications in SPL. Capillary action absorbs the ink (red) into the AFM tip. As the cantilever tip is dragged in contact with the substrate, a water meniscus is formed, which pulls the ink onto the substrate via molecular transport

Scanning Probe Lithography (SPL) is a lithographic technique which involves the use of the aforementioned AFM. As pictured below in Figure 14, SPL is a set of methods to pattern materials on the “nano-” scale with the AFM scanning probes, specifically with Dip-Pen Nanolithography (DPN). DPN is a basic nanolithography technique which has a plethora of existing research wherein an AFM cantilever tip creates patterns directly on a range of substances with a variety of “inks”. This process resembles dipping a quill or a fountain pen in ink prior to writing. These surface patterning scales are under 100 nm, which is truly indicative of nanoprinting.

Scanning Probe Lithography is a technique which uses LbL deposition with the bottom up approach. This method of LbL SPL was heavily involved in a study published in May 2016 from the University of California, Davis. In this study, SPL techniques via LbL deposition was utilized for two experiments, both of this this paper will cover. The first trial, depicted in Figure 15 shows the applications in printing lines and walls.

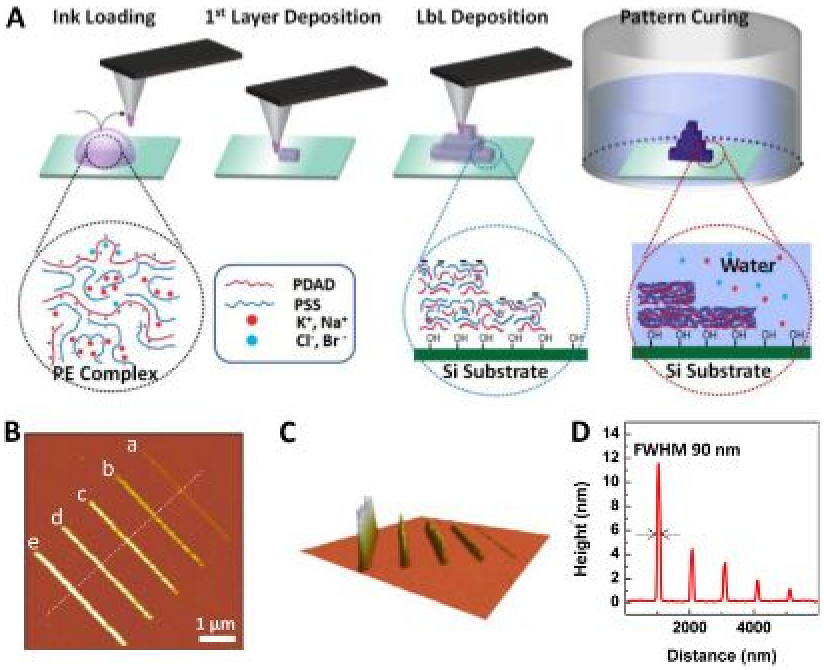


Figure 15.

(A) Shows the printing procedure from collecting ink to the subsequent layer depositions

(B) Shows the Top View of the finished walls

(C) Shows the Side View of the finished walls

(D) Dimensions of the finished walls

From this first experiment, LbL SPL was a success in that according to Figure 15, the DPN AFM cantilever was able to load the ink as well as deposit the multiple layers followed by pattern curing to obtain a finished product. The lines as shown in the multiple different view angles were a proven success in being able to print in the nanoscale. Five lines with increasing heights were printed ranging from 0.9 nm to 11.8 nm. This is extremely significant in that this print is technically subnano into the picometer range. The aforementioned study had the increasing height with the increasing number of passes (10, 32, 64, 128, and 256 passes for each of the lines). This test had employed the usage of the AFM cantilever tip (AC-240 Olympus) with a spring constant of $k = 1.7\ N/m$ and had a point load of $P = 20\ nN$ at the tip. The lines also had generally the same scaled thicknesses (75 nm, 80 nm, 90 nm, 88 nm, and 90 nm) with the increasing passes.

The second test involved printing three-dimensional structures rather than lines. As mentioned before, 3D nanoprinting should have the versatility of 3D design support rather than mere lines and walls. Figure 16 exhibits the LbL approach in SPL for printing square pyramids.

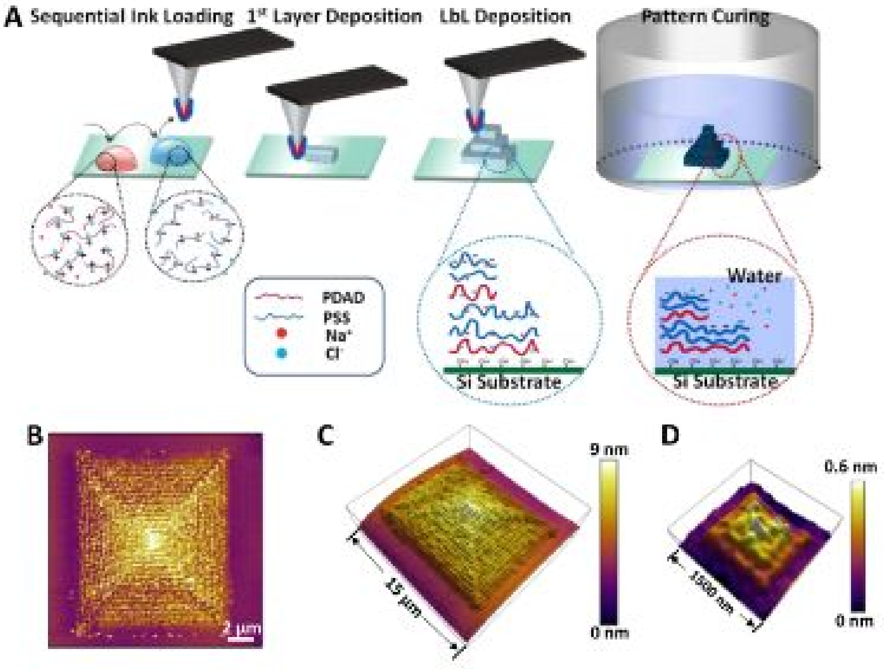


Figure 16.
(A) Shows the printing procedure from collecting ink to the subsequent layer depositions
(B) Shows the Top View of the finished structure
(C) Shows the large scale view of the structure
(D) Shows the small scale view of the structure

From the second experiment, LbL SPL was successful due the fact that as shown in Figure 16, the DPN AFM cantilever was able to load and deposit the multiple layers with capillary and molecular transport respectively, followed by curing to obtain a finished structure. The structural view as shown in the multiple different view angles were proven successful in being able to print in the nanoscale. Printing took around 20 minutes and had 15 layers of squares. These squares were printed LbL with bottom up as a decreasing size. This test had employed the usage of the AFM cantilever tip (AC-240 Olympus) with a spring constant of $k = 1.7\ N/m$ and had a point load of $P = 20\ nN$ at the tip. These squares had dimensions ranging from 500 nm to 1250 nm in side lengths, each with a layer height of 0.4 nm.

This study utilized polyelectrolyte materials with AFM based delivery techniques and was able to successfully print desired geometries with LbL printing. This was also one of the first published studies on nanoprinting structures besides straight lines and/or walls. This pioneered nanoscale printing discoveries in three dimensions and is looking for process improvement to optimize surface chemistry, delivery efficacy in the three dimensional nanoenvironment, and to improve throughput with multiple and high speed AFM tips to faster prints. This study, which cites the next, subsequent study states that further miniaturization of 3D printing to the nanoscale dimensions is the next “Holy Grail” of printing capabilities.

ELECTROSPINNING

Scanning Probe Lithography (SPL) has the capability for creating truly nanoscale three dimensional nonlinear structural prints. SPL Dip-Pen Nanolithography, however, requires extreme accuracy in alignment and has great difficulty controlling the meniscus shape when collecting or depositing ink to the substrate. Electrojetting was developed as a result to combat the shortcomings of the SPL DPN. Electrojetting, uses nanofibers emitted from the liquid droplet under an electric field. Basically, nanofibers would be extracted out via electric manipulation. This however, had its over drawbacks in that major difficulties from the unstable nature of electrified nanojets due to the effect of Coulombic Repulsion from the same charges of the nanofibers. The issues of electrojetting then paved way for the development of electrospinning. Electrospinning, as shown in Figure 17. employs the principles of electrojetting with a conducting microline to control the instability of the whipping jets, chaotic due to the same polarity of the jets. This, unlike the SPL is not a lithographic method of printing. This study was published in 2014 from the Seoul National University and showed how electric as well as

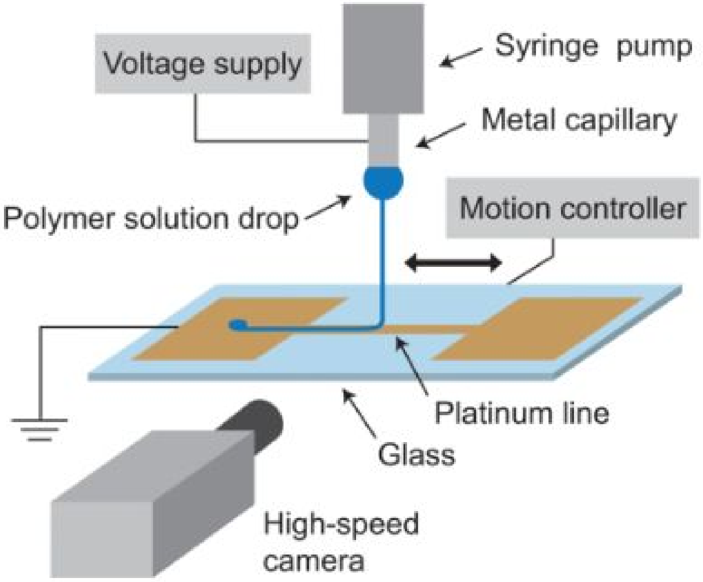


Figure 17. Electrospinning as shown with the charged platinum line (brown) to allow the chaotic polymer solution drop to be placed on the proper line.

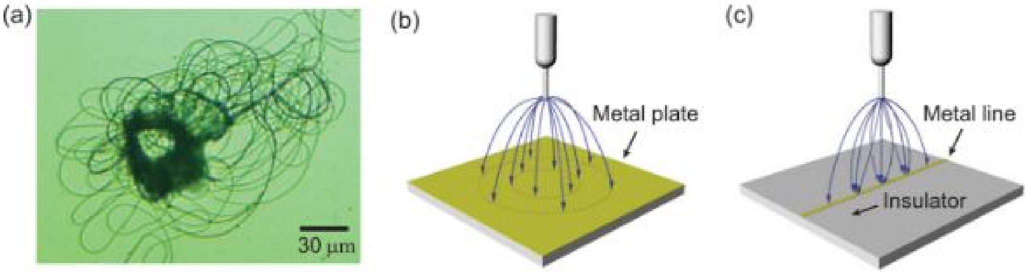


Figure 18. Effects of electric field distribution on nanofiber deposition
(a) Chaotic bundle of nanofibers
(b) Nanofibers on a plate ground
(c) Nanofibers on line ground on an insulated plate

electromagnetic principles can be used in conjunction with the mechanical aspects of ink deposition from printing to create controlled structures. Figure 18 above shows how applied controlled electric field distributions can pattern nanofiber deposition. From the depiction, it is evident that electrospinning techniques can be applied successfully to control random chaotic nanofiber bundles from a deposition sources such as a syringe pump to lay out proper patterns wuthe electric field distribution control tactics. This study, shown in Figure 19 below, unlike the previous one only produced straight lines and and walls, albeit in a faster and more controlled approach with more precision.

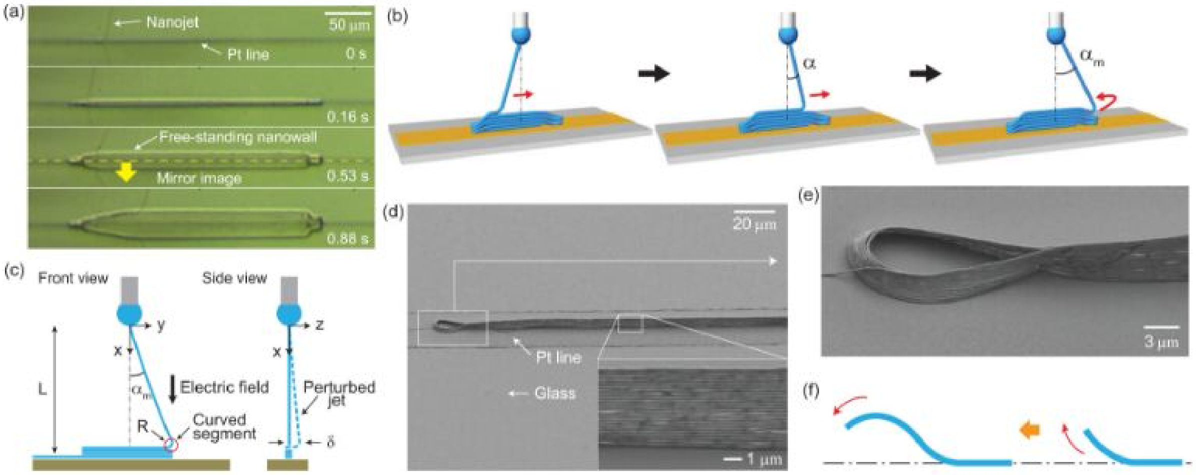


Figure 19. Electrospinning testing schematics and results
(a) Prints
(b) As the jet stream approaches the ends, the line gets “looped” and “spun” as such
(c) Schematic of the nanojet that is about to spun so that the end (red circle) does not break off and so the line deposition is continuous
(d) SEM imaging of the ends of the nanowall
(e) Closer view of the SEM imation of the ends of the nanowall

Figure 19 displayed shows the full technique of electrospinning to print nanowalls. This technique is very effective in creating straight line structures and walls because of its ability to do so quickly with the use of electric field applications and being able to "spin" or loop at the ends. As the jet stream approaches the endsm the line gets looped in such a manner in order to ensure that the end does not break off and so that the line is continuous. A close up of the description is delineated below in Figure 20.

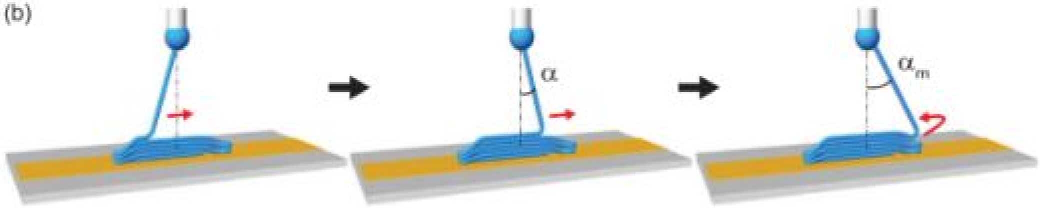


Figure 20. Close up of the electrospinning technique

As Figure 20 shows, the study only printed nanowalls and the technique discussed so far lacks the capability to produce structures of more dimensions. As α approaches $α_m$, the jet turns around and makes the loop. The nanojet loses charges as it is deposited and hits, making contact with the metal ground. The jet stream then gains a charge of the opposite polarity to attract the following nanojet stream, allowing the new stream to be attracted and to stick to the previous stream laid down. As the jet then reaches the other end, the jet turns around as α approaches $-α_m$ and repeats the process. For this study, the Nanojet of 180 nm diameter was moving as a rate of 30 mm/s to create a 4.5 micron tall, 220 micron long nanowall. The nanojet had an oscillation frequency of 68 Hz, which means that it took around 0.18 seconds to stack 25 lines, which is at a speed significantly greater than that of the SPL DPN.

This study used electrospun polymer solution nanojets focuses onto a thin metal electrode line. Not only was this study on electrospinning able to successfully create linear free standing nanowall structures, but also able to do so in a significantly faster time than that of the previous methods of nanolithography. Other methods which could achieve similar results include Ion Etching. Ion Etching is, however a subtractive process rather than the aforementioned Electrospinning, an additive process. Ion Etching also requires more labor and material intensive, and effort in that it requires the substrates, films, masks, and even more machinery. Electrospinning offers a more economical approach in that it requires only the machine with the metal ground platform, print material, and a power supply.

BLOCK COPOLYMER SELF ASSEMBLY

Block copolymers self assembly is relatively new and unique technique for printing multidimensional nanostructures. Block copolymers uses the idea of microphase separation to fabricate nanoscale structures based on properties of material polymerization. Microphase separation is the concept when incompatibility among substances due to their molecular covalent bonds prevent them from demixing macroscopically, and as such the blocks form nanoscale structures. The self assembly process as a result of these microphase separation of copolymers is influenced by the Flory-Hugins interaction parameter, χ, the degree of polymerization, N, and the volume fractions of the blocks, f. Studies have shown that the segregation strength, χN of the copolymers determines whether or not the substances will allow microphase separation or intermixing. For example if the segregation strength of idea symmetric block copolymers is greater than 10.5, the composition will microphase. If the segregation strength is less than 10.5, the blocks will mix.

Block copolymer self assembly is a very promising technique for the future of nanoscale fabrication. The idea purpose of this technique is to create 2D patterning to create templates that allow for many nano-sized applications such as dielectrics and . As research for this progressed, the potential of block copolymer self assembly became apparent in multidimensional nanofabrication as it's inherent nature is 3D. This transforms the top-down and bottom up approach of previous 3D printing techniques of nanomanufacturing into less effort with a single step. After fabricating 3D nanostructures, they can be combined to form more integrated parts for various applications. As this technique furthers along, it will become more reliable and make nanotechnology much easier to implement.

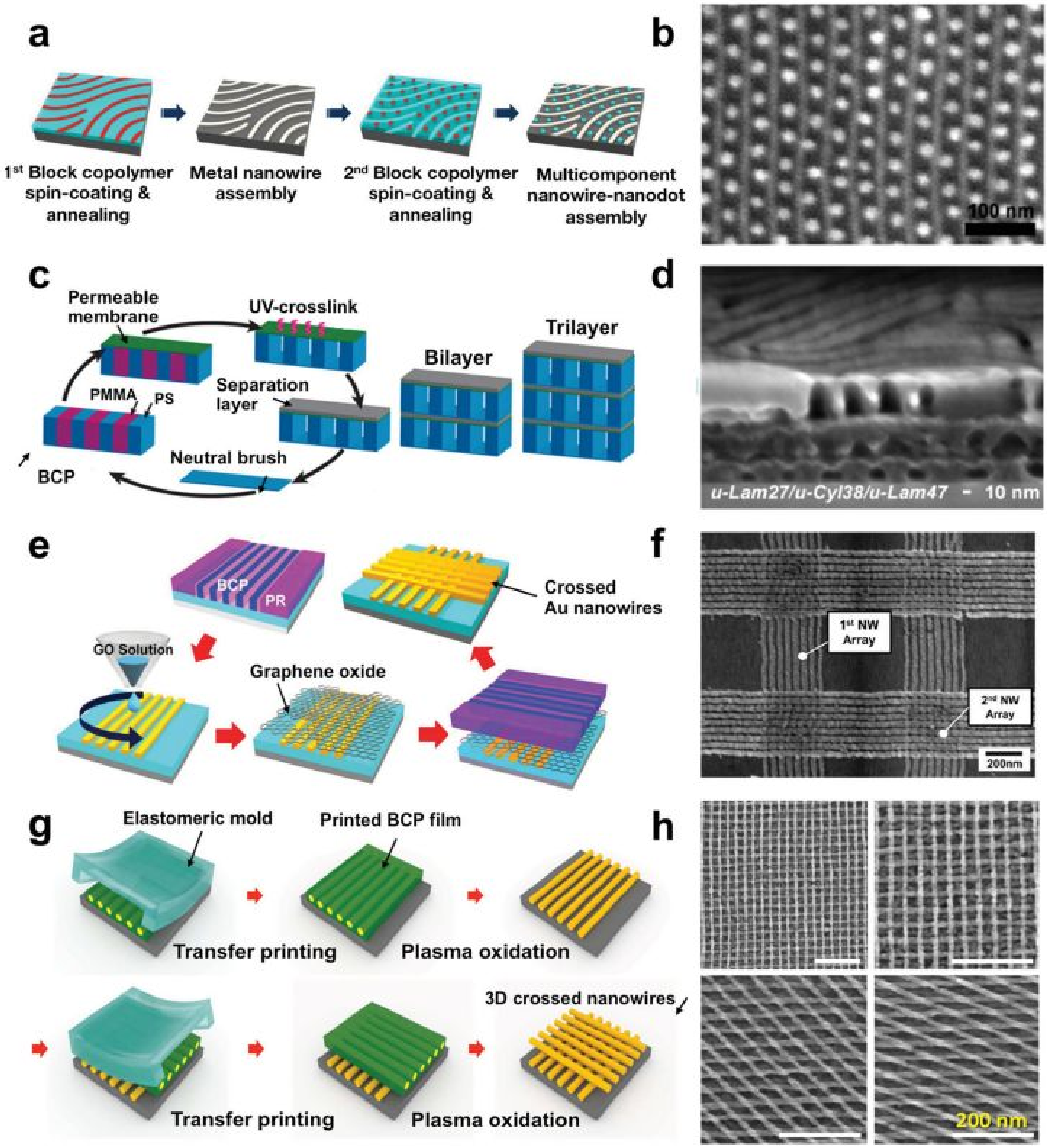


Figure 21. 3D Structures built up sequentially using BCP

With block copolymer self assembly, there are a variety of techniques that have been studied to produce full 3D structures. Figure 21 below shows a few techniques under this idea. The first technique, shown in Figure 21a and 21b, shows the Sequential Assembly. With this method, a sphere-forming poly(styrene-block-4-vinylpyridine) block copolymer is templated using metal nanowires in an array to create patterns and transferred to another layer. This technique can create a variety of patterns and designs through templating, coating, and annealing processes. The second techniques shown in Figure 21c and 21d shows multilevel nanostructures separated with a thin layer that allows stacking of adjacent block copolymer structures. Figures 21e and 21f uses a chemically modified graphene layer deposited on Au nanowire patterns to build a 3D array of nanowires. Lastly, Figures 21g and 21h show the Nanotransfer printing of block copolymers which uses an elastomeric mold made with topographic trenches used to transfer prints of block copolymer films. With this technique, the in-plane orientations can be controlled and layers of these prints can be stacked to form multilevel structures of various orientations.

The results of various studies and experiments show that block copolymers are extraordinary in their ability to create small 3D structures in one step. These structures can include helical structures, patterned surfaces, multilevel structures, cylindrical arrays, etc as shown in Figure 22. They can also range from sizes of 25-250 nm making it promising in what it can accomplish. Significant potential impacts of block copolymers was initially to create 2D etch masks that can be used as templates for other applications but it has the capability of microdomain manipulation through various techniques that allows precise registration and orientation.

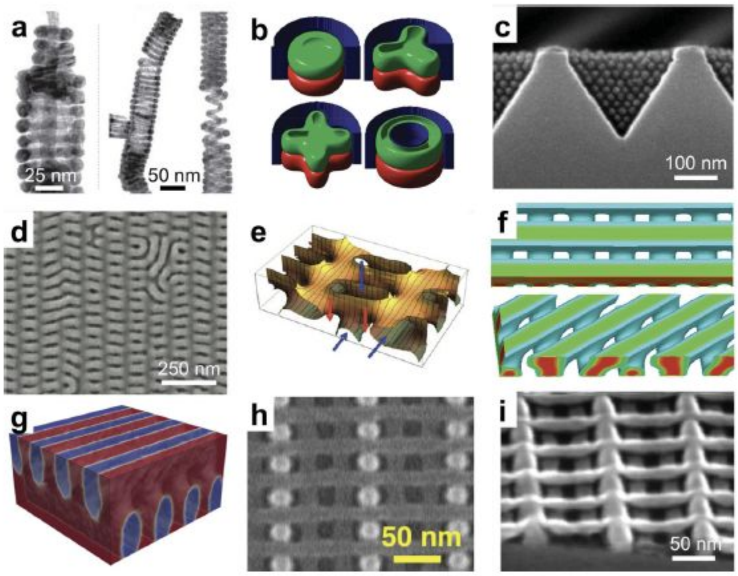


Figure 22. Various 3D structures built in one-step.

With its vast range of possibilities, block copolymers can be used in almost any nanoscale application including integrated circuits, photonic optical crystals, membranes, ultracapacitors, photovoltaic cells/batteries, sensors, catalysts, and many more. With possibilities comes challenges and with block copolymers still being a new idea of interest, a lot is still to be improved. One major set back is that there is a lack of control for error due to these fabrications being natural and single-stepped. If something was to go wrong, the nanofabrication would have to be performed again with some changes. Other issues includes high-throughput template fabrication and annealing, high-interaction parameter block copolymers required for smaller feature size, and a lack of development models and automation tools. Work and research is still needed to be done but its potential is what drives its progress.

CONCLUSION

Three-dimensional stereolithographic nanoscale printing and additive nanomanufacturing paves the way for more advanced industrial manufacturing techniques and has many applications in the future development for better systems for large manufacturing corporations to efficiently and effectively save time and capital in the long run, As of right now in the present day, 3D printing and additive manufacturing is still in its infancy, and may be still considered a novelty for hobbyists. Despite this, many private industries as well as public institutions are looking to improve this process due to its potension in rapid product generation and fast prototyping. Additive manufacturing is projected to one day in the future eliminate the need for the traditional multi-industrial assembly line with a single step fully automated process. Current shortcomings and drawbacks of macroscale printing can be further improved if not eliminated one day in the future with the introduction of nanoscale applications and nanotechnologies to additive manufacturing.

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