High-Precision Three-Dimensional Printing in a Flexible, Low-Cost and Versatile Way: A Review

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Abstract

High-precision three-dimensional (3D) printing for fabricating the arbitrarily, complex 3D microstructures with a resolution of a few microns or below are attractive across a broad range of applications. Advances have been made in the field of high-precision 3D printing, however, there are still many challenges and drawbacks that need to be overcome in order to print high-precision and high-quality 3D microstructures in a relatively flexible, low-cost and versatile way. This review summarizes some promising high-precision 3D printing technologies, including direct ink writing (DIW), two-photon polymerization (TPP), and electrochemical fabrication (EFAB). Herein, we mainly focus on the materials used in high-precision 3D printing and their applications reported so far. At the same time, we also put forward a comprehensive view of their developments and challenges, which providing a benchmark for future research and development of high-precision 3D printing technologies.

Keywords: High-precision; 3D printing; Flexible; Low-cost; Versatile.

Received: 6 August 2021; Accepted: 6 September 2021.
Article type: Review article.

1. Introduction

Three-dimensional (3D) printing, also known as additive manufacturing (AM), is a general term for a class of technologies that can realize the direct transfer from 3D models to real objects by the unique ways of accumulating materials layer-by-layer.[1] Various raw materials currently used in 3D printing involve concretes, ceramics, metals, polymers, and edible materials, and as a result the application fields include buildings, handicrafts, aerospace, biomedicine, electronic, micro-electromechanical systems (MEMS), semiconductors, foods, etc.[2-8]

With the advancement of human science and technology, the immutable trend toward miniaturization leads to an irreplaceable role of high-precision 3D printing (with a resolution of a few microns or below) in the field of high-tech industries. To date, there is an enormous variety in high-precision 3D printing technologies, mainly related to high-energy beam-based (e.g. focused electron/ion beam induced deposition (FEBID/FIBID)[9]), photopolymerization-based (e.g. projection micro stereolithography (PµSL)[10]), two-photon polymerization (TPP)[11], extrusion-based (e.g. ink jet printing (IJP)[12], direct ink writing (DIW)[12], electrohydrodynamic printing (EHDP)[13], and electrodeposition-based (e.g. electrochemical fabrication (EFAB)[7], electrochemical printing (ECP)[14]) methods. In FEBID/FIBID, the precursor molecules are induced to dissociate by high-energy electron/ion beam, thereby depositing and forming 3D microstructures. The typical minimum feature size of FEBID/FIBID is a few tens of nanometers.[9] PµSL has a resolution up to 0.6 μm,[10] which is based on area projection triggered ultraviolet (UV) photopolimerization. TPP is based on the non-linear two-photon absorption (TPA) triggered photopolymerization.[11] Compared with PµSL, TPP has higher printing resolution (sub-100 nm, but poor throughput) induced by a femtosecond pulsed laser. IJP is a method based on the layer-by-layer deposition of a liquid material in droplet form,[12] and is mainly used to prepare low-complexity 3D microstructures. EHDP employs high voltage to eject polymers with high-resolution features in the form of fibers or droplets,[13] and is usually used to print 2D micropatterns and low-complexity 3D microstructures. In DIW process, the extruded fibers are stacked layer by layer according to a predefined configuration to form a 3D microstructure.[12] Compared with IJP and EHDP,

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DIW has the characteristics of low cost, flexibility and a wide range of raw materials. However, in most of the existing studies on DIW, the feature sizes of 3D microstructures are in the range of tens of microns to hundreds of microns, and only a few of the researches have feature sizes that can reach several microns or below. ECP fabricates a 3D microstructure by locally electodepositing individual metal and alloy dots as the microjet rasters,[14] and it has poor throughput. EFAB combines the semiconductor manufacturing and AM, it can realize the mass production of high-complexity 3D microstructures through pattern deposition, blanket deposition, and planarization, layer by layer.[7] However, it relies on a cumbersome set of sub-processes.[15,16] Note that although great progress has been made in the high-precision 3D printing technologies, the realization of high-precision, high-complexity, and low-cost 3D microstructures for a specific 3D printing technology still faces challenges.

Many good review articles have been published on 3D printing technologies, and also on the raw materials or applications in 3D printing.[7,17-26] However, rare review article reports high-precision 3D printing technologies that are used to fabricate high-complexity truly 3D microstructures with a resolution of a few microns or below. Moreover, combining 3D printing technologies, materials, and applications in a relatively flexible, low-cost and versatile way is important for the future researches, and has not been reviewed previously. And this review may fill this gap.

This review focuses on promising high-precision 3D printing technologies that are being used to fabricate high-complexity truly 3D microstructures with a resolution of a few microns or below in a relatively flexible, low-cost and versatile way. In Section 2, we will briefly introduce the fundamental aspects of these promising high-precision 3D printing technologies, including direct ink writing (DIW), two-photon polymerization (TPP), and electrochemical fabrication (EFAB). In Section 3, we will discuss systematically materials and applications of these high-precision 3D printing technologies. The material type and its applications will be highlighted and discussed comprehensively for each high-precision 3D printing technology. In Section 4, we point out challenges that remain to be addressed, and provide a comprehensive view of future trends of these 3D printing technologies. At last, in Section 5, we make a general summary. Hopefully, this review will help researchers and engineers to comprehensively understand the recent advancements and challenges in high-precision 3D printing technologies, and inspire new ideas and research directions.

2. High-precision 3D printing technologies
In this review, high-precision 3D printing means the dimensions of at least one feature are in the micron scale or below. A rough classification (including forming principle, outstanding feature and printing resolution) of high-precision 3D printing technologies is shown in Fig. 1. Note that although FEBID/FIBID and EHDP can achieve the highest precision,[9] the associated high costs and low fabrication rates greatly limit their applications. Some of these high-precision 3D printing technologies either require higher costs or are difficult to realize the manufacture of high-complexity truly 3D microstructures. Among them, some 3D printing technologies offer enormous potential for achieving high-complexity truly 3D microstructures, while at the same time in a relatively flexible, low-cost, and versatile way. Specially, i) Direct ink writing (DIW), it is a technology based on material extrusion, and has a wide range of materials, a quick manufacturing speed, as well as the potential high precision (lateral dimension: 200 nm[27]). ii) Two-photon polymerization (TPP), it is a technology that relies on a femtosecond pulsed laser to excite photosensitive materials to undergo polymerization, and may be a good candidate to achieve the feature sizes of sub-100 nm level (for example, 65 nm[28]) and offset the diffraction limit. iii) Electrochemical fabrication (EFAB), it organically combines additive manufacturing (AM) with semiconductor manufacturing, and has an ability to mass manufacture millions of high-precision components (layer thickness: 2 μm[29]) simultaneously, which may compromise the costs of its cumbersome sub-process set. More detailed characteristics of these promising high-precision 3D printing technologies are shown in Table 1.

2.1 Direct ink writing (DIW)
DIW is extrusion-based 3D printing technology, in which a viscoelastic ink (a Non-Newtonian fluid with the shear-thinning behavior[31,32]) is extruded through a specific needle in a filamentary form, then undergoes rapid solidification to sustain its shape even without any support underlying layer(Fig. 2a). The inner diameter of the needle used largely

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<td>Extrusion</td>
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<td>Template</td>
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<td>No</td>
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<td>Material range</td>
<td>Wide</td>
<td>Limited</td>
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<td>Customized flexibility</td>
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determines its printing precision, ranging from hundreds of nanometers to millimeters. Therefore, it has the ability to fabricate the arbitrary complex 3D structures in a flexible, inexpensive and potential high-precision mode. Over the past few decades, DIW has become widely popular and attracted more interests from the researchers attributing to its excellent advantages, for example, without templates, low cost, flexibility, large-range raw materials.[33-36]

### 2.2 Two-photon polymerization (TPP)

TPP, as a nonlinear direct laser writing process, which uses a femtosecond pulsed laser to focus into the photosensitive materials tightly through a high numerical aperture objective lens, and triggers polymerization as well as cross-linking reaction at the focal point of the laser beam based on the nonlinear two-photon absorption (TPA) (Fig. 2b). Due to the chemical reaction in the center of the focus caused by two-photon excitation, and the ability to break through the limitation of diffraction limit, TPP can easily produce ultra-fine structures. The free radicals[37] are going to be generated during the TPA process, which can initiate polymerization and cross-linking of the polymer monomers, so that the reactive regions are not dissolved to a developer. The volume of polymerized and cross-linked region is called a voxel, which determining the resolution of 3D structures. Its size is usually very fine because of the quadratic dependence of TPA probability on the photon fluence density.[38] The determinants of voxel size include the threshold energy, the laser power, the

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**Fig. 1** Classification of high-precision 3D printing technologies.

**Fig. 2** Schematics of high-precision 3D printing technologies: (a) DIW. (b) TPP. (c) EFAB.
exposure time, the numerical aperture, and the refractive index of materials, which have been theoretically estimated by K-S Lee et al. [39] Until now, TPP has been a powerful technology to fabricate the arbitrarily complex 3D structures even at the sub-100 nm level. [28,49]

2.3 Electrochemical fabrication (EFAB)
EFAB, as a novel technique for fabricating high-precision metal 3D structures, which combines instant masks to electrodeposit metal 3D microstructures layer-by-layer. [30] The 3D model is divided into multilayer planar photomask files by a professional layered software. [10] Multiple instant masks that containing the plane figure structure are produced by utilizing lithography process. [15] A 3D structure is produced after the repeated processes of electrodeposition and planarization, and the final etching process. As shown in Fig. 2c, specifically: i) The use of instant masks to perform pattern deposition on a conductive substrate depends on the reduction of metal ions in the hollowed-out position of the insulator between anode and cathode. ii) A blanket deposition is performed by using another metal plate as anode. iii) Planarization for controlling the thickness of the completed layer. iv) Repeat these steps to accumulate pre-designed number of layers, which consists of structural materials and sacrificial materials. v) After that, an assembled 3D metal structure will be fabricated by removing the sacrificial materials. EFAB process combines the flexibility of a 3D printing design approach with the ultra-high precision and mass production of semiconductor manufacturing, resulting in complex metal structures that no other approaches can achieve. It can realize the batch fabrication of intricate metal 3D structures or devices measuring millimeters to centimeters in overall size with feature sizes from microns to tens of microns on a wafer.

3. Materials and applications
3.1 Direct ink writing (DIW)
The outstanding advantage for DIW is adjustable raw materials due to flexible design of ink, which brings unlimited possibilities for application. A suitable ink requires to have non-Newtonian fluid behavior with shear thinning, [41] that is, the viscosity decreases with the increasing shear rate, which ensures smooth extrusion of the ink. At the same time, an appropriate storage modulus is also required to enable the ink to maintain its shape after extrusion. A vast variety of inks have been implemented in DIW process, including ceramic inks, bio-inks, edible materials, polyelectrolyte complexes, metallic inks, and sol-gel inks. [31,32,34,42-44] The widespread scope of application of DIW has involved the fields of foods, [42] ceramics, [44] aerogels, [26,32] energy storage, [45,46] biological engineering, [36,47] smart robots, [48] and environmental remediation. [49] However, the precision of DIW is usually maintained within the range of tens to hundreds of microns in most of the reported studies. [26] The main limitation is that the ultimate diameter of the microneedle used is completely dependent on the ink itself. The dramatic changes in types of ink have greatly expanded the application potential of DIW and laid a good foundation for the preparation of high-precision 3D structures by DIW technology. To date, DIW has been developed with several inks that potentially fabricated the high-precision 3D microstructures, including metallic inks, [43] polyelectrolyte complexes, [58] and sol-gel inks. [51]

Metallic inks
Metals have excellent electrical conductivity, good mechanical capacity, and high-temperature resistance. Many studies have shown that DIW technology can be used to 3D print metal parts or devices. [43,52,53] These inks composed of metallic species (metal or metal oxide nanoparticles, metal salts, etc.) and organic species are directly printed into 3D structures by controlling the ink rheology, and then the 3D-printed structures are subjected to high-temperature treatment to remove the organic species and further reduce the size. [52] Therefore, utilizing such inks for DIW is of great significance in the field of high-precision 3D printing, such as microelectronic circuits or devices. Jennifer A. Lewis et al. [43] demonstrated that silver nanoparticle inks realize the omnidirectional printing of flexible, stretchable, and spanning microelectrodes in air. The planar microelectrode arrays were printed on silicon wafers through a cylindrical microneedle (the diameter was 1 μm), resulting in a minimum width of ~2 μm. The printed silver microelectrodes could be further reduced in size by annealing, and the electrical resistivity dropped sharply with the increase in temperature. Additionally, they also printed Sn-doped indium oxide (ITO) microelectrode. [53] 1D planar array of ITO microelectrodes were patterned through a microneedle (the diameter was 1 μm). After annealing at 570 °C in air, the resulting ITO microelectrodes were 1.9 μm in width and 210 nm in height. Moreover, they demonstrated the ability to self-supporting printing that span gaps. Based on this, 3D microperiodic arrays were printed, and these rods appeared to be approximately cylindrical ( filament diameter of ~1 μm). Furthermore, Eric et al. [54] printed 3D photonic crystals (3D PCs) by using titanium alkoxide and titanium diisopropoxide bisacetylacetonate (TIA) as a printable ink. After the pyrolysis, the sample was converted into a 3D micro-periodic TiO2 structure with the width of filaments was approximately 520 nm, at the same time, this 3D micro-periodic structure displayed an exceptionally broad peak width of ~26% and an intense reflectance peak of 98% at λ = 2.9 μm.

Polyelectrolyte complexes
Polyelectrolyte complexes are the association complexes formed between oppositely charged particles, which are formed by electrostatic interactions between oppositely charged polycions. [55] Concentrated polyelectrolyte complexes have gained widespread attention because of their suitable rheology for DIW process, and have been extensively reported to be used in 3D printing high-precision structures, such as templates, tissue engineering scaffold, and other potential
functional devices.\cite{50,56,57} To make a printable ink composed of the concentrated polyelectrolyte complexes, individual component must be mixed together at a nonstoichiometric ratio and under ionic strength conditions.\cite{58} Jennifer A. Lewis et al.\cite{56,58,57} found that the concentrated polyelectrolyte complexes (with 40-50 wt% polyelectrolyte in aqueous solution) composed of poly(acrylic acid) (PAA) and poly(ethylenimine) (PEI) have an appropriate viscosity (about 5-150 Pa s$^{-1}$) for deposition through microcapillary nozzles. The 8- and 16-layer woodpile structures (the lateral dimensions from 250 μm × 250 μm to 500 μm × 500 μm, and the in-plane center-to-center rod spacings of 2.8 μm and 4.0 μm, and a rod diameter of 1 μm) were printed (Fig. 3a) and the Si hollow-woodpile photonic crystals were prepared by using the above 3D woodpile structures as templates (Fig. 3b).\cite{56} Specially: i) The polymer 3D woodpile structure was coated with a thin silica layer (~100 nm) via a SiO$_2$ chemical vapor deposition (CVD) process at room temperature. ii) Then the woodpile structure was completely removed after thermal treatment, resulting in a SiO$_2$ hollow-woodpile. iii) After a Si CVD process, a thin Si layer (~100 nm) was respectively deposited on the inside and outside of the SiO$_2$ tubular array, resulting in a hollow-woodpile photonic crystal composed of Si/SiO$_2$/Si trilayer coating. Indeed, these hollow-woodpiles polyelectrolyte scaffolds can be printed into arbitrary complex high-precision 3D templates through DIW technology, which has great potential for high-precision 3D printing of materials that cannot directly meet DIW requirements.

**Sol-gel inks**

Sol-gel ink is the most widely used type of ink in the DIW process, because concentrated solutions containing polymers usually exhibit the shear-thinning behavior during sol-gel process.\cite{33} As a result, such inks have widespread scope of application that mainly involves environment,\cite{31} energy,\cite{59,61} and tissue engineering.\cite{31,51,62} Many studies have demonstrated DIW’s ability to print arbitrarily complex 3D structures by using sol-gel inks.\cite{26,63,64} However, the high-precision 3D printing by using DIW process still faces huge challenges. Robert et al.\cite{53} suggested the 3D printing of microperiodic hydrogel scaffolds by utilizing an acrylamide-based sol-gel ink for tissue engineering. The 3D hydrogel scaffolds were composed of 1-μm filaments and 5-μm spaces, which were patterned into the face-centered tetragonal structures (Fig. 4a). Furthermore, the 3T3 murine fibroblast cells experiment exhibited its great application potential in cell culture, separation and screening (Fig. 4b). This capacity to print hydrogel scaffolds with microscale features opens a new avenue for tissue engineering. Additionally, sol-gel inks with 3D network internal structure exhibit the shear-thinning behavior and have good compatibility with DIW technology.\cite{32} therefore, such inks have great potential in 3D printing aerogel. It is worth noting that there is still a certain gap between the precision of the current reports on 3D printing aerogels and the high-precision requirements mentioned here, however, some studies have found that there is a lot of room for improvement in accuracy by carefully adjusting the ink rheology.\cite{32,60} The resulting 3D structure combines the nanostructures of aerogel and the customizable macrostructures of 3D printing, demonstrating a unique multifunctional structure that spans seven orders of magnitude: from nanometers to millimeters.\cite{32,52} The detailed process diagram of DIW 3D printing aerogel is shown in Fig. 5.\cite{31}

### 3.2 Two-photon polymerization (TPP)

Since it was first reported as a technique for microfabrication in 1997, TPP has been widely considered to be able to fabricate 3D micro/nanostructures, and it is favored in the fields of optics,\cite{40} magnetics,\cite{65} and biology.\cite{66} A typical TPP material system consists of:\cite{67} (i) one or the mixture of monomers/oligomers, cross-linking to form the final micro/nanostructures; (ii) photoinitiators, providing the free radicals to induce polymerization; (iii) a solvent. The material system is harsh, because it should have efficient two-photon absorption (TPA) chromophores, as well as be transparent in visible and near infrared (NIR) regions. Here, we cited some

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**Fig. 3** An example of DIW 3D printing of concentrated polyelectrolyte complexes. (a) 3D woodpile structures and (b) 3D Si hollow-woodpile photonic crystals. Reproduced with permission from [56]. Copyright 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
Fig. 4 An example of DIW 3D printing of sol-gel inks. (a) The 3D hydrogel scaffolds and (b) 3T3 fibroblasts plated on hydrogel scaffolds. Reproduced with permission from [51]. Copyright 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

examples of TPP materials suitable for fabrication of 3D micro/nanostructures, including photoresists, protein-based biomolecules, and hybrid materials.

Photoresists
Photoresists are divided into positive-type and negative-type photoresists. For positive-type photoresists, laser beam exposure causes chain scission to shorten units, as a result the exposed areas can be dissolved and washed away in the development stage. The positive-type photoresists, such as AZ 9260 and AZ IPS-6050 (MicroChemicals GmbH), are frequently used to efficiently manufacture hollow structures because processing can be achieved by removing the small parts of the total areas, which are widely used for the preparation of micro/nanoscale 3D templates (Fig. 6).[68,69] For negative-type photoresists, laser beam exposure results in cross-linking and curing of monomer chains, as a result the unexposed areas can be dissolved and washed away in the development stage. Therefore, these photoresists, such as SU-8 (MicroChem), can be used to directly generate 3D micro/nanoscale structures (Fig. 7a).[70]

Fig. 5 The schematic diagram of 3D printing aerogel by using DIW process.
Protein-based biomolecules materials
Proteins have the complex structure composed of 20 different amino acids, and there are many functional groups on their surface (e.g. amino (–NH₂), carboxyl (–COOH), carbonyl (–CHO)), which provides reactive ends capable of chemically joining two or more units. Proteins are type of biomacromolecules, therefore, 3D structures based on proteins shows special biocompatibility. Chan et al.⁷¹ systematically investigated the effects of bovine serum albumin (BSA) protein voxel morphology and fabricated 3D protein microstructures and micropatterns with sub-micrometer features by TPP process, as shown in Fig. 7b. Three square-based piers of micrometer size (4 μm × 4 μm) were prepared, and two nanosized doublelayer suspending bridges (<800 nm width < 800 nm thickness) were interconnected. Besides, other proteins, such as gelatin,⁷² collagen,⁷³ and fibrinogen,⁷⁴ can be also designed to be combined with photoinitiators and crosslinkers for use in bioapplications.

Fig. 6 Examples of positive-type photoresists as 3D templates by TPP. (a) AZ 9260. Reproduced with permission from [68]. Copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) AZ IPS-6050. Reproduced with permission from [69]. Copyright 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
Hybrid materials

Hybrid materials are a class of materials in which multiple elements co-exist within a single phase. This type of materials can be customized to select the added material elements according to the requirements of special application fields, which realizes the flexibility of material selection. For example, Georg et al.\cite{40} prepared a 500 nm period woodpile photonic crystal with feature sizes less than 100 nm by using an organic-inorganic zirconium-silicon composite doped with the quencher 2-(dimethylamino)ethyl methacrylate. And the period woodpile photonic crystal shows clear photonic stop bands in the wavelength region between 450 nm to 1000 nm. Zhong et al.\cite{65} incorporated metal oxide nanoparticles (Fe$_3$O$_4$) into the photosensitive materials, and the minimum average line width varied between 110 nm and 180 nm, the Qingdao University logo, a magnetic hydrogel micro-rod, and a magnetic hydrogel micro-nail were fabricated successfully. Hu et al.\cite{75} combined pentaerythritol triacrylate (PETA) with gold chloride hydrate (HAuCl$_4$·3H$_2$O) to fabricate complex 3D Au-containing nanocomposites with line width as small as 78 nm. The arbitrary complex 3D microstructures prepared include ring structures, interlinked helix structures, ellipse structures, pyramid structures and woodpile photonic crystal structures (Fig. 7c).

3.3 Electrochemical fabrication (EFAB)

EFAB process stands out substantially when 3D micro-components/assemblies depend on complicated 3D microstructures, multiple moving parts, no assembly, and mass production. It has a wide range of applications in monolithically-manufactured micro-devices and the prototyping of integrated systems, which is an ideal technology for mass production of robust 3D metal micro-parts/micro-devices composed of multilayers with thickness of single layer from 2 to 25 μm. Since it was developed by Adam Cohen et al., EFAB technology has become the trademark of Microfabrica Inc. (formerly MEMGen Corp).\cite{15}

The suitable materials for EFAB process should be metal or metal alloys with excellent electrical conductivity.

There are typically three structural materials developed by Microfabrica Inc., including Valley-120, Edura-180, and Palladium.\cite{16,76,77} Valley-120 is a nickel cobalt (Ni-Co) alloy, which is used as a primary structural material due to its good compactness, corrosion resistance, great mechanical properties and short-term biocompatibility. Edura-180 is an electroplated rhodium (platinum (Pt) group metal) formulation,
which is widely used in the field of medicine and electronics owing to its sufficient biocompatibility, excellent mechanical properties, and great corrosion resistance. Palladium is also the noble platinum (Pt) group metal, which serves as excellent biocompatibility. The most common sacrificial material is copper (Cu), which can be selectively etched relative to the structural materials.[16] In addition, the electroplating solutions need to be specially prepared according to the used materials. Other additives, such as adhesives, buffer solution, and anti-pinhole agents also need to be introduced to enable the electrodeposition process to proceed.[77] Microfabrica Inc. gave many examples of 3D micro-devices manufactured with EFAB technology, including transformers, helical inductors, variable capacitors, two-axis mirrors, micro-combustors, toroidal inductors, hybrid couplers, and medical devices.[17,78,79] Their overall sizes are a few millimeters, and they are composed of many layers with a layer thickness in the range of 2 to 25 μm, which can realize integration of complicated 3D microstructures, multiple moving parts, and without assembly.

4. Challenges and future trends

4.1 Direct ink writing (DIW)

Up to now, the precision of most reported 3D-printed structures by DIW process is still in the order of tens of microns and hundreds of microns, although a few have high precision of sub-micron to several microns. The most fundamental reason is that the use of microneedles (with an inner diameter of a few microns or below) is limited by the ink formulation. Therefore, the development of novel ink formula that has suitable rheology for ease of microneedle extrusion is the key to the printing of high-precision 3D structures. However, most of the inks that meet the requirements of microneedle extrusion have a low viscoelastic modulus (for example, storage modulus: $G' < 10^5$ Pa), and the direct extrusion of these inks via microneedles may lead to poor formability. The key to addressing this challenge is to achieve rapid solidification of inks after extrusion. Thanks to the flexibility of DIW process, some additional strategies combined with DIW process are adopted to address this challenge, such as heat treatment,[55] deposition reservoirs,[57] catalyst atmosphere compensation,[31,80] UV assists,[81] and supramolecular templates,[82] which may give a novel route to the high-precision 3D printing technology in the future. The volume shrinkage caused by the temperature change after solidification also helps to further improve printing resolution to a certain extent.[32,82] However, this accessibility to high resolution depends on material itself. The volume shrinkage either leads to a denser structure, enhancing its mechanical properties, or causes new cracks in structure, causing an opposite side. In addition, the development of the finer microneedles that can withstand high squeezing force will greatly help improve printing resolution. Most recently, 3D-printed aerogels[36,31,32] using DIW technology have received wide attention due to the combination of hierarchical nanoporous aerogels and customizable periodic 3D printing, while getting rid of the mold dependency. At the same time, DIW 3D printing hydrogel flexible material[83] and shape memory polymer material[84] will have great demands in many fields such as soft robots, intelligent devices, and biomedicine.

4.2 Two-photon polymerization (TPP)

Although several studies have reported that fabricated features as small as 100 nm can be obtained by using this technology. However, the resolution limit highly depends on the material system and the laser system. The size of individual voxels is controlled by the photopolymerization materials, the power and scan speed of the laser writing beam. Efforts need to start from above-mentioned aspects in order to obtain the higher resolution. Highly efficient photoinitiators and monomers/polyimers with large TPA cross-section and high photoinitiation efficiency will significantly improve printing resolution.[90,91] The photopolymerized material must have sufficient hardness to maintain a finer 3D structure itself. And sufficient stability to cope with the volume shrinkage caused by change from monomer to polymer is also essential, which significantly improves the printing resolution. At the same time, the precise control of printing parameters such as laser power, processing speed, hatching, and slicing distance to match the appropriate material systems is also essential. Another critical issue of TPP is the processing time. The serial point-by-point scanning mode has a serious negative impact on processing period, which dramatically impedes its widespread use in various applications, especially involving larger structures or mass production. Rapid processing methods should be developed for the industrial mass production. Some preliminary rapid processing methods, such as projection-based hierarchical parallelization through spatial and temporal focusing ultrafast laser,[85] and parallel TPP processing and shot exposure processing by spatial light modulator (SLM),[86-88] have emerged, which are valuable for improving the throughput of TPP process. Furthermore, most studies on TPP are limited to the radical-initiated polymerization of acrylates. And most of the TPP materials suitable for 3D micro/nanoscale structures are proprietary materials, it is difficult to modify to add active components for customized functionality. Particularly, continuous progresses in protein-based biomacromolecules are expected to realize 3D mimic complex structures that can replace the organism's own tissues or organs. Additionally, printing objects or structures that contain inorganic components and have microstructures on the order of several nanometers (which can reduce the weight of structural parts) are also advantageous. Therefore, hybrid materials with flexible selectivity and customized functional diversity also have important research value for special fields.

4.3 Electrochemical fabrication (EFAB)

The design freedom of additive manufacturing (AM), coupled with the high precision and mass production of semiconductor manufacturing, makes EFAB an unprecedented innovative
technology that has an ability to mass manufacture millions of high-precision components without assembly. There are multiple independent sub-processes in EFAB process, including structure layering, instant masking fabrication, electrodeposition, planarization, and etching.\(^{[15,16]}\) As a result, EFAB technology relies on the perfect integration of these multiple independent sub-processes, and its complexity increases with the increase in the number of layers manufactured. Especially when manufacturing single micro-components, multiple independent sub-processes make EFAB inefficient and costly, which brings huge challenges to laboratory research. Therefore, this technology is usually used to prepare millions of micro-devices in batches to compromise processing costs.\(^{[15]}\) The unique layer-by-layer manufacturing mode poses huge challenges to the inter-layer alignment, especially for the preparation of high-precision planar geometry for each layer. Additionally, layer-by-layer manufacturing mode also produces anisotropic mechanical properties. The structural designs need to consider the stability of 3D structures and the full entry of etching solvents (e.g. a hollow sphere with etching access hole). Two keys to improving resolution are involved. One is to minimize the layer thickness, which depends on the precise control of planarization process and the precise positioning of each layer. The other is to minimize the single-layer geometry, which comes from the micro-holes/channels formed by the photolithography process. EFAB technology has an unprecedented ability to manufacture arbitrarily complex 3D metal micro-devices, especially the preparation of micro-devices with multiple moving parts suitable for surgical operations and MEMS devices.\(^{[16,77]}\) In the future, research aimed at these challenges will have a breakthrough in improving the efficiency, quality, and resolution of EFAB process. Furthermore, the development of EFAB process requires the investment of time and resources. Therefore, further development will depend on technological breakthroughs and application opportunities.

5. Conclusions

High-precision three-dimensional (3D) printing has become a truly disruptive force in many industries. Many high-precision 3D printing technologies up to now have been developed to respond the demand for fabricating the arbitrary, complex, and high-precision 3D microstructures. This paper presented a review on the promising high-precision 3D printing technologies, including direct ink writing (DIW), two-photon polymerization (TPP), and electrochemical fabrication (EFAB), that are being used to fabricate arbitrarily high-complexity truly 3D microstructures with a resolution of a few microns or below, as well as in a relatively flexible, low-cost and versatile way. The materials suitable for the preparation of high-precision 3D microstructures and their applications have been highlighted separately for each high-precision 3D printing technology. Some challenges and future trends are also raised in this review. High-precision 3D printing provides a facile route to fabricate the arbitrary, complex, and high-precision 3D microstructures. Most notable of all, these promising high-precision 3D printing technologies open up a new route for 3D microstructures with arbitrary design and microscale in a relatively flexible, low-cost and versatile way.

Acknowledgements

Thanks for the support of the National Key Research and Development Program of China (2017YFA0204600) and the National Natural Science Foundation of China (11874284).

Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

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584, 387-392.


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