

## Recent advancements and applications in 3D printing of functional optics

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## ABSTRACT

Various kinds of optical devices have been designed for unique functionality based on a deeper understanding of optical principles. Recently, the research of functional optics has become a hot topic due to their wide usage in diverse fields. However, the structural complexity and multi-material distribution of advanced optical devices far exceed the fabrication capability of traditional manufacturing techniques, which inevitably hinders the further development of functional optics for various promising applications. As a revolutionary advanced manufacturing technology, additive manufacturing (AM) has demonstrated its potential to produce multi-material, multi-scale and multi-functional optical devices for excellent performance in imaging, sensing, displaying, and light modulating. Here, recent achievements in additive manufacturing of functional optics including lens, optoelectronics, photonics, and metamaterials were reviewed. The investigation covers the design scenarios, material selection, 3D printing strategies, and property evaluation. Current challenges, prospective research topics, and future promising applications of 3D printing of next-generation functional optics are discussed at the end.

## 1. Introduction

Optics is an important branch of science that studies the generation, propagation, and display of electromagnetic radiation in a wide range of wavelengths ranging from terahertz wave, infrared, visible light, to ultraviolet, as well as the interaction with matter [1,2]. The instruments that produce, manipulate, and detect light are optical elements. The newly developed functional elements enable the functionalities such as illuminating, sensing, coloring, and displaying to be directly embedded in the casing or mechanical structure of an interactive device [3]. Thus, common mechanical movements such as sensing displacement, push, pressure, rotation, linear movement, and acceleration can be detected [4,5]. For example, digital holography for displaying and recording optical information has numerous potential applications in microscopy, 3D tomographic imaging, 3D reconstruction of the biological structure of biological structures and more [6]. Tangible objects are used to extend the display and interaction areas of the desktop, touch screen, and interactive interface through fiber optic bundles [7]. Benefiting from these functional optical elements, large-area displaying, flexible

optical sensing, novel illuminating, and other optical electronics embedding can be realized and implemented in high-fidelity, high-response, and highly customized interactive devices [3]. However, functional optical devices are cost-intensive and impractical to produce through traditional manufacturing methods due to the requirements of high precision, micro-scale and high integrity. Besides, the reproducibility and customization of quality and size cannot be guaranteed.

Optical materials change the direction and phase of light by means of refraction, reflection, transmission, and etc., under the influence of external fields (light, electric and magnetic fields, sound, temperature, pressure, etc.), so that light can be transmitted according to predetermined requirements, or absorbed and transmitted through a certain wavelength range, thereby changing the intensity and spectrum of light to achieve the purpose of detection, modulation and energy conversion [8,9]. The optical materials include polymers, metals, ceramics, and nano-composites [10]. The polymers are mainly used for optical applications such as windows and lenses, as they have a wide range of transparency with a refractive index between 1.3 and 1.75 as shown in Fig. 1a. Polymer optics can be produced with the material such as Polycarbonate, Styrene, CR-39, or Zeonex E48R by embossing, die

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Nomenclature			
AM	Additive manufacturing	SPPs	Spiral phase plates
PMMA	Polymethylmethacrylate	THz-TDI	Terahertz time-domain imaging
DIW	Direct ink writing	FDM	Fused deposition modeling
SLA	Stereolithography	UV	Ultraviolet
SLS	Selective laser sintering	LED	Light emitting diode
TPP	Two photon polymerization	DLW	Direct laser writing
MLAs	Microlens arrays	SLM	Selective laser melting
RMS	Root mean square	LIFT	Laser induced forward transfer
THz	Terahertz	PDMS	Polydimethylsiloxane
NA	Numerical aperture	PμSL	Projection micro-stereolithography
DLP	Digital light processing	GRIN	Gradient refractive index
M/NLAs	Micro/nano lens arrays	CA	Contact angle
FF	Fill factor	E-jet	Electrohydrodynamic inkjet printing
FOV	Field of view	SEM	Scanning electron microscopy
MTF	Modulation transfer function	LCP	Laser catapulting
IR	Infrared	CMOS	Complementary metal-oxide-semiconductor
MBD-MA	Methacrylic derivative of 7-nitrobenz-2-oxa-1,3-diazole	LD	Laser diodes
SMF	Single-mode fiber	PLA	Polylactic acid
EBP	Extrusion-based 3D printing	SMF-LP	Single-mode fibers-lens-periscopes
poly-TPD	Poly[N,N'-bis(e-butylphenyl)-N,N'-bis(phenyl)-benzidine]	QD	Quantum dot
AgNP	Silver nanoparticle	CdSe/ZnS	Selenide/zinc sulfide
PCL	Polycaprolactone	PEDOT:PSS	Poly(ethylenedioxythiophene): polystyrene sulfonate
EGBE	Ethylene glycol butyl ether	EGaIn	Eutectic gallium indium liquid metal
CPC	Compound parabolic concentrator	SCs	Solar cells
BCP	Block copolymers	ABS	Acrylonitrile butadiene styrene
RLP	Resonant laser printing	PIC	Photonic integrated circuit
PCB	Printed circuit board	OVD	Optical variable devices
TE	Transverse electric	CdS	Cadmium sulfide
		TM	Transverse magnetic
		HDDA	1,6-Hexanediol diacrylate
		OAM	Orbital angular momentum

casting or injection molding processes [11]. Although these methods have the capability of mass production, it is relatively difficult to accurately control the temperature, injection pressure, and injection speed during the manufacturing process [12]. Metals, such as aluminum, copper, gold, and silver, exhibit high reflectance, and various metals are used to fabricate optical substrates or mirrors (Fig. 1a and b). For example, electroless nickel are usually coated on the surface of optical devices to reduce reflection losses and increase optical damage thresholds [13]. In terms of ceramics, the glass-like fused silica glass (SiO<sub>2</sub>), soda-lime-silica glass, sodium borosilicate glass and lead-oxide glass are frequently used to make optical devices such as telescopes, microscopes, and binoculars [10]. The raw glass shows low reflectance and high emissivity value (Fig. 1b), and the production of glass must be carefully and strictly controlled to ensure its purity and the pre-set parameters to meet the desired characteristics [10]. Nano-composites have been successfully fabricated in bioinspired structures with improved mechanical and electrical properties [14–17]. Bioinspired nano-composites can also be embedded into optical substrates to enhance the optical performances such as high refractive index and high transparency [18]. By integrating nano-composites, such as ZrO<sub>2</sub> nanoparticles [18], ZnO nanoparticles [19], Sol-gel organic-inorganic composite [20], and etc., into polymer or ceramic matrix materials, optical properties of optical devices, including absorption, fluorescence, and wide range refractive index, can be improved dramatically [21]. More nanocomposites with excellent optical performance are still needed to be studied and further applied to practical production.

There are many problems such as time-consuming, labor-intensive, and material-wasting, in the fabrication of optical devices using traditional manufacturing approaches. Additive manufacturing (AM), which is also known as 3D printing, is an emerging manufacturing technology with advantages such as high dimensional accuracy, structural

complexity, cost-effectivity, flexibility, consistency, and risk reduction. Currently 3D printing technologies are widely applied in the fabrication of optical devices on different scales using optical materials (Fig. 1c) [22]. For example, fused deposition modeling (FDM) is one of extrusion based printing techniques in which an object is built by melting and pulling out thermoplastic filaments through a nozzle and further depositing material layer by layer to get the final shape [23]. Thermoplastic polymers and nanocomposites, such as polymethylmetacrylate (PMMA), polyethylene, polypropylene are widely used to fabricate microwave and terahertz lenses by using such FDM printing process [24]. PolyJet 3D printing is developed based on the ink jetting, where liquid photopolymers are dropped and cured by ultraviolet (UV) light. Instead of being limited to planar shape, optical devices (such as waveguides, and photonic crystals) with complex 3D structures can be successfully fabricated using PolyJet with photocurable materials [25,26]. Direct ink writing (DIW) is another ink-based technique, where ink can be extracted from a nozzle like a fluid due to the low viscosity with applied shear stress. Since it works at mild ambient temperatures and without drastic chemical reactions, light emitting diodes (LEDs), photonic crystals, and optical windows can be produced using DIW with acrylates, epoxies, conjugated polymers, and conductive inks [27]. In stereolithography (SLA), the ultraviolet light beam is focused on the surface of the liquid photopolymer resin, and whole layer of optical material can be solidified after one time exposure [28–30]. SLA enables the fabrication of optical devices like microlenses, optical sensors, and meta-materials with sophisticated microstructures using photocurable acrylates, epoxides, ceramic slurry, and nanocomposites [23]. Direct laser writing (DLW) uses nonlinear multi-photon absorption induced by ultrafast laser pulses to further increase the resolution of SLA based 3D printing, and it offers a high spatial resolution (<1 μm with two-photon polymerization). Many optical components, including microlens arrays,

objective lenses, shafts and optical sensors, can be produced by DLW due to its high precision [23]. Selective laser sintering (SLS), where the powder is piled up layer-by-layer and laser is performed to sinter powder to form 3D structures. Metal powders, polymer powders and ceramic powders can be used in SLS to fabricate diffractive terahertz band (THz) lenses, Fresnel, and fractal lenses. 3D printing optical devices can break through the limitations of traditional planar patterning methods, making it possible to fabricate micron-scale 3D helical structures, photonic crystals, beam-driven submicron probes and confocal imagers [23]. 3D printing has the advantage of nearly unbounded design freedom coupled with the capability to be manufactured in a continuous process with additional flexibility of materials to be directly printed on a variety of substrates resulting in a functional, ready to use component [31,32].

This article aims to provide a view of recent progress of 3D printing of functional optics. The most promising approaches are reviewed, with focus on ready-to-use optical materials, traditional optical fabrication process, additive manufacturing process and applications of fabricated optical devices. 3D printed materials and structures related to optical applications are presented, such as multiscale lenses, optoelectronics, photonics and metamaterials (Fig. 2). In the last section, current status, outstanding advantages, solvable drawbacks, and promising perspectives of 3D printing technologies for functional optics are presented and discussed.

## 2. 3D printing of optical lens

3D printed optical lenses with diameters ranging from the macro-scale ( $>1$  mm) to the nanoscale ( $<1$   $\mu$ m) in addition to the direct printing of multi-scale objectives on optical fibers have unprecedented potential in the realm of optics and related applications. However, the fabrication of high-quality optical components requires sub-nanometer

features with good surface control to ensure desired optical performance and well-established fabrication methods, such as precision injection molding [33] and micro-precision machining [34] are both time-consuming and costly processes to achieve these requirements. 3D printing technologies have recently evolved beyond rapid prototyping, becoming an attractive tool for the fabrication of industrial-quality optical components that are lightweight, complex, and cost-effective [35]. Previous works have demonstrated that 3D printing of optical lenses using two-photon polymerization [36], ink-jet printing [37], micro-stereolithography [38], direct ink writing [39], and laser-induced forward transfer [40] can overcome current limitations in conventional fabrication methods. Particularly, freeform optical surfaces and microlens arrays (MLAs) have numerous functionalities including imaging, illumination, and beam-shaping technologies, but enabling such optics is limited by the ability to design, fabricate and test such surfaces [41,42]. Recent improvements in 3D printing technologies, allowing highly controlled surface morphologies with sub-100 nanometer resolution, providing simple solutions for printing optics, refractive and diffractive elements, and integrated optical systems, opening possible applications otherwise unachievable [43]. This section reports on current progress of 3D printing technologies and their advantages over current fabrication methods on the fabrication of optical lenses ranging from nanoscales to macroscale.

### 2.1. 3D printing of macroscale lens

3D printing technologies have demonstrated the capability to create a variety of freeform optical components with submicron features and good optical performance [22]. Two parameters that are of crucial importance in manufacturing high-quality optics are dimension accuracy and surface smoothness. In recent works, femtosecond DLW has

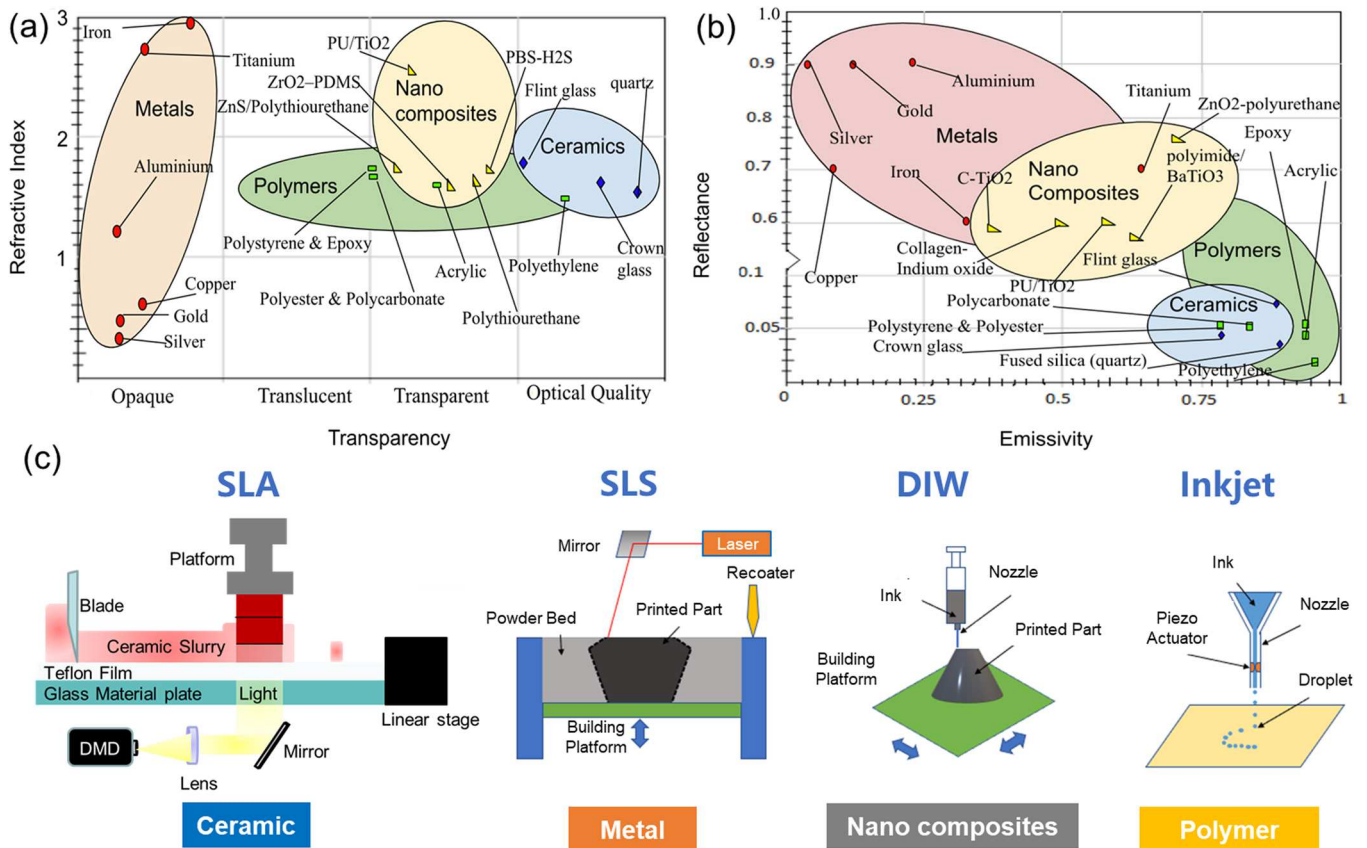
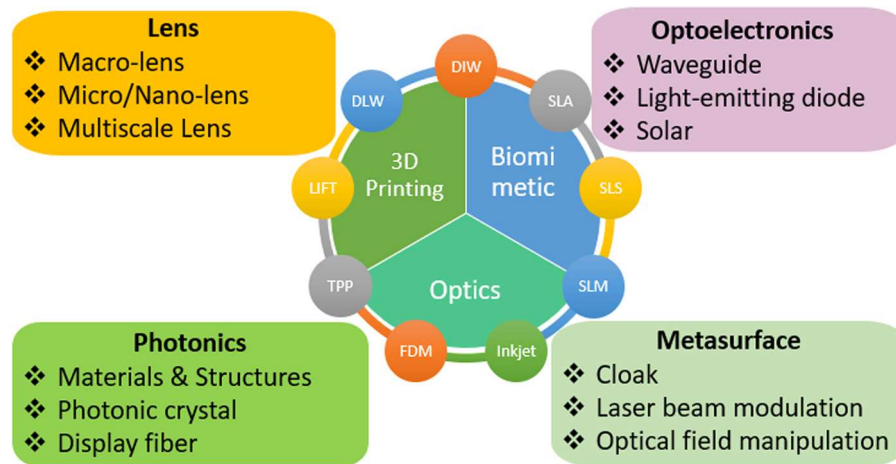


Fig. 1. Optical properties of the material and relevant 3D printing processes for the fabrication of optical components. (a) Refractive index vs transparency; (b) Reflectance vs emissivity; and (c) Schematic diagrams of the most common 3D printing technologies for the fabrication of optical material.



**Fig. 2.** Overview of 3D printing of functional optics; 3D printing of (1) optical lens for imaging (Section 2); (2) optoelectronics for sensing (Section 3); (3) photonics for colorful display (Section 4); and (4) optical metamaterial (Section 5).

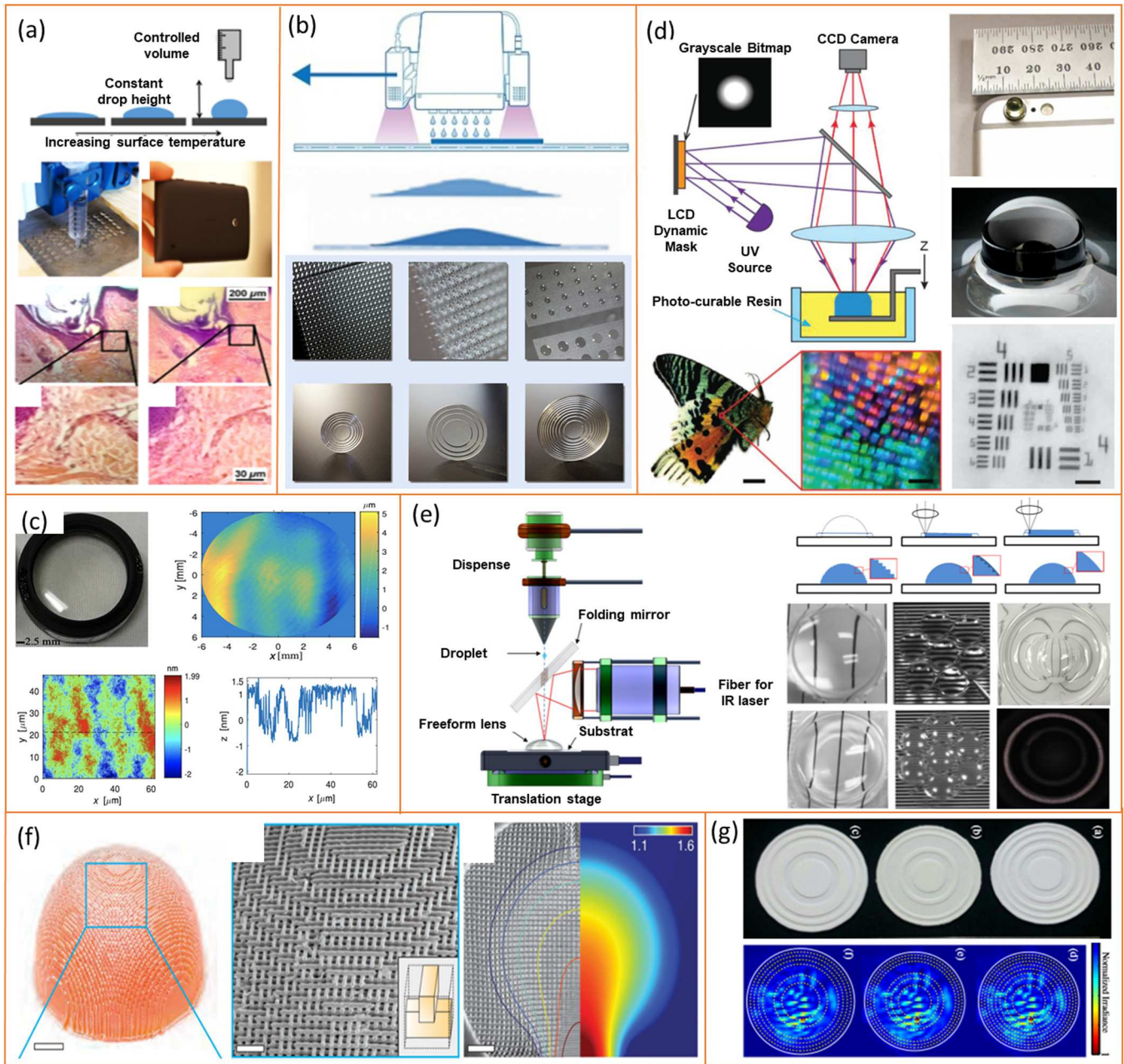
exhibited the required nanoscale resolution, using ultra-short bursts of laser radiation to obtain subwavelength (less than that of visible light) surface smoothness and sub-voxel ( $<100$  nm) accuracy [44]. However, this bottom-up 3D printing technique is limited in producing macroscale optical components due to the direct addition of nanoscale voxels which can be both expensive and time-consuming when printing customized lenses with diameters larger than 1 mm. Therefore, a noticeable trade-off exists between voxel precision with desired surface roughness and the fabrication speed for millimeter scale optical lenses. Recently, the use of polydimethylsiloxane (PDMS) as an optically transparent constituent for macroscale lenses over commonly used photoresists has become an attractive material for the use of drop-on-demand 3D printing to generate complex surface morphology required for excellent optical performance. For example, Sung et al. developed a hanging droplet inkjet printing process with a heat-assisted substrate that exhibited controlled surface morphology of the 3D printed lens with achievable imaging resolution of  $1\ \mu\text{m}$  when applied to a smartphone camera, being able to clearly resolve skin cells and human hair when compared with a traditional microscope (Fig. 3a) [45]. Higher temperatures accelerate the curing process of the PDMS lens, which provide promising advantages in the realm of 3D printed optics. The customization of focal length, lens diameter, and contact angle can be achieved based on the temperature of the substrate and sequential addition of droplets. Another approach was developed by Luxexcel 3D printing technologies as a solution to the strict tolerances of high transmissivity and design customization, necessary for ophthalmic laboratories, by developing an inkjet 3D printer that deposits tiny droplets of UV-curable resin (photoresist) that form smooth surfaces via fluid flow and merging before curing in to 3D lenses (Fig. 3b) [46]. Additionally, the post-manufacturing technology can apply anti-reflective, UV, and hard coatings to the lenses thus enhancing their optical and mechanical performance [46]. Furthermore, Assefa et al. optimized the shape, surface roughness, and optical performance of a 3D printed centimeter-scale lenses, through an iterative process of wavefront error readings to correct for surface profile deviations, using the Luxexcel Printoptical technology with an aperture of  $\sim 12$  mm [47]. As shown in Fig. 3c, the fabricated lenses exhibited an root mean square (RMS) roughness of  $0.9 \pm 0.3$  nm and optical performance of  $143.7\ \text{lp mm}^{-1}$  using a green band-pass filter [47]. Currently, the fabrication is capable of printing 4–8 lenses per hour which showcases vast advantages for rapidly printing high-quality industrial-grade optics, overcoming the wasteful and costly drawbacks of conventional fabrication methods using grinding or polishing [46,47].

Alternative methods for rapid production of macroscale lenses have been realized through projection micro-stereolithography (PμSL) which

utilize UV-curable photoresist material in a layer-by-layer building process facilitated. Chen et al. demonstrated the use of synergistic effects between PμSL and meniscus equilibrium post-curing to obtain optically smooth surfaces, corresponding RMS of 6.8 and 5.8 nm for the center and peripheral regions of the lenslet, and sub voxel accuracy for customized aspherical lenses resulting in significantly faster fabrication speeds of  $24.54\ \text{mm}^3\ \text{h}^{-1}$  [48]. Advantages in nano-feature structures led to excellent optical performance, integrating the lens to a smartphone obtained microscopic images of a sunset moth's wings (Fig. 3d) [48]. Moreover, Hong et al. devised a modified 3D printing approach that uses a pulsed IR-laser to thermally cure optical silicones into free-form optics using a hybrid method of layer-by-layer and drop-on-demand processes to create plano-convex, plano-concave, and a freeform donut lens with surface roughness  $< 20$  nm and imaging resolutions of  $36\ \text{lp mm}^{-1}$  (Fig. 3e) [49]. Freeform optics using optical silicones show several advantages such as strong UV-stability, non-yellowing, and high transmission compared to UV-curable material, making them suitable for application in LED lighting and optical imaging [49].

The THz in the spectrum of electromagnetic radiation is becoming one of the most important regions due to unique adsorption fingerprints, which can characterize molecular vibrational modes and provide valuable information otherwise not accessible in other frequency bands. Although the THz regime is still in its infancy, 3D printed modified THz gradient refractive index lenses (GRIN) with scalable features and index variation is in advancing the capabilities and optical applications of the THz frequency band. For example, Zhou et al. fabricated a highly accurate modified Luneberg GRIN lens using PμSL that possessed a continuous index from 1.1 to 1.64 using “woodpile” like structures that could achieve resolutions close to the diffraction limit of 0.4–0.6 THz (Fig. 3f) [50]. In comparison to previously mentioned optical lenses, THz optics can be manufactured from a multitude of plastic materials but similarly require tight tolerances necessary for high quality imaging. Besides, diffractive THz lenses have recently been proposed to exhibit comparable or even higher performance in controlling THz waves. For example, diffractive THz lenses, Fresnel, fractal, and Fibonacci, were fabricated using SLS with polyamide granular powders as the base material, achieving functionality at 0.625 THz (Fig. 3g) [51]. These works achieved superior control of THz wave trajectories, which has been previously considered to be difficult, enabling integration of compact THz optics for future applications in THz frequency imaging. Overall, these studies show vast improvements in the fabrication of customized spherical, aspherical, and freeform macroscale lenses with adjustable focal length, complex geometries, and multiple functionalities using 3D printing technologies with time-efficiency and low-cost.





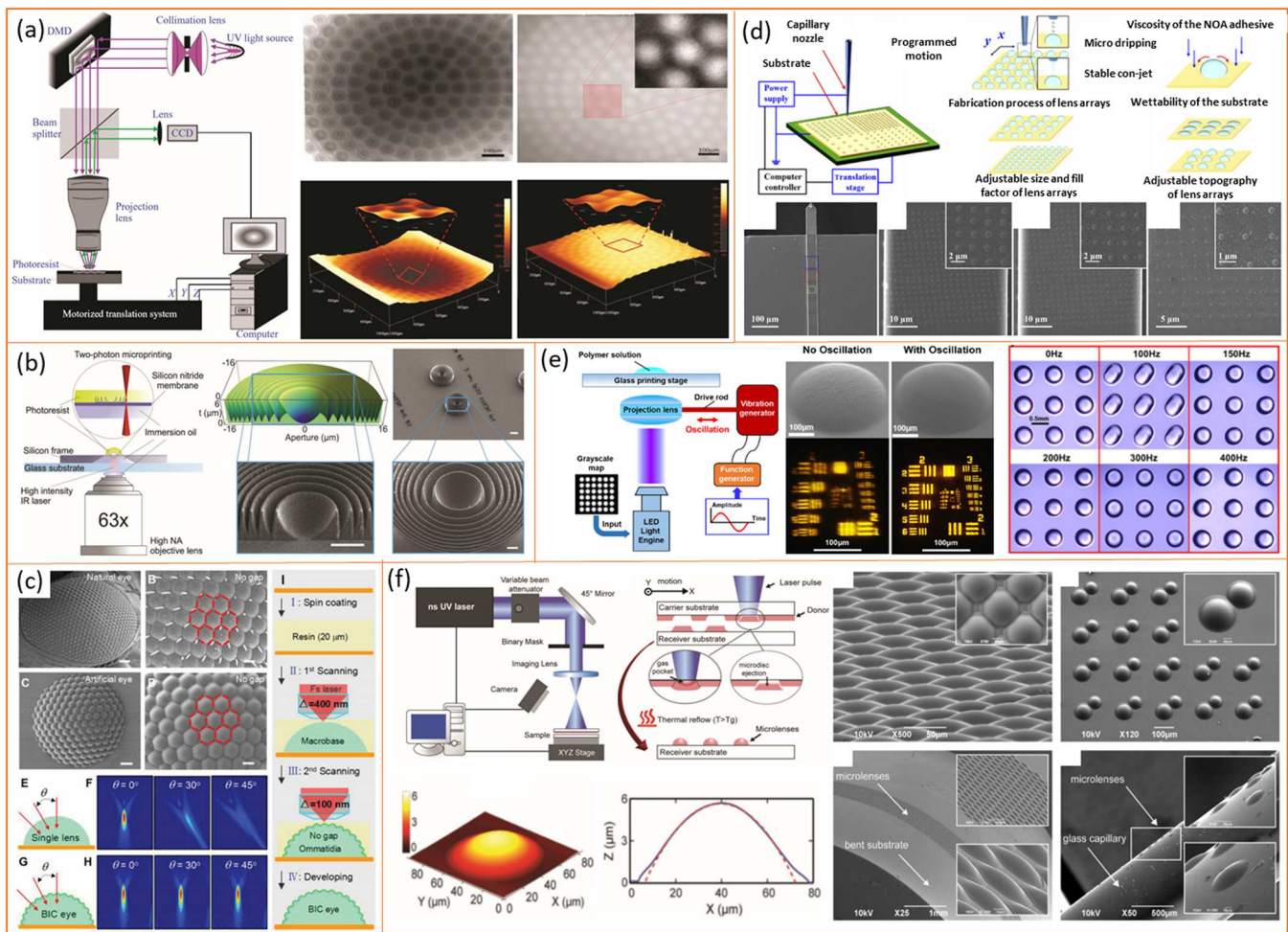
**Fig. 3.** 3D printing and imaging of macroscale lenses. (a) Schematic of the fabrication of lens using inkjet printing process, and application of lens to a smartphone capable of microscopic imaging of human skin and hair follicle; Copyright from Ref. [445]. (b) Luxexcel printing technology shown with optical lens arrays and Fresnel lens; Copyright from Ref. [446]. (c) 3D printed lens with optical microscopic measurements of the surface profile; Copyright from Ref. [447]. (d) The printing process of lens using PuSL and the focusing image of fabricated lens; Copyright from Ref. [448]. (e) Hybrid process of inkjet-DLW to fabricate plano-convex, plano-concave, and donut shaped lenses; Copyright from Ref. [449]. (f) THz optical lens with SEM images of woodpile design to generate gradient refractive index; Copyright from Ref. [50]. (g) Fresnel lens manufactured using SLS and their respective normal irradiance. Copyright from Ref. [51].

## 2.2. 3D printing of micro and nanoscales lens

MLAs have become a staple in the world of optics with applications ranging from beam shaping [52], optical tweezers [53], and integral imaging [54]. Traditionally, MLAs are planar structures and there are a lot of drawbacks in the fabrication of MLAs using methods such as diamond milling and soft lithography. For example, diamond milling process is the point-to-point method, leading to low time-efficiency in the fabrication of MLAs at the cost of required precision. Recent studies have been proposed to fabricate high-quality optics using 3D printing with faster fabrication speeds and lower material costs, leading to improved accuracy of micro and nano features. Particularly, customized

lenses with steep gradients, highly controlled surface roughness, and complex microstructures, which are hard to produce using traditional manufacturing technologies, can be successfully built by using advanced 3D printing technologies.

For example, double grayscale maskless lithography, using two 3D energy profiles and spatial light modulators as a digital mask, was developed to fabricate highly precise curved MLAs with 138 surface lens lets on a  $1024 \mu\text{m} \times 768 \mu\text{m}$  spherical surface (Fig. 4a) [55]. The surface roughness and focal length of fabricated PDMS MLAs were 10.4 nm and 11.6  $\mu\text{m}$  respectively, thus exhibiting good optical performance [55]. The PDMS cured MLA inherently suffers from undesired deformation of the microstructures during the replication process that lead to unwanted



**Fig. 4.** 3D printing of micro/nanoscale lenses. (a) Double gray-scale maskless printing set-up with two different energy profiles and fabricated curved MLAs; Copyright from Ref. [55]. (b) TPP printed Kinoforms with sub-wavelength features; Copyright from Ref. [56]. (c) 3D printing of curved MLAs using two stage scanning of TPP technologies to create eye lens; Copyright from Ref. [57]. (d) E-jet printing of micro/nanoscale lens with adjustable surface profile via changing wettability and viscosity of printing material; Copyright from Ref. [58]. (e) MLAs with modified geometries with increasing frequencies fabricated by DLP using oscillation generators; Copyright from Ref. [59]. (f) SEM images of MLAs on bent, curved, and flat substrates fabricated by 3D LCP method; Copyright from Ref. [60].

distortions and surface profile deviations [55]. Despite these deviations, the demonstrated fabrication shows several advantages to creating curved microstructures which can be widely applied to biosensors, optical fibers, and photon collection [55]. DLW and multiphoton polymerization are some emerging technologies for the fabrication of MLAs with complex structures. For example, a kinoform, a perfect phase-shifting lens, was fabricated using DLW to generate high-quality parabolic surfaces and nanoscale features that could focus up to 100% of incoming X-rays (Fig. 4b) [56]. Moreover, in the work on the replication of biological compound eyes, a fabrication concept that precisely defined smaller voxels with optical smoothness of  $\sim 2.5$  nm at the peripheral regions of the microlenses while larger voxels at the base of the structure were put forward to reduce the overall fabrication time to less than 10 h (Fig. 4c) [57]. Moreover, inkjet printing has been demonstrated for the direct addition of UV-curable adhesives to numerous substrates with good flexibility of optical parameters, focal length and numerical aperture (NA), and homogeneities of lenses [58]. These critical parameters depend on the wettability of the substrate and viscosity of the droplets in controlling the overall surface morphology and contact angle (CA) of the lens. Zhou et al. demonstrated an electrohydrodynamic inkjet printing (E-jet) to fabricate microscale and nanoscale lens arrays, with average diameters ranging from  $64 \mu\text{m}$  to  $120 \text{ nm}$ , with excellent optical performance on an atomic force microscopy cantilever using a stable cone-jet printing mode (Fig. 4d) [58]. Through precise control of

several parameters, including tip diameter, voltages, printing time, wettability, and viscosity of adhesives, the optical performance of M/NLAs can be further optimized to achieve super resolution imaging for flexible optics and large-scale nano meta-lenses.

Recently, researches have focused on investigating 3D printing technologies for the mass production of MLAs with superior optical performance requiring compactness with good shape fidelity. One such approach is digital light processing (DLP) assisted by mechanical oscillations to print concave and convex MLAs with surface roughness of about  $1 \text{ nm}$  and imaging resolution of  $1.639 \mu\text{m}$  linewidth in a single light exposure (Fig. 4e) [59]. Single grayscale patterns are projected onto a glass printing stage that contains the uncured photoresist, typically on the order of  $1\text{--}3 \text{ s}$ , coupled with a linear vibration generator which oscillates the projection lens diagonally, MLAs with excellent shape accuracy and smooth surface profiles were successfully fabricated under  $200 \text{ Hz}$  oscillation [59]. Although this study presents one advantageous route for mass fabrication of MLAs, the performance of MLAs in optoelectronics and photon collection efficiency is limited by its fill factor (FF). Besides, a novel approach named 3D laser catapulting (LCP) method, like laser induced forward transfer, exploits high-energy laser pulses to transfer polymeric material on to a donor substrate in the form of microdiscs, and then followed by a thermal reflow process above the glass transition temperature to build plano-convex MLA (Fig. 4f) [60]. Due to a high spherical morphology, MLAs fabricated through LCP

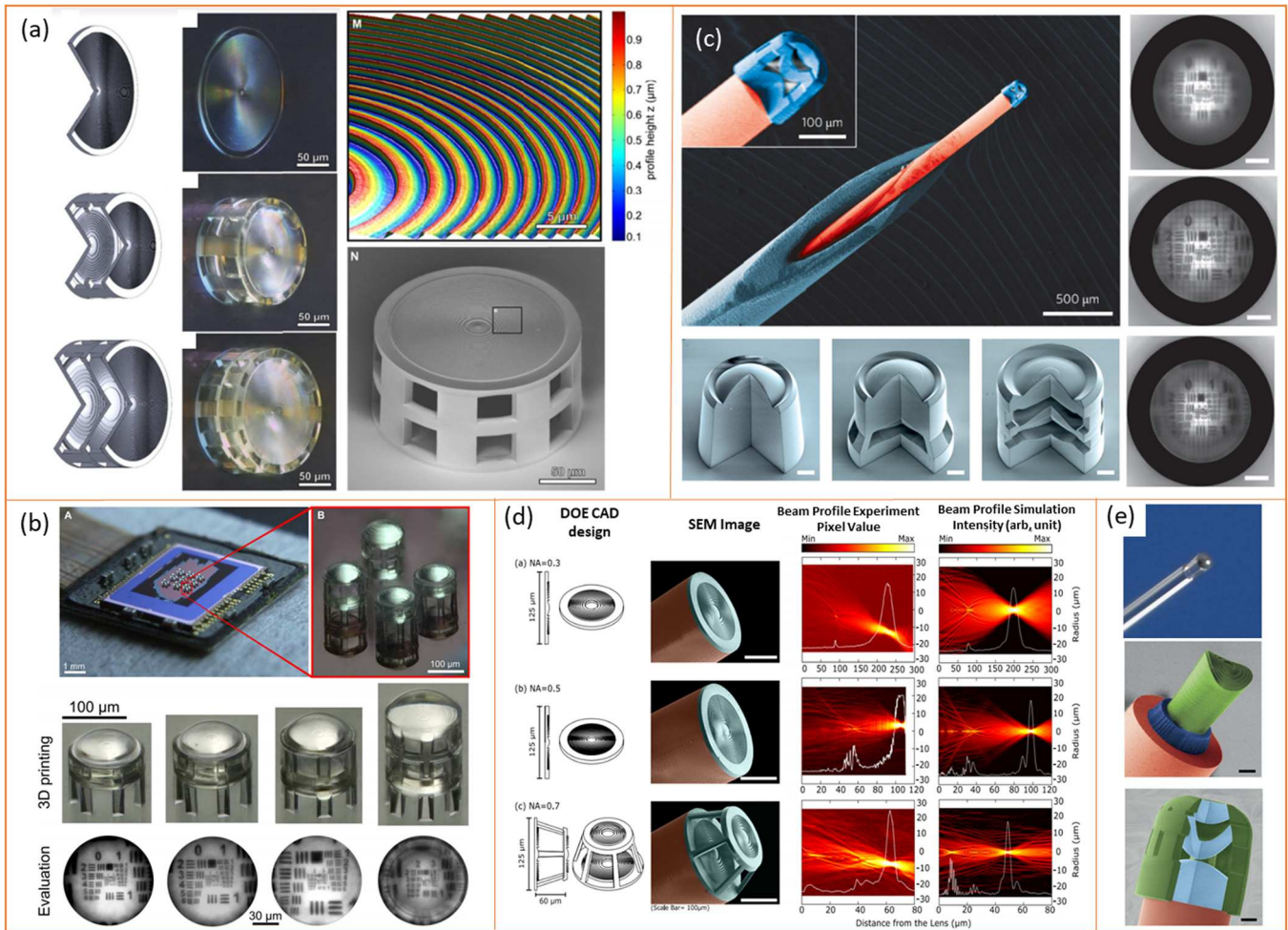


exhibit low aberration and surface roughness, resulting in functionality for imaging and microscopy application, thus providing great advantages over conventional fabrication methods [60]. 3D printing provides unprecedented design flexibility through cost reduction and rapid manufacturing. However, challenges still exist in the implementation of commercially available MLAs via 3D printing technologies for high throughput microscopy components and industrial grade optical components. Therefore, further investigations should focus on formulating new materials for the fabrication of MLAs to enhance additional functionality by increasing durability, robustness, and damage resistance. Besides, integration of post-processing, such as sintering, and addition of infusing silica nanoparticles, carbon or ceramic coatings, could unlock unique applications in the field of optics.

### 2.3. 3D printing of multiscale lens

Multi-aperture or compound lenses fabricated through 3D printing are advantageous over traditional fabrication methods, such as nano-imprinting or micromachining. Because microscale optical devices such as hybrid free-form optics, refractive-diffractive components or Fresnel lenses can be directly printed on optical fibers, highly complex optical systems with superior resolution can be created using 3D printing in a single step process. For example, Thiele et al. developed a compact

imaging system with 3D printed stacked diffractive lenses, composed of a singlet, doublet, and triplet with diameters of 180  $\mu\text{m}$ , 140  $\mu\text{m}$ , and 180  $\mu\text{m}$  respectively, exhibited near aberrations free imaging and sub-micron resolution in the visible spectrum with 580 nm line spacing at wavelengths of 550 nm and a 60-degree field of view (FOV) [61]. As depicted in Fig. 5a, the flat diffractive doublet stacked lens surface profile shows good optical smoothness without a staircasing effect in phase relief regions which directly impact efficiency and imaging performance [61]. Due to the small size of the flat diffractive lenses, print times of approximately 15 min could be achieved utilizing a minuscule amount of materials overcoming challenges previously mentioned in point-to-point based DLW [61]. Additionally, Thiele et al. developed a foveated imaging system, consisting of four aberration corrected air-spaced multi-lens objectives of varying FOV, 20, 40, 60, and 70 degrees, was directly printed using TPP on a CMOS image sensor exhibiting an angular resolution of  $> 2$  cycles/degree in the center of the image through modulation transfer function (MTF) measurements (Fig. 5b) [62]. The 3D printed multi-lens imaging system exhibits high resolutions towards the center of the image while retaining a full 70-degree FOV [62]. Overall, multi-lens objective arrays can provide improved functionality to optical devices for endoscopy and robotics, and give detailed image information near the center of the image supporting details in a wide FOV.



**Fig. 5.** 3D printing of multiscale lenses. (a) Single, double, and triple stacked diffractive lenses with SEM images and measured surface profile characteristics; Copyright from Ref. [61]. (b) Images and focusing quality evaluation of  $2 \times 2$  objective lenses with varying FOV; Copyright from Ref. [62]. (c) Multi-interface refractive lens in supporting material (blue) attached to an optical fiber (red). SEM images of singlet, doublet, and triplet lens with 90-degree slice along with respective measured imaging performance; Copyright from Ref. [63]. (d) CAD model of diffractive optical elements directly printed on optical fiber with respective beam intensity in the axial direction; Copyright from Ref. [64]. (e) Freeform lenses directly printed on optical fibers including: polarization control, diffractive-refractive element, and imaging optical element on the facet of optical fiber; Copyright from Ref. [65].

Recent development in 3D printing technologies opens new routes for multiscale lens objective fabricated by femtosecond DLW that can be translated into micro-optical and nano-optical systems by directly 3D printing on substrates such as optical fibers for imaging and optical trapping applications using highly transparent photoresists. With an optical quality smoothness less than 15 nm RMS roughness, a 3D printed multi-lens objective, which is depicted on the end of an optical fiber, consists of five refractive interfaces that correct aberrations and show improvements to resolving power of 500 lp/mm [63] (Fig. 5c). Quantitative optical performances of the 3D printed singlet, doublet, and triplet lenses can be carried out by imaging the USAF 1951 test target [63]. Moreover, 3D printing technologies have been used to fabricate Fresnel lenses and diffractive lenses on the tips of single-mode optical fibers for optical tweezer applications, where designing compact microscale and nanoscale optical components are crucial to the overall performance. In a particular study, three different numerical apertures, 0.3, 0.5, and 0.7 with focal lengths of 200  $\mu\text{m}$ , 100  $\mu\text{m}$ , and 50  $\mu\text{m}$  respectively, are demonstrated in a dual fiber setup to serve as a highly stable optical trapping device at low light powers (220  $\mu\text{W}$ ) for dielectric particles with diameters ranging from 1  $\mu\text{m}$  to 500 nm in water (Fig. 5d) [64]. The primary advantage of a dual fiber set up with 3D printed diffractive Fresnel lenses is the capability of producing high working distances and high-fidelity features since only 3D printing provides unbounded complexity to the optical design for diffractive optical elements, leading to increased trapping stiffness and highly accurate trapping systems for applications in single cell and particle manipulation [64].

Free form optics fabrication via 3D printing techniques, such as DLW, TPP, Inkjet, can be applied to construct a variety of optical elements including diffractive optical elements, beam shaping optics, and polarization filters can be integrated on a single mode fiber with sub-micrometer accuracies that are otherwise unachievable using conventional fabrication methods [65]. DLW not only allows for the creation of free-form optics on optical fibers but also enables to print optics on various substrates such as light emitting diodes (LEDs) and other light emitting structures that require complex customization and design freedom, allowing the generation of multi-functional objectives with two or more diffractive optical elements (DOE) or refractive surfaces, which greatly improve optical performance in a fast and cost-effective

process [65]. As shown in Fig. 5e, a beam collimation lens, saddle shaped Fresnel lens for beam shaping, and multi-lens objective are printed on a single mode [65]. In addition to DLW, inkjet printing has been used to fabricate spherical microlens and MLAs on the facet of single mode fibers by depositing a single droplet of UV-curable resin onto the end of a fiber, and sub-100  $\mu\text{m}$  diameter lenses can be built for potential use in biochemical sensors for clinical diagnostics and environmental monitoring [66]. The 3D printing of optical components with high resolving power on micro to nanometer scales offers new insight to applications in microimaging, sensors, and microscopic objective lenses.

## 2.4. Summary and outlook

3D printing has opened a plethora of opportunities in the field of optical lenses, providing high fabrication quality and superb resolution, compared to traditional fabrication methods, which are time consuming, wasteful, and costly. The summary of printing resolution, printing methods, and printing materials for optical lens is shown in Fig. 6. Benefiting from rapid prototyping and optical repairs, the capability of fabrication on-demand lenses with imaging and surface smoothness using 3D printing enables various new applications, comparable to commercially available lenses. Additionally, 3D printing can generate freeform optical lenses with complex geometries otherwise not achievable for applications that require powerful imaging systems. However, there are certain drawbacks and challenges in 3D printed optical lens such as time consuming, surface quality, and limited material selection. For example, femtosecond DLW takes hours or days to fabricate a single optical component under nanometer scale voxels required for high accuracy, which is unrealistic for mass production industrial optical devices. Furthermore, good optical performance is optimized by minimal surface profile deviations and large-scale optics, such as those used for space telescopes that are unable to be realized with current 3D printing technologies. Since photoresistive materials are used widely in most 3D printing process and they are not as transmissive as traditional optical materials, such as glass. Besides, it also produces a yellowish hue because of the addition of photoinitiators. Thus, future studies in 3D printing of optical lenses should focus on development of mass production of optics as well as the development of a broad range of suitable materials that allow for more transmission and improved

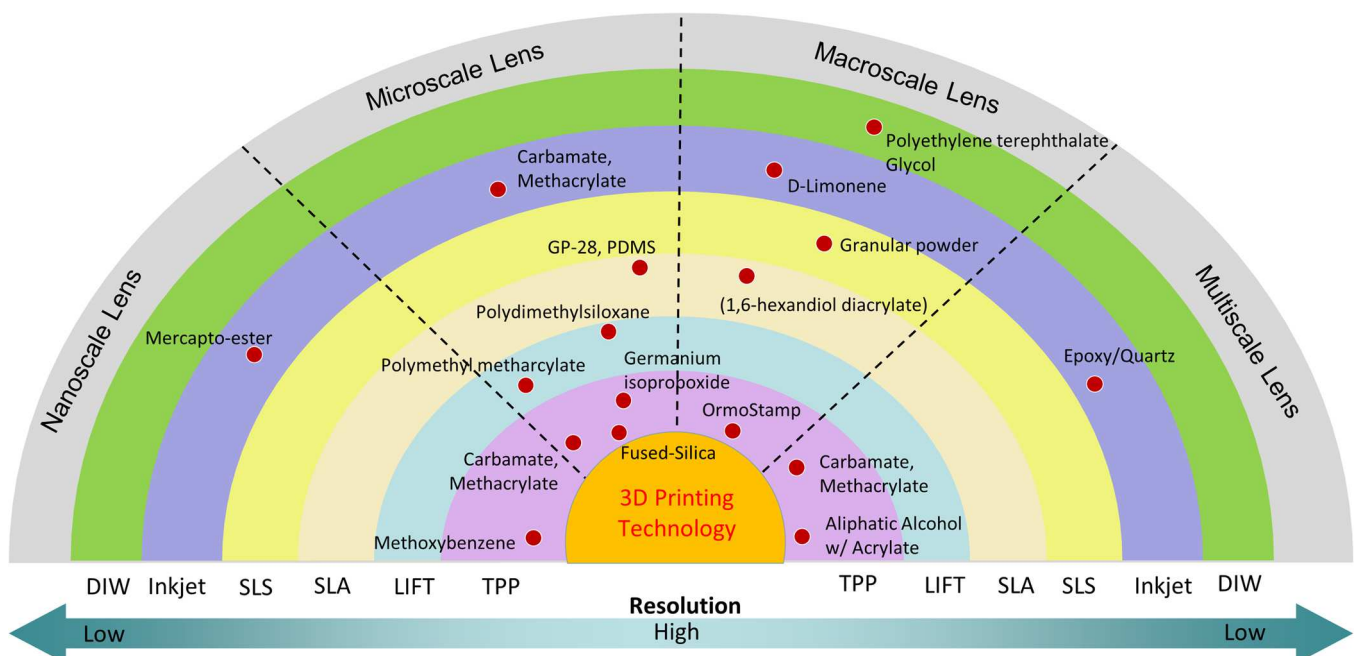


Fig. 6. Schematic diagram showing the materials and 3D printing methods used in the fabrication of nano-, micro-, macro-, and multiscale optical lenses.



mechanical strength with the addition of scratch resistant coatings. 3D printing technologies provide possibilities to rapid fabricate customizable optical lenses that display superior optical performance using low-cost materials with high reproducibility and precision in the future.

### 3. 3D printing of optoelectronics

Optoelectronics are electronics devices used for emitting, transmitting, detecting or modulating light which includes not only visible light but also invisible forms of radiation [67]. Basically, optoelectronic devices are transducers converting photons into electrons, light into an electronic current or vice versa. With the booming of electronics, optoelectronics also has been applied in various fields, such as infrastructures, military services, automatic access control systems, medical industries and so on. Currently, the mainly used optoelectronic devices contain waveguides, LEDs, laser diodes (LD), photodetectors, and solar cells [68–71]. Optical waveguide is one type of optoelectronic device, which is a physical structure guiding electromagnetic waves in the optical spectrum [71]. The common types of waveguides are optical fibers, planar waveguides, channel waveguides, and transparent waveguide. The applications of waveguide are diverse, for example, the transmission of light over long distances can be achieved by optical fibers. Waveguide can also be used on photonic integrated circuits to guide light between different optical components. LED, a commonly used light source, is a semiconductor emitting light while current flows through it. As current flows through the LED, electrons recombine with electron holes in the semiconductor then release photons as a form of energy [68]. The generated wavelengths of modern LEDs are not limited in visible light, but also available across infrared (IR) and UV. Generally, diodes are made of several layers of raw semiconductor material as thin as 0.5  $\mu\text{m}$ , with one layer contains excessive electrons while next one has electron holes [70]. The difference between these two layers will cause the above process of light or invisible radiation generation. LD is similar to LED, and in LD the photon will strike the atom and compel it to release the similar photon, which will form the light beam [72]. The light emitted by LD is coherent and monochromatic, and LD is widely used in optical communication systems, laser detection, laser printing and laser scanning, and medical fields. Photodetector transforms light photons into electrons by a P-N junction, which is exactly the opposite of LEDs [73]. Photodiodes and phototransistors are two common examples of photodetectors. Based on its operation principle, photodetectors are often used as sensors in automatic control systems, such as light control systems in automobiles. Solar cells have the same energy conversion function as photodetectors, the difference is that solar cells store some electrical energy transformed from light energy while photodetector does not [74]. Obviously, solar cells have become an essential tool to exploit solar energy. Currently, these optoelectronic devices have been applied in various fields, and more and more research are focused on the development of fabrication technologies of those devices. Among different advanced manufacturing approaches, 3D printing, as a novel fabrication technology, has great potential in producing optoelectronic devices. In the following sections, the recent progress of 3D printing of optoelectronic devices will be discussed.

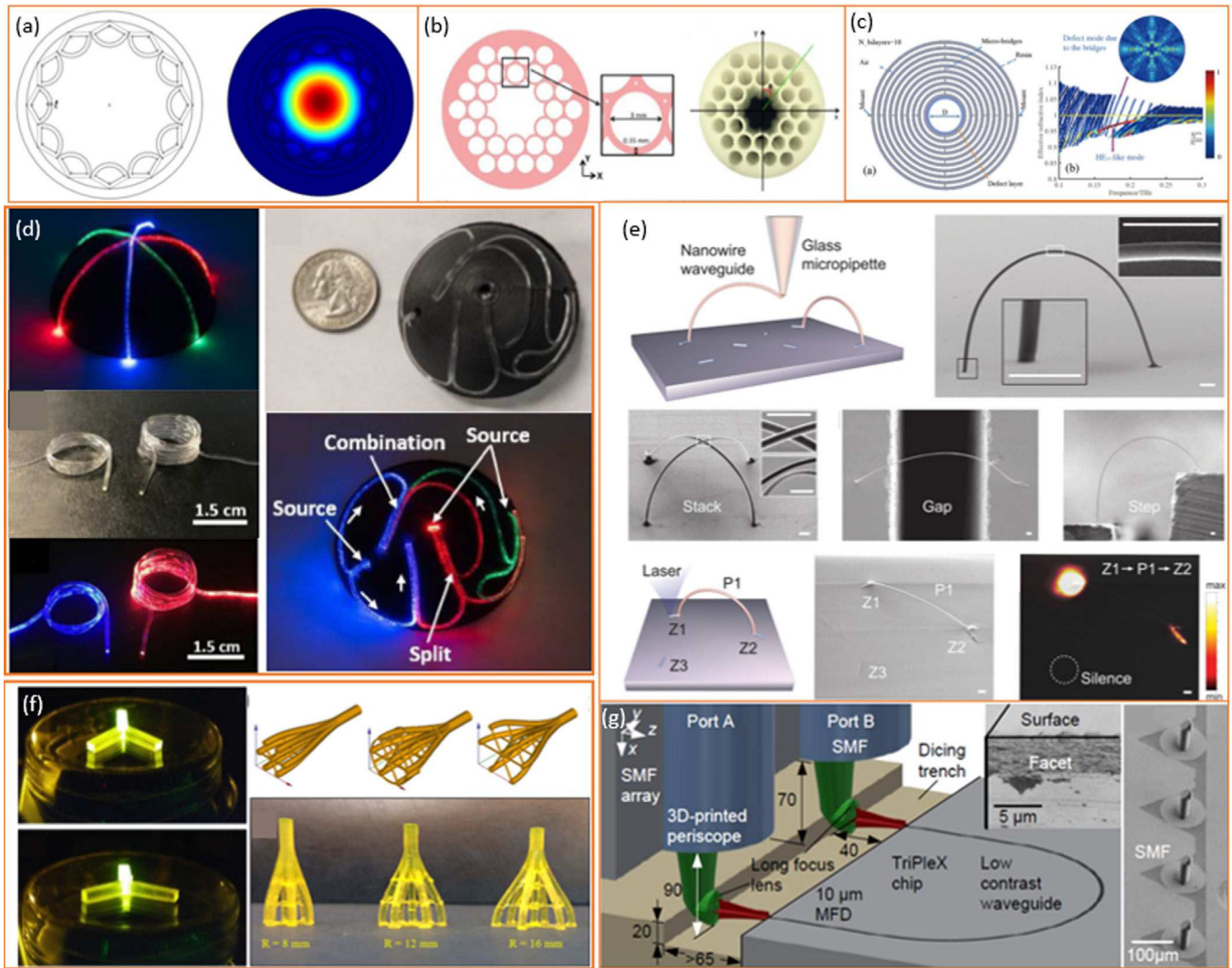
#### 3.1. 3D printing of waveguide

Waveguides have been extensively used in different areas, such as biochemical sensing, biology imaging and broadband communication. In order to enhance the performance of waveguides, the development of THz waveguide has become a hot topic. THz waveguide has capabilities to extend probing depth of the surface waves to longer distances. Although waveguides working in THz environments have demonstrated low power loss, the manufacturing community has been struggling to fabricate such device that meet the criteria such low loss, low cost, and easy processing [75]. Even though several fabrication approaches have been reported, there are still many challenges during the waveguides

fabrication processes containing high temperature and hazardous hot-draw processes, micromachining work flows, hand assembly and draw tower [75]. These fabrication techniques are not ideal for precise reproduction of waveguides with designed structures. For example, the fabrication of Kagome photonic crystal fiber requires to integrate with multiple processes, including stacking of capillary tubes, casting into a micro-structured mold, extrusion, and the integration of multiple processes increase the difficulty of precise reproduction. Benefit from advantages of 3D printing technologies, the reproduction of waveguide with complicated structures can be easily accomplished by using digital models.

For instance, Li et al. fabricated hollow waveguides with biodegradable polylactic acid (PLA) using FDM. Their cross-section design of the hollow waveguide is shown in Fig. 7a and the printed hollow waveguides exhibited low loss ( $0.015\text{ cm}^{-1}$ ) at 0.1 THz [76]. Based on Kagome photonic crystal structure, waveguide (Fig. 7b) was fabricated with VeroWhitePlus polymer using commercial PolyJet 3D printing technology (Objet30 prime, Inc.) [77]. Although the size of waveguides is limited due to the fabrication capability, the waveguides, which is mechanically formed by two sections, still maintain excellent performance, exhibiting an average power loss of  $0.02\text{ cm}^{-1}$  for 0.2–1.0 THz and minimum power loss  $0.002\text{ cm}^{-1}$  at 0.75 THz [77]. Apparently, 3D printing fabrication method greatly simplifies the fabrication process of complicated waveguide devices without sacrificing the performance. Apart from the studies mentioned above, Li et al. fabricated hollow core THz Bragg waveguides by using SLA [78]. This type of waveguide is designed as a periodic sequence of low- and high-refractive index multilayers surrounding a hollow core with printing resin, where PlasClear and Asiga serve as a high-refractive index layer while air serves as a low-refractive index layer (Fig. 7c). The bilayer thickness is 512  $\mu\text{m}$  with a predicted fundamental bandgap centered at 0.18 THz. The waveguide core size is set at 4.5 mm to realize an effectively single mode operation within the fundamental bandgap region [78]. This waveguide has the ability to monitor the optical properties of thin films and powders. Besides, Udofia et al. presented a novel 3D printing method for customization of optics with a soft and stretchable thermoplastic polymer [79]. An extrusion-based printer is developed and Clear Ballistic gel is used as printing material [80]. Waveguide and splitter and combiner circuits can be printed on a 3D conformal surface using this novel 3D printing approach (Fig. 7d).

Besides, one superiority of 3D printing compared with mostly traditional fabrication technologies is the nano-scale manufacturing of complex structures. Based on meniscus-guided 3D writing, Pyo et al. developed a precise and versatile nano-scale 3D printing method for fabrication of optical waveguides [81]. Polystyrene with high transparency and high refractive index is used as passive waveguiding material [81]. The newly developed approach provides the possibility to connect polymer nanowire waveguides with any objects, and it can achieve stacked interconnection without physical contact, which allows simplification of photonic circuit designs and increase of density of integration [81]. This technique accomplishes optical interconnections in flexible or stretchable photonic devices (Fig. 7e) [81], and the printing precision can meet the requirement in nanofabrication, which is vital for diverse optical components like wavelength multiplexers and splitters [81]. In addition to the high resolution, various material selections provide researchers more freedom to develop optical waveguides using 3D printing. Frascella et al. take advantage of photoluminescent dye to print waveguides and splitters by using SLA printing process [82]. Bisphenol A ethoxylate (2 EO/phenol) diacrylate and Omnirad 819 are used as photocurable monomers and photoinitiator respectively [82]. Methacrylic Derivative of 7-nitrobenz-2-oxa-1,3-diazole (MBD-MA) is synthesized to be photoluminescent dye [82]. Different concentrations of MBD-MA were tested to print waveguides and evaluate their transmittance (Fig. 7f) [82]. Besides, Trappen et al. demonstrated a novel approach to fabricate a specific waveguide used as an optical probe using DLW (Fig. 7g) [83].



**Fig. 7.** 3D printing of waveguide. (a) Schematic of 0.1 THz low-loss 3D printed hollow waveguide; Copyright from Ref. [76]. (b) 3D printed low-loss THz waveguide based on Kagome photonic crystal structure; Copyright from Ref. [77]. (c) Schematic of the 3D printed THz Bragg waveguide and band diagram of the Bragg waveguide; Copyright from Ref. [78]. (d) 3D printed waveguide on a dome and spiral waveguides before and after coupling to LEDs; Copyright from Ref. [79]. (e) 3D printing of photonic nanowires; Copyright from Ref. [81]. (f) Fluorescence pictures of the waveguides illuminated at one end of the waveguide and circular cross section optical waveguides with different radii; Copyright from Ref. [82]. (g) Wafer-level probing of a SiN waveguide using a standard single-mode fiber (SMF) array with 3D-printed lensed periscopes; Copyright from Ref. [83].

Commercially available material IP-Dip works as photoresist, and slicing and hatching writing distances are both set to 100 nm [83]. The 3D printed single-mode fibers-lens-periscopes (SMF-LP) probes for coupling to silicon nitride and silicon photonic on-chip waveguides have demonstrated high coupling efficiency [83].

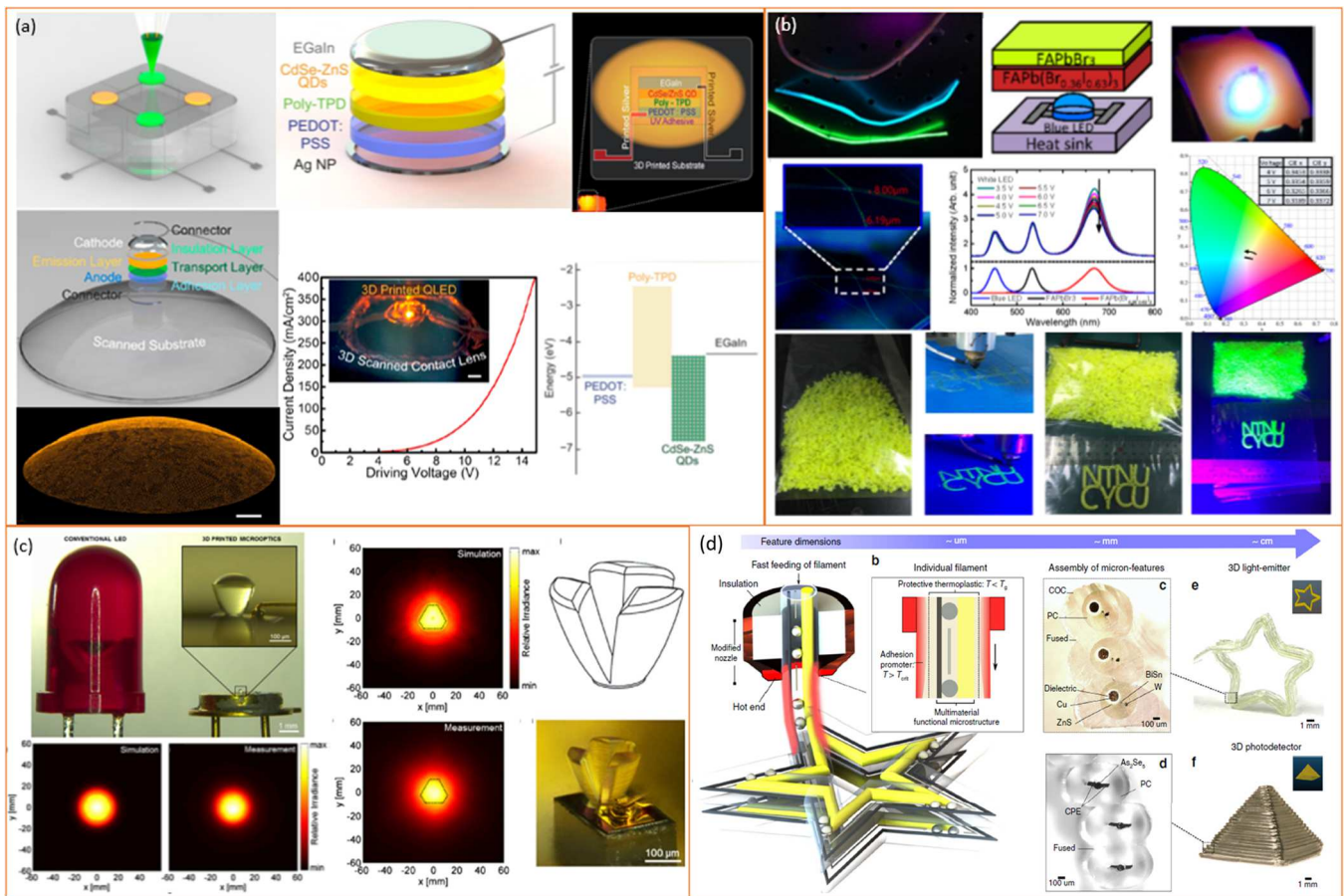
### 3.2. 3D printing of LEDs

The conventional fabrication process of LEDs has a long and complex routine, which limits the further development of novel LEDs. Current developments in 3D printing method have provided a tool to construct LEDs in an unconventional way. Because of the booming of 3D printing technologies and printing materials developments, more and more research works are focused on the area of 3D printing of LEDs, which leads to the fast-growing research field. For example, Kong et al. reported a 3D printed quantum dot (QD) LED using extrusion-based 3D printing (EBP) technology (Fig. 8a) [27]. In the 3D printed QDLEDs, the emission layer is made by cadmium selenide/zinc sulfide (CdSe/ZnS) core-shell QDs, poly[N,N'-bis(e-butylphenyl)-N,N'-bis(phenyl)-benzidine] (poly-TPD) is hole transport layer, and poly

(ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) is the transparent anode, surrounded by a sintered silver nanoparticle (AgNP) ring metallic interconnect and a eutectic gallium indium liquid metal (EGaIn) cathode [27]. The fabrication of QDLEDs proves the concept of combining active nanoelectronics by using EBP based printing process, which show the versatility in printing different types of material. Aside from developing 3D printing process for LEDs fabrication, some researches focus on the materials exploration in 3D printing of LEDs. Thermoplastics, which are widely used as filaments in FDM printer, were tested to be protective encapsulation materials for HC(NH<sub>2</sub>)<sub>2</sub> 2PbBr<sub>3</sub>(FAPbBr<sub>3</sub>) and FAPb(Br<sub>0.36</sub>IO<sub>0.63</sub>)<sub>3</sub> perovskite nanocrystal [84]. Because of the low melting point, filaments made by the composite perovskite nanocrystal/polycaprolactone (PCL) were prepared and the objects printed using such filaments showed fluorescence [84]. As shown in Fig. 8b, perovskite nanocrystal/PCL based optical filaments were firstly prepared using 3D printing pen and the filaments were further loaded into the nozzle of a FDM printer to fabricate film-based LEDs, which is complicated to fabricate using traditional methods [84].

Besides, Thiele et al. fabricated on-chip LED optics using TPP process [85]. As a result of trade-off between writing time and accuracy, the





**Fig. 8.** 3D printing of LEDs. (a) 3D Printed QLEDs; Copyright from Ref. [27]. (b) Image of filaments prepared from perovskite nanocrystal/PCL composites under UV irradiation, schematic diagram and photograph of the white LED and small pieces of the composites; Copyright from Ref. [84]. (c) 3D printed non-conventional collimator optics; Copyright from Ref. [85]. (d) Micro-structured multi-material filament, and 3D printed light-emitter and light-detector; Copyright from ref. [88].

layer spacing in the experiment was set at 100 nm. Both the 3D printer (Photonic Professional GT from company Nanoscribe GmbH) [86] and printing material (IP-S) [87] used in the experiment are commercially available [85]. Two types of non-conventional collimator optics were printed on top of a chip (Fig. 8c). This work demonstrates the fabrication precision and geometric shape freedom of the TPP process. Additionally, Loke et al. designed two types of micro-structured and multi-materials filaments [88]. One was designed for light-emitting, and another was designed for light detecting. The developed filament structures and materials are shown in Fig. 8d. These filaments can be directly extruded from a typical FDM printer (200  $\mu$ m printing resolution) to build 3D light-emitter and 3D photodetector (Fig. 8d) [88].

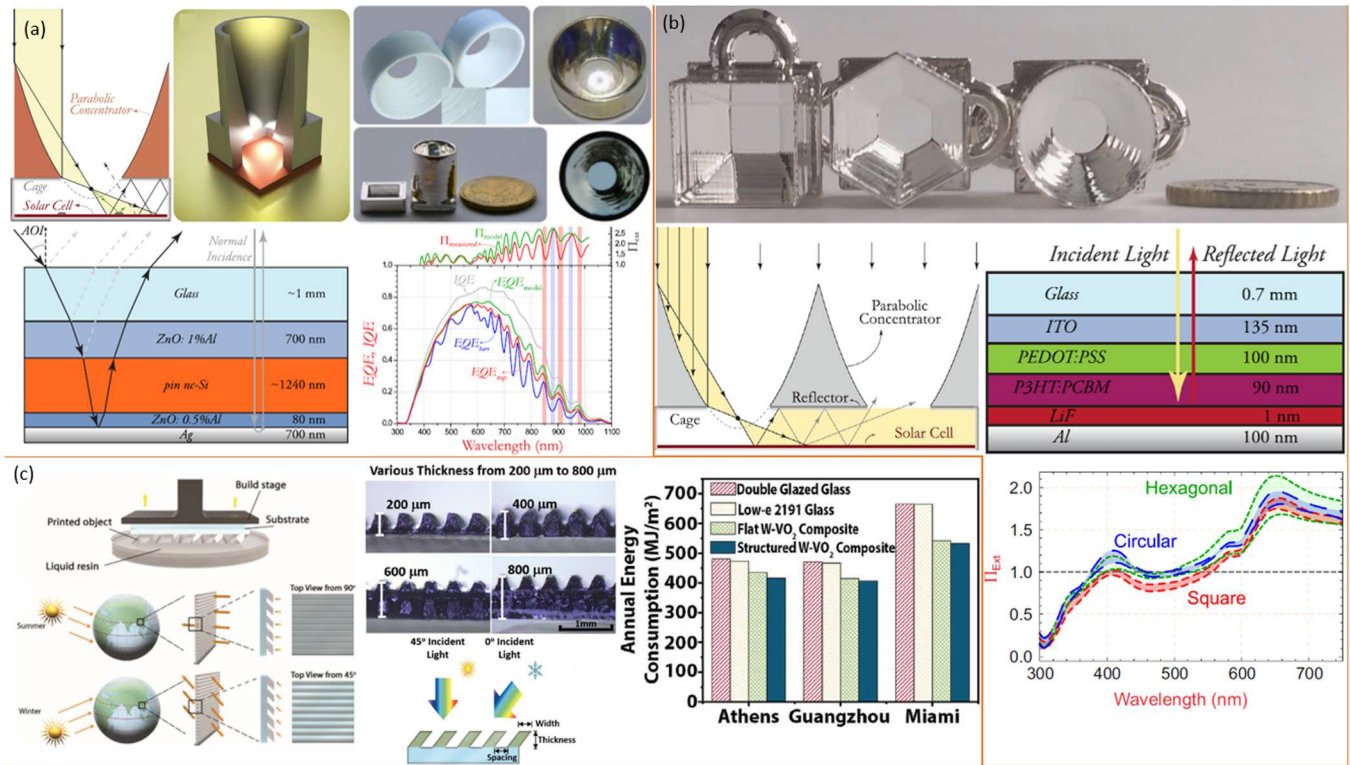
### 3.3. 3D printing of solar cell

The demand for rechargeable, reusable energy sources grows rapidly as the Earth's supply of invaluable fossil fuels diminishes. Solar cells (SCs) are gaining attention worldwide for various applications due to their environmentally friendly, superior photoelectric conversion efficiency, and stability. Currently, SCs are manufactured mostly using traditional deposition approaches, which is hard to achieve the fabrication of complex inner structures and further hinder the applications of SCs. 3D printing provides a promising tool to construct bioinspired structures with advanced material for various applications [31,89]. It is necessary to understand how to fabricate the SCs with enhanced properties and energy conversion efficiency using advanced 3D printing technologies, which remains a critical challenge for solar manufacturing research. For example, Lu et al. used inkjet printing technology to

fabricate SCs and further explored the performance of 3D-printed SCs [90]. The printing ink is consist of PEDOT:PSS [90], glycerol, and ethylene glycol butyl ether (EGBE). The experimental results show better uniformity in film thickness and density and smoother surface than the ones using PEDOT:PSS without any additives (Fig. 9a) [91]. Wider materials selections in 3D printing provide scientists and engineers with more possibilities to improve the properties of SCs.

Currently, energy conversion rate of SCs is only around 14–19% [94], and significant research effort has been devoted to 3D printing of SCs accessories to improve the energy conversion rate of SCs [92–95]. For example, Dijk et al. has studied 3D printed external light traps and concentrator arrays for SCs [92]. Different structures of light traps of SCs were designed and printed with acrylonitrile butadiene styrene (ABS) using Ultimaker [95], which is a commercial FDM 3D printer (Fig. 9b) [96]. Because ABS permits the printed part to be vapor smoothed by exposure of saturated acetone vapor [92], the 3D printed cage and compound parabolic concentrator (CPC) can be coated with silver for high reflectance [92]. Different types of CPC, including square, hexagonal and vertically truncated structures, were designed and printed using the same 3D printing procedure [92]. Experiments results showed the energy conversion of SCs has been improved by 3D printed external light trap and concentrator arrays. Moreover, smart glass, whose light transmission properties can alter in response to temperature, light and so on, is an interesting research area of the SCs in the future. For example, Zhou et al. [93] developed custom-designed tilted 1D grating-shape composite structures composed of polymer and vanadium oxide ( $\text{VO}_2$ )/W-doped  $\text{VO}_2$  nanoparticles on glass substrates [93]. These developed glass substrates are aiming to apply in different latitude cities



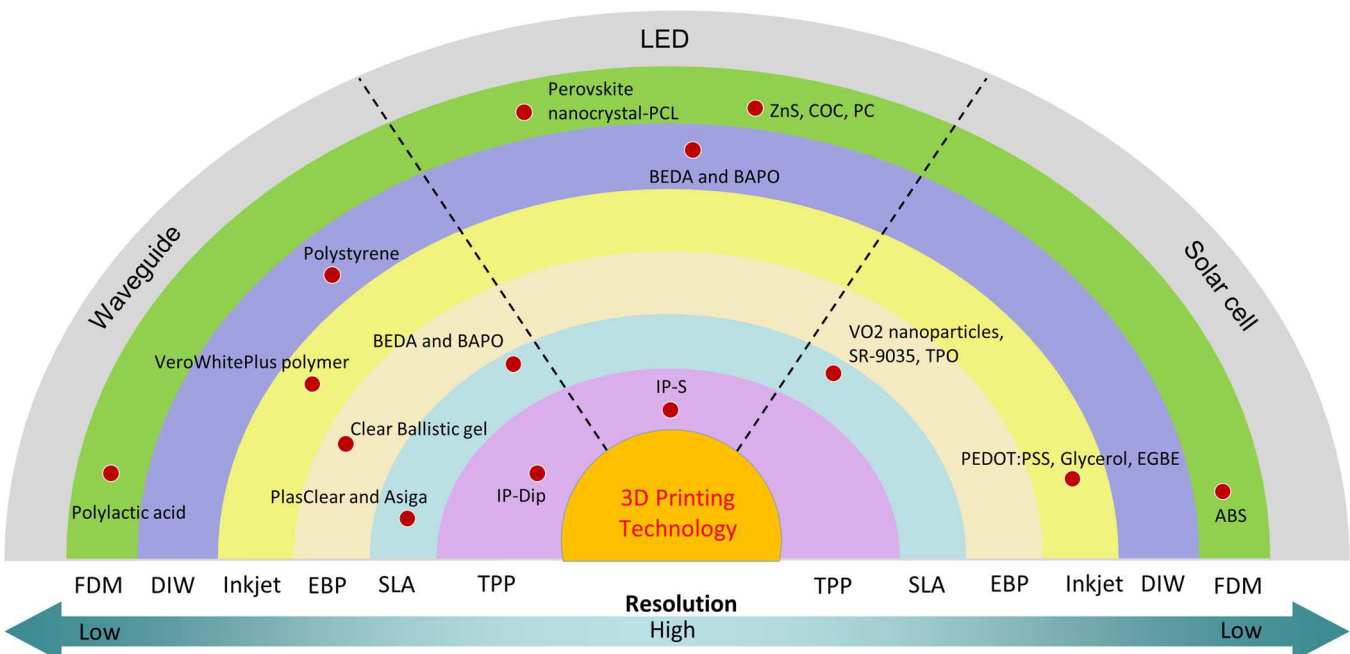


**Fig. 9.** 3D printing solar related components. (a) Schematic illustration and 3D printing of the external light trap of a SC, and efficiency comparison with and without external light trap; Copyright from Ref. [91]. (b) 3D printed square, hexagonal and circular parabolic concentrators of SCs with silver coating and efficiency comparison; Copyright from Ref. [92]. (c) 3D printed smart windows; Copyright from Ref. [93].

because of the consideration of solar elevation angle. The schematic illustration of conventional flat films and structured polymer-VO<sub>2</sub> composite are shown in Fig. 9c, and these microstructures were accurately printed by using SLA based 3D printing technology [93]. 3D printing provided the possibility to make customized designs of glass substrates for different latitudes due to flexibility and elegance of this type of technology.

### 3.4. Summary and outlook

Optoelectronics play an important role in the optical field, and traditional manufacturing technologies meet bottle necks in the fabrication of optoelectronics for the efficiency improvements. For instance, the traditional fabrication approaches are nearly impossible to produce waveguides with complex inner structure features. 3D printing has



**Fig. 10.** Schematic diagram showing the materials and 3D printing methods used for the fabrication of waveguide, LED and solar components.

opened plenty of opportunities for the development of novel optoelectronics, since it allows more freedom in structure design of optoelectronics such as waveguides, LEDs, and solar components. With the development of 3D printing processes, micro or nanoscale features can be fabricated using advanced 3D printing processes, which create the possibility for manufacturing photonic integrated circuit (PIC) and QDs. Currently, most of 3D printing technologies are developed to fabricate low-volume and customized optoelectronics product with complex structures and high accuracy which is hard or even impossible for other manufacturing methods. 3D printing facilitates the customization of optoelectronics, which is essential for the improvement efficiency. The summary of 3D printing processes, resolution, and materials used in fabrication of waveguide, LED and solar components is shown in Fig. 10. Even there are many progresses in the 3D printing of optoelectronics, a lot of material which are widely used in traditional manufacturing of optoelectronics still are hard to processes by using current 3D printing approaches. Although a growing number of commercially available materials have appeared in different 3D printing technologies, it is still necessary to develop new 3D printing process to fabricate the well-developed materials used for the fabrication of optoelectronics by traditional approaches. Moreover, more efforts are needed to put by researchers and engineers to test different solutions or material mixtures to explore the optimal combination and concentration for 3D printing of optoelectronics.

#### 4. 3D printing of photonics

3D printing is also highly applicable to the field of the fabrication of photonics. In electronics, electrons are used to send signals, but in photonics photons are manipulated to send these signals instead of electrons [97]. Photonics is being utilized in various fields such as consumer electronics, biomedical, manufacturing and entertainment on a larger scale [98]. Photonics can be applied to more than just sending signals to electronics, it can also be used in 3D imaging to capture scenes. For example, Lippmann scheme proposes to use an opto-electronic matrix sensor to capture a multitude of 3D images instead of only capturing the color radiance of a light beam with photographic film [99]. There are also many examples in nature that can provide insight into ways of changing the color reflected by an object via photonics. Xu et al. used polyacrylamide inverse-opal hydrogel to synthesize a material with special properties that changing its structural color in response to the amount of chemicals present in a liquid, such as alcohol, that it was exposed to [100]. In addition to capturing the color and radiance of light, photonics can also be used to manipulate light for display purposes. For example, inspired by spider silk, optical ballistic gel makes it possible for light to be manipulated in three-dimensional space, allowing for various applications in art, beam splitting, combiner circuits and optical encoding [79]. Light has been interacting with nature for millennia and there are many ways to manipulate light with the help of unique material system and structures, such as changing color capability of chameleons and structural color of fireflies. Natural materials, such as plant cellulose, chitin, and animal silks have their own way of manipulating light that can be observed [101]. Besides, photonics has an immense number of applications, where various forms of light manipulation can be performed through silk string, optical ballistic gels, reflection proteins, and various other biological inspired artificial materials [102]. Due to the unique properties of material, it allows a large number of explorations that can be done by using 3D printing to further extend the field of photonics.

##### 4.1. 3D printing of material and structures for structural color

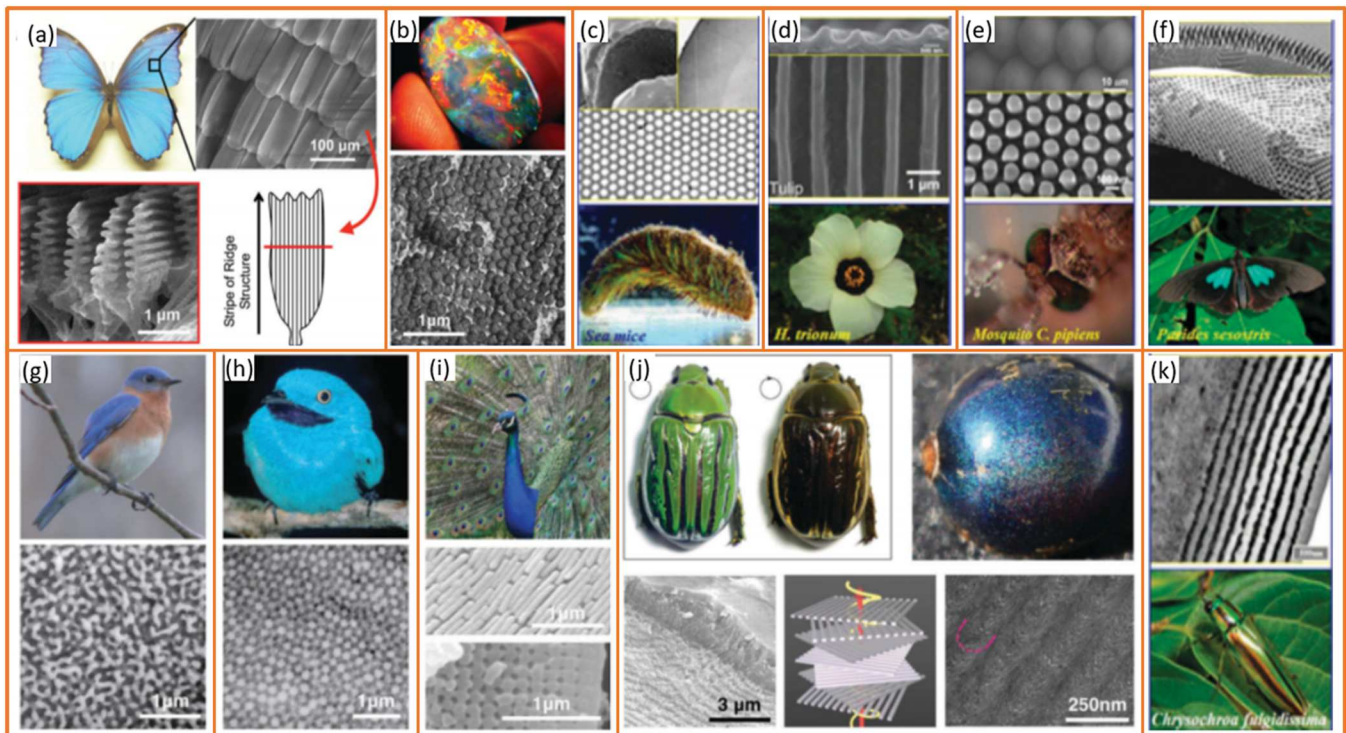
The colors from the visible light spectrum can be displayed in three different ways: absorption, emission, and structural colors [103]. Many organisms in nature possess discrete micro or nanostructures that are colorless or transparent but display color because of unique features

[104]. As shown in Fig. 11, the natural structures exhibit a variety of optical properties such as scattering, reflection, polarization, diffraction, and refraction [104]. Scattering structures found in nature are colloidal systems of multi-materials that rely on their different refractive indices to mimic reflective properties in every direction thus scattering the light (Fig. 11a–c) [104]. Changing the sizes and arrangements of the materials into a random or organized fashion determines the color and shade [104]. Diffraction gratings are grooved sheets that consist of ridges that close in size to the wavelengths of light in the visible spectrum (Fig. 11d–f) [104]. Making these ridges smaller than the wavelengths of light, they become anti-reflective gratings and create saturated colors [104]. Moreover, some types of structures found in nature are photonic crystals which are ordered to control how light is propagated through subwavelength structural lattices (Fig. 11g–i) [104]. Multilayer reflection is stacks of thin films with different refractive indices to create constructive interference and reflection (Fig. 11j, k) [104]. Fabricating these structures found in nature falls into top-down and bottom-up strategies [105]. The most common top-down strategies include lithography and layer by layer deposition [105]. Lithography can control the patterning of dielectric materials on micro scales [105]. Masked lithography follows a projection pattern for printing while maskless prints patterns via etching or serial writing [105]. Layer by layer deposition creates sheets of film that are stacked with high and low periodic alternating refractive indices [105]. Bottom-up methods focus on self-assembly and biomimetic templates [105]. Self-assembly methods contain components such as copolymers, colloids, and liquid crystals that combine to create structures with optical properties [105]. The biomimetic template method utilizes the deposition of material onto templates to create replicas or inverses structures of the templates and their optical properties [105].

Several different 3D printing methods have been used to achieve structure colors by mimicking the natural structures and material systems. For example, self-assembling nanostructures was developed by Boyle et al. and bioinspired structures could be printed using commercial FDM 3D printer with color appearance (Fig. 12a) [107]. In this work, block copolymers (BCP) synthesized from wedge-type polymers dodecyl and fluorobenzyl by using ruthenium-mediated ring-opening metathesis polymerization, and the dendritic BCP's self assembles into a photonic crystal-like structure during 3D printing [107]. The wavelength of structural color can be modulated by adjusting the molecular weight of BCP [107]. The printed structures possess optical properties that can guide certain frequencies of light through a tube while removing other frequencies [107]. Zhou et al. designed a printing paste system in which nanostructures could be self-assembled and non-iridescent structural colors can be further produced on textiles such as clothing (Fig. 12b) [108]. This technique is more environmentally friendly than traditional printing of textiles because it does not require a lot of wastewater to apply the pigment-based inks [108]. Deposition was used to create 3D color images with high brightness, high resolution, and saturation (Fig. 12c) [109]. The three-layer system is started with depositing 100 nm of silver onto a silicon wafer by electron-beam evaporation, followed by 45 nm of silica dielectric material and final layer of 25 nm of silver applied by a Kurt Lester sputterer [109]. Then the top layer is milled into a triangular lattice pattern where hole to hole measure and hole size determine colors using focused ion beam milling process [109]. Lastly, a 5 nm silica overlayer is put on to protect the 3-layer system from degrading in air [109].

Besides, Liu et al. found that it was difficult to make nanostructures using two-photon beam lithography, so they proposed a system to create woodpile micrometer structures and shrink them via heating in an argon gas environment (Fig. 12d) [110]. Color is formed based on such lattice constants, and when shrinking the structures, the lattice constants reduce and colors with lower frequencies are archived [110]. When combining several lattice structures like pixels, full-colored objects can be created [110]. Abid et al. used mask-less two beam interference lithography to create 3D textured hierarchical ordered nanostructures





**Fig. 11.** Structures found in nature that produce structural color. (a) Morpho-butterfly with ridges which have a lateral profile that look like Christmas trees; Copyright from Ref. [105]. (b) The arrangement of silica spheres in the opal creates iridescent colors; Copyright from Ref. [105]. (c) The marine worm, the Aphrodite, has cylindrical periodic hair structures; Copyright from Ref. [106]. (d) Some flowers, such as the Hibiscus trionum, contain a 1D grating structure; Copyright from Ref. [106]. (e) Mosquitos and other insects have this 2d grating structure for anti-reflection and self-cleaning; Copyright from Ref. [106]. (f) The Parides sesostris, has an inverse opal structure to get iridescent colors; Copyright from Ref. [106]. (g) The Sialia sialis, have tubular nanostructures; Copyright from Ref. [105]. (h) The Cotinga maynana, have spherical structures; Copyright from Ref. [105]. (i) Peacock feathers contain keratin with photonic crystals of melanin; Copyright from Ref. [105]. (j) Beetles polarized iridescence because of cellulose fibrils and chitin structures; Copyright from ref. [105]. (k) Many things in nature contain period multilayers shown; Copyright from Ref. [106].

(Fig. 12e) [111]. The two beam interference lithography uses an angle multiplexed exposure and scanning to get exact exposure control of the structures on a nanoscale [111]. These printed structures are flexible to design and arrange in 3D space to produce a wide variety of structural colors that could mimic polarization, iridescence, and direction of reflectivity [111]. Jiang et al. came up with a method to use biological structures to create images (Fig. 12f). In this work, they focused on stacking red, green, and blue sheets of the printed material to get a total of 729 different colors [112]. The sheets were printed using an inkjet process with an ink made of  $\text{TiO}_2$  nanoparticles [112]. A grating surface was first made by using nanoimprinting, followed by dropping the ink onto the grating surface and then putting a laminate index-matching polymer on top [112]. This technique can create transparent color images that only show color when white light is directly applied to them [112]. This can be used in optical variable devices (OVD) on identification cards because it would be difficult to replicate or manipulate preventing any tampering [112].

Moreover, structural color can be self-assembled by post destruction using self-healing mechanism (Fig. 12g) [113]. These self-healing color nanostructures could replace other 3D printed materials that can easily decompose [113]. Zhu et al. presented a novel printing process called resonant laser printing (RLP) to fabricate the structural color (Fig. 12h) [114]. Electron-beam lithography and dry etching were firstly used to treat a silicon wafer and then coated it with anti-stiction into a layer of polymer substrate called Ormacomp [114]. After this, the Ormacomp layer was then cured via UV light and separated from the silicon wafer template [114]. A Ge film is then evaporated onto it via an electron beam evaporator and then resonant laser was utilized to process Ge. The strong on-resonance energy of the laser irradiation increased the lattice temperature locally in an extremely short time which led to rapid

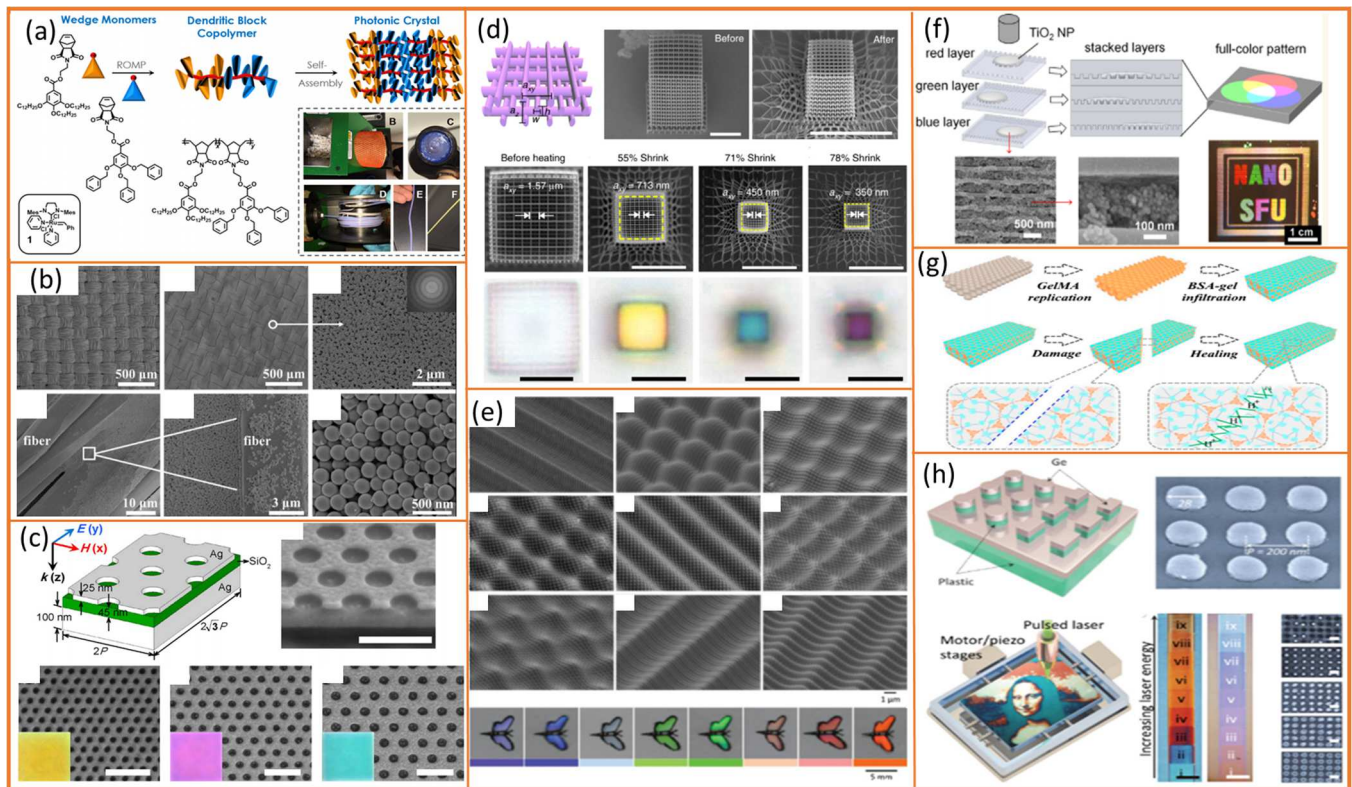
melting. Surface energy-driven morphology changed with associated modification of color appearance because of rapid melting. This printing process creates full-colored images from non-iridescent nanostructures that have resolutions higher than 100,000 DPI [114].

#### 4.2. 3D printing of photonic crystal for colorful patterns

The hair structures of sea mouse (*Aphrodita aculeata*) can prevent the propagation of light through it [104], because the internal refraction of photonic crystals, where light is refracted and reflected depending on the indices of refraction of the materials used [115]. Transparent materials structured periodically with spacing about the same size as the wavelength create a photonic bandgap that filters out photons with specific energy levels and frequencies from entering into the structure and in return reflected back [116]. It is also noted that the materials used to make the photonic bandgap are often dielectric and have different dielectric constants contained within them [117]. If these structures are designed with specific features, such as line or point, they can cause trapping or waveguiding of light [116]. The photonic bandgap allows for many specific optical properties to be achieved that are impossible to realize through conventional optical research methods [117]. To print photonic crystals, there are two fabrication strategies including lithography (top-down) and self-assembly (bottom-up) [104,116,117]. The lithography techniques consist of the electron beam, x-ray, nanoimprint, photo lithography, and holographic lithography, and the self-assembly of the colloidal crystals are made of materials such as hydrogel and responsive polymers in suspension [104]; [116,117].

Several research groups employed an inkjet printing process and self-assembly to get 2D and 3D photonic structures to display information or images which have many applications in anti-counterfeiting. Liu et al.





**Fig. 12.** Printing processes and structures for structural colors. (a) Photonic crystal self-assembly additive manufacturing process; Copyright from Ref. [107]. (b) SEM images of screen-printed structural colors on fabric; Copyright from Ref. [108]. (c) SEM images of deposition printed structural colors; Copyright from Ref. [109]. (d) Visualization of structural colors through heat shrinking photonic crystal woodpile structures; Copyright from Ref. [110]. (e) Hierarchical nanostructures printed using 2 beam interference lithography; Copyright from Ref. [111]. (f) Schematic for structural color printing using transparent gratings; Copyright from Ref. [112]. (g) Hydrogel self-healing structural color manufacturing method; Copyright from Ref. [113]. (h) Laser printing structural colors onto dielectric materials method; Copyright from Ref. [114].

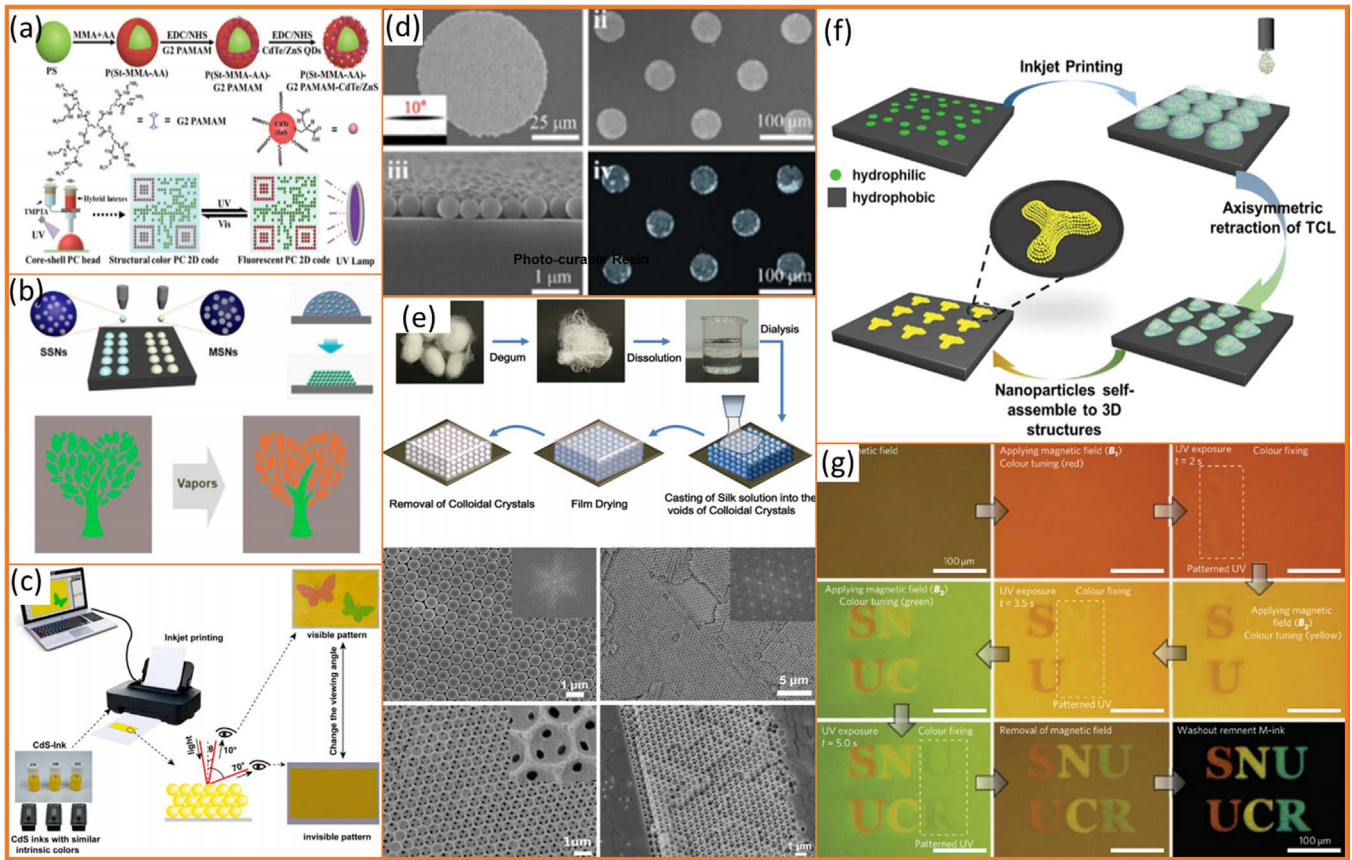
demonstrated an electrohydrodynamic printing process using microfluidic technology (Fig. 13a) [118]. The core-shell microspheres with polystyrene were used as the core and poly(methyl methacrylate co-acrylic acid) was used as a shell [118]. Using this process, structures such as multi-signal photonic crystal 2D code patterns with fluorescent capabilities can be produced quickly [118]. Besides, Bai et al. developed a photonic structure material that changed color after vapors deposition (Fig. 13b) [119]. The mesoporous silica colloidal nanoparticle based ink was inkjet onto a substrate with some pattern and then nanoparticles were self-assembled [119]. When the printed substrate was exposed to an ethanol-based vapor, part of the image changed color so that the information could be easily hidden using these responsive colloidal photonic crystals [119]. Wu et al. found a way of creating these photonic structures on regular copy paper using a commercial inkjet printer (Fig. 13c) [120]. Cadmium sulfide (CdS) particles were dispersed into a solvent consisting of deionized water, ethyl glycol, glycerol, and ethanol [120]. They also developed a way to print single and double color patterns that can be designed with different colors which were determined on viewing angle [120]. In the absence of any external stimulus, invisible patterns can become visible simply by looking from specific angles. [120]. Nam et al. used a silica particle solution mixed with formamide to create images that have the ability to cover and over by changing and tuning light illumination, background, and viewing angle (Fig. 13d) [121]. The droplets were injected onto a substrate and photonic crystals were formed after dry and self-assemble processes [121]. The surface wettability of the substrate and the chemical composition of the solvent determines the final size and color of the photonic crystal [121].

As shown in Fig. 13e, a silk fibroin solution made from raw silk fibers was used to cast into a colloidal crystal template to create an inverse opal film [122]. The colloidal crystal was grown from monodispersed

polystyrene colloidal spheres with evaporation induced self-assembly [122]. When the solution has been cast into the template filling the gaps, chemical etching was used to remove the template and generated the opal film [122]. Special structures were designed to create bi-structural colors that cause bi-reflections of light by refusing two different frequencies of light to pass through the film [122]. Wu et al. developed a material solution consisting of monodispersed polystyrene-methyl methacrylate-acrylic acid nanoparticles upon a hydrophobic surface with hydrophilic dots on it (Fig. 13f) [123]. After the hydrophilic dots were arranged in the pattern on the hydrophobic surface, the solution was injected onto the surface and began to self-assemble into 3D structures [123]. Kim et al. developed a three-phase material called M-ink involving superparamagnetic colloidal nanocrystal clusters, solution liquid, and photocurable resin (Fig. 13g) [124]. The superparamagnetic colloidal nanocrystal clusters can be arranged using a magnetic field which further determined the color [124]. After a specific color has been chosen, the M-ink was exposed to UV light through maskless lithography [124]. So multi-color patterns and images can be created through this up scalable technique with repetitive tuning and fixing capability [124].

#### 4.3. 3D printing of optical fiber for display

Optical fiber, as a type of optical component, has been commonly used in different areas including illumination and display, transmission of light, sensing and so on. Optical fibers can be divided into two categories: glass optical fibers and plastic optical fibers. Most glass optical fibers are made from silica while others are made from other types of glass, such as fluoride glass, phosphate glass. The traditional method used in optical fiber manufacturing is preform and pulling. Three



**Fig. 13.** Printing processes of photonic crystal structures. (a) Electrodynamics printing process with microfluidic technology; Copyright from Ref. [118]. (b) Inkjet printing vapor responsive colloidal photonic crystals; Copyright from Ref. [119]. (c) Printing structural colors on paper using inkjet printer; Copyright from Ref. [120]. (d) Inkjet printing of mono-layered photonic crystals; Copyright from Ref. [121]. (e) Silk fibroin photonic crystal process; Copyright from Ref. [122]. (f) Printing of patterned photonic crystals; Copyright from Ref. [123]. (g) Structural color generation by magnetically tuning images; Copyright from Ref. [124].

chemical vapor deposition methods, which are inside vapor deposition, outside vapor deposition and vapor axial deposition, are used to make a large diameter preform. After the preform is finished, it will be placed in a device known as a drawing tower to form typical long and thin fiber. Normally, the long and thin fiber will be coated with an optical cladding protecting the core from moisture and various physical damage. Obviously, due to the fabrication capability of these methods, the design freedom of optical fibers is limited. The emergence of 3D printing technology provides the fabrication of optical fibers with an alternative choice.

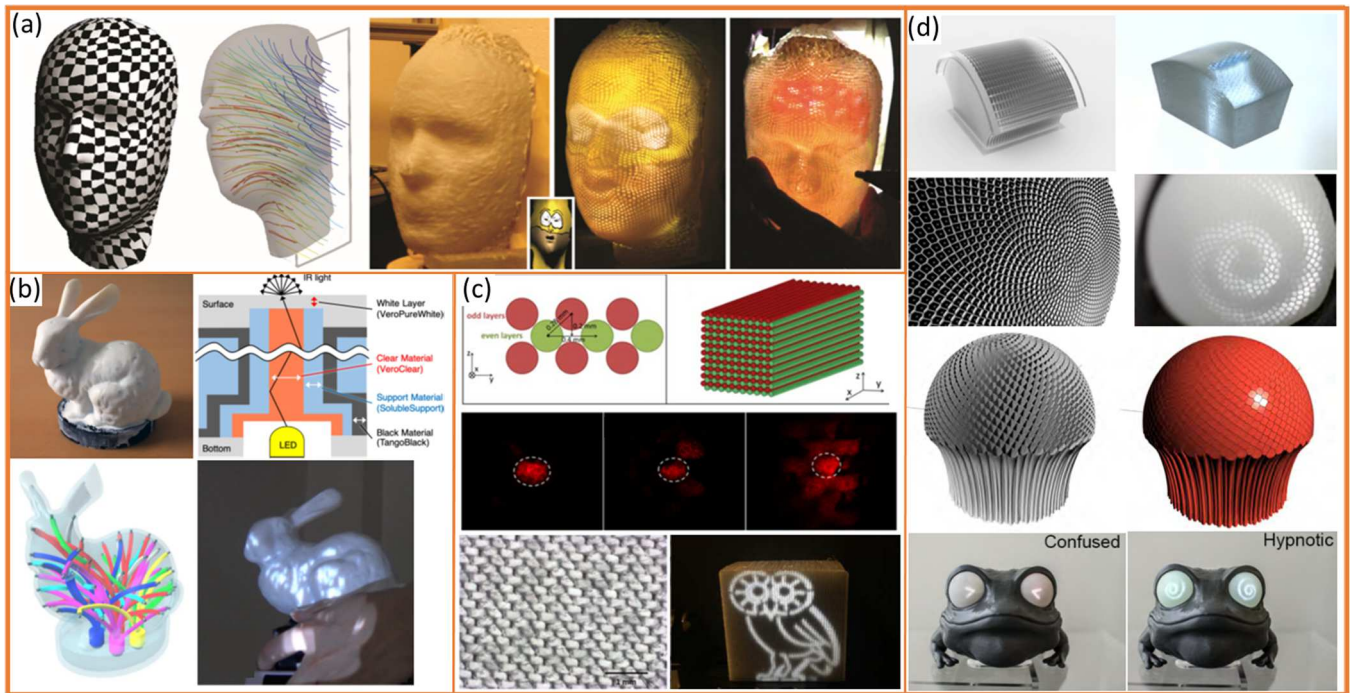
The traditional way of fiber imaging is based on fiber bundles. The fibers are first manufactured individually and then are packed into a bundle. By using both heat and external forces, the bundle is shaped into desired form which may cause defects in the final product. Compared with traditional manufacturing methods, multi-material 3D printing can be used to avoid the global deformation steps during the fabrication of optical fibers. For example, PolyJet 3D printer (Objet Connex 500) is utilized to fabricate optical fibers using two different materials including acrylic and cladding (Fig. 14a) [125]. In this work, several complex structures can be produced due to the high freedom of fabrication capability. Similarly, Tone et al. used the same 3D printing technology to produce 3D printed objects embedded with optical fibers (Fig. 14b) [126]. Because of the freedom and multi-material fabrication capability, the internal waveguide structures and the external 3D shape can be fabricated at the same time. FDM is another 3D printing method that is widely used in optical fiber manufacturing. For instant, Wang et al. built fiber optic faceplates using 4 different transparent filaments including ColorFabb XT-clear, Taulman3D Tech-G, Taulman3D t-glase, Ultimaker CPE and they further evaluated the optical transmission and

contact-induced crosstalk of printed samples (Fig. 14c) [127]. Besides, Brockmeyer et al. developed a 3D display surface based on 3D printed optics [128]. They use PAPILLON which is a technology for designing 3D curved display surfaces acting as information display and sensing human touch as their design tool [128]. Based on the 3D-printed display fibers, they developed interactive eyes for different characters as shown in Fig. 14d [128]. Overall, 3D printing is a promising fabrication method to produce optical fibers for imaging, and it inspires novel design of optical fibers for imaging. Compared with other fabrication technologies, 3D printing simplifies the fabrication procedure and can be utilized in the fabrication of various types of optical fiber devices. Especially, multi-materials printing technology enables the fabrication of optical fibers by using only one process. However, current 3D printed optical fibers are limited for professional applications because of its resolution and the transparency of the printing material. More researches related to new 3D printing technology and materials will be conducted to solve these challenges.

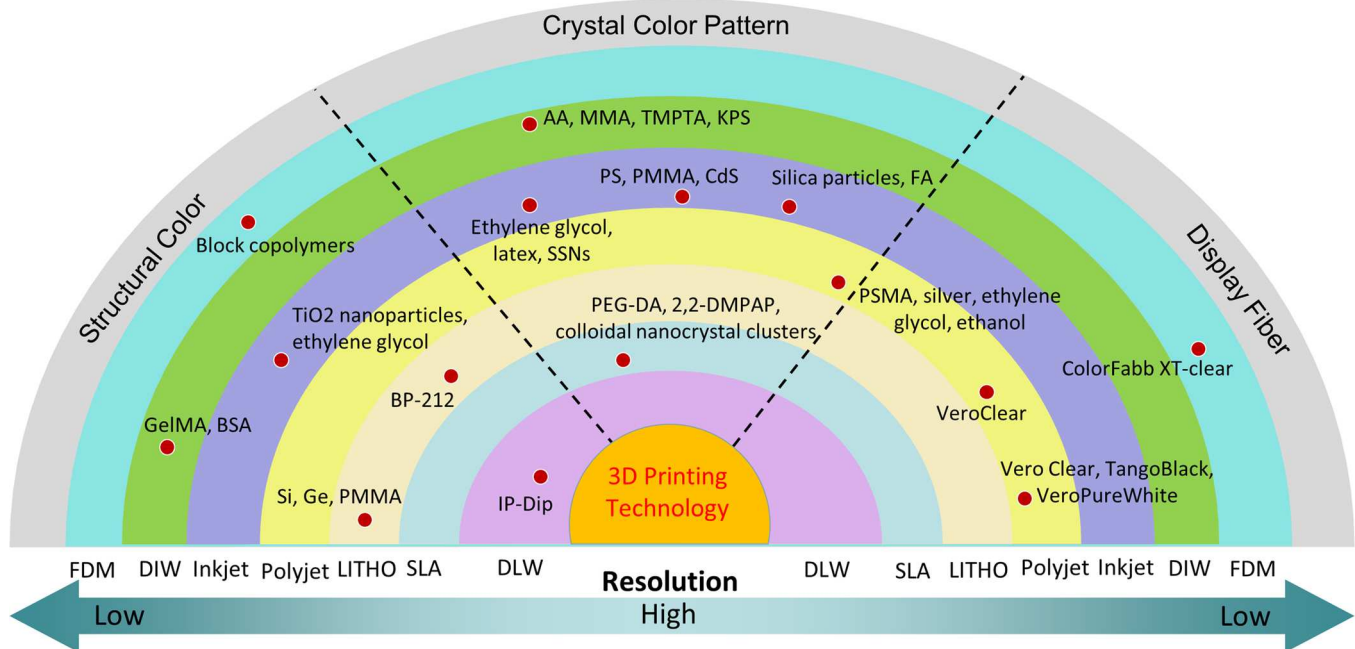
#### 4.4. Summary and outlook

Photonics is the study of the manipulation of photons and light. Structural colors, photonic crystals, and optical fibers are all subjects within the scope of photonics for display. The micro and nanostructures follow a set of optical rules which determine the way light propagates. In this section, each of them was discussed and current status of 3D printing of photonics were shown. 3D printing processes and materials used in fabrication of structural color, crystal color pattern, and display fiber are all summarized in Fig. 15. Several top-down and bottom-up printing processes have been developed to create structural colors that mimic





**Fig. 14.** 3D printing of optical fiber for display. (a) 3D printed pipeline to create displays of arbitrary shape; Copyright from Ref. [125]. (b) The external and internal structures of the printed objects; Copyright from Ref. [126]. (c) Printing procedure, output end images and microscope image of fiber optic faceplate and image guiding capability of 3D printed faceplates; Copyright from Ref. [127]. (d) Ruled display surfaces, spheric display surfaces, PAPILLON production pipeline and dynamic animated eyes with PAPILLON; Copyright from Ref. [128].



**Fig. 15.** Schematic diagram showing the materials and 3D printing methods used in 3D printing of photonics for display.

natural structures and material systems which are highly energy-efficient and possess amazing optical properties such as scattering, reflection, polarization, diffraction, and refraction. Layer by layer deposition, lithography, self-assembly, and biomimetic templates are used to create structures such as multilayer reflectors, scattering structures, diffraction gratings, and photonic crystals. In terms of photonic crystals, they use a photonic bandgap to control the light that propagates through, and they are commonly fabricated by inkjet printing based self-

assembly. As for optical fiber, multi-material 3D printing technologies show advantages and the printed optical fibers can be used in different applications, such as sensing, illumination, communications.

### 5. 3D printing of optical metamaterial

Optical metamaterials are materials with novel artificial structures composed of subwavelength units. Optical metamaterials have



extraordinary physical properties that cannot be discovered by natural materials, such as negative refractive index, negative permeability, negative dielectric constant and inverse doppler effect [129,130]. The properties of metamaterials are determined not by the intrinsic properties of the unit materials, but also by the shape and distribution of the unit structures [131,132]. By adjusting the size and arrangement of cell structures, the working frequency and electromagnetic response characteristics of optical metamaterials can be controlled respectively. Metamaterials have great application prospects in stealth technology, optical field control, communication technology, sensor technology and so on [133]. The permittivity and permeability of optical metamaterials can be adjusted in the range of positive, zero and negative numbers to realize the regulation of electromagnetic field. Through the design of resonance unit, it can be applied to stealth cloak, super diffraction limit lens imaging, perfect absorber and other fields [130].

The traditional manufacturing methods, such as etching and machining, have limitations on the fabrication of optical metamaterials. Printed circuit board (PCB) is composed of periodic arrangement of metal structure units printed on the dielectric substrate, which is widely used in the manufacturing of metal resonant metamaterials. However, copper-containing etching solutions are prone to cause irreparable pollution to the environment and are only suitable for the building of a 2D plane of the microwave band, which limits the development of the 3D cell structures and the extension of the optical wave band of metamaterials [134]. In the etching process, photosensitive polymer is made into a certain pattern of anti-corrosion film, and the desired pattern is further formed on the surface of the sample through the exposure of focused electron beam. The high cost and long period of etching technology limit the large-scale manufacturing of complex 3D metamaterial [135]. In term of machining, such as wire cutting, micro milling and other technologies, macro 3D structures are formed by removing the material. However, machining is difficult to meet the accuracy requirements of complex cell array, and the production repeatability is poor [136]. Hence, the traditional manufacturing processes are not competent for the manufacturing and precision control of large-scale metamaterials. 3D printing brings new opportunities to develop optical metamaterial [137]. The 3D printed optical metamaterials have achieved good results in practical applications, such as optical stealth and optical field control. Based on the principle of transform optics, the distribution of electromagnetic parameters is designed to guide the electromagnetic wave around the space surrounded by the stealth cover and reconstruct it to the shape of incident. The wave guiding process is equivalent to the situation that there is no interference to the propagation of electromagnetic wave inside the invisibility cover, which realizes perfect invisibility [138]. The optical metamaterials can process the wave front with sub wavelength spatial resolution, and achieve specific functions, such as high efficiency and large angle bending light to focus, fully control the phase and polarization of light, and adjust the orbital angular momentum [139]. In addition to the control of traditional light field, the research of optical metamaterials has been extended to the generation and control of quantum light. In this section, the current status of 3D printing of optical metamaterials and structures are discussed.

### 5.1. 3D printing of metamaterial for cloak

The appearance of metamaterials with negative refractive index makes the parameters of the medium change continuously and achieve the effect of perfect control. Based on the form invariance of Maxwell's equation, the concept of spatial deformation is introduced, and a corresponding relationship between constitutive parameters and spatial deformation is established. This relationship is designed to guide the electromagnetic wave around the shelter without reflection and loss, so as to achieve stealth. With the optimization of structure design and the improvement of machining accuracy, the application scope of this stealth technology is extended from microwave band to visible light

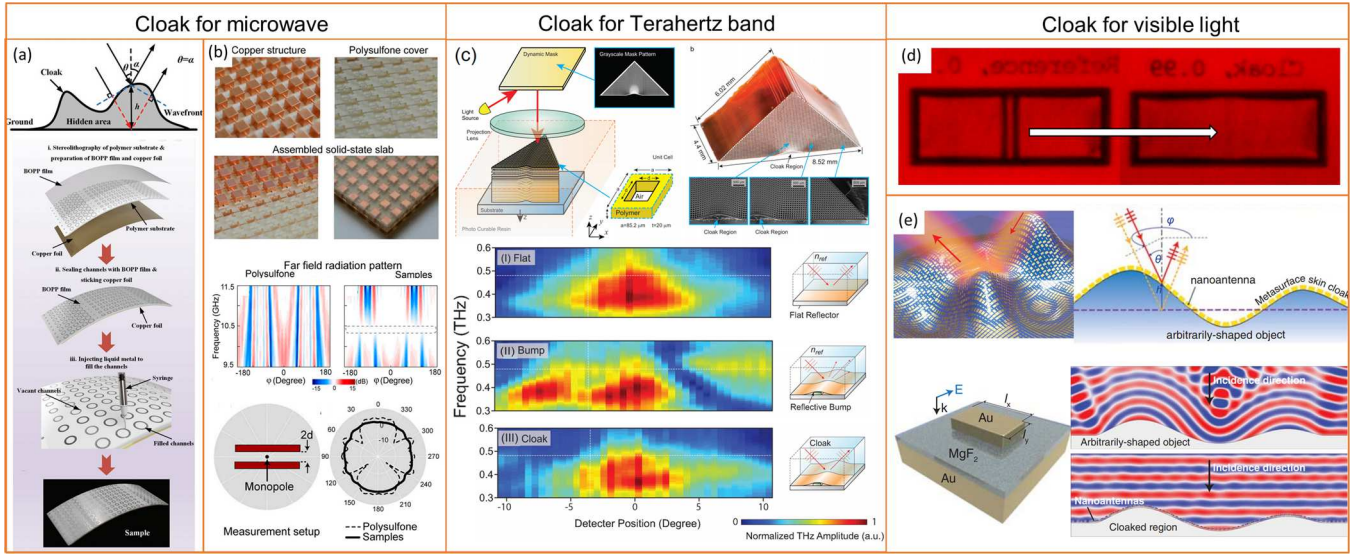
band, from micro-object to macro-object, and the stealth cloak itself is developing towards ultra-thin and flexible direction.

By combining 3D printing technology with liquid metal injection molding, an ultra-thin arched stealth carpet cloak suitable for microwave band was developed. The substrate was printed by SLA, and the channel was sealed with polypropylene film. Then gallium indium tin alloy was injected into the channel to form a metal ring. The cloak can suppress the additional strong scattering of bump in the range of 43° transverse magnetic (TM) polarization, 37° transverse electric (TE) polarization bandwidth and 28° angle span, and achieve good stealth characteristics. The application of 3D printing technology makes the substrate stable enough to maintain delicate phase distribution and is suitable for arbitrary geometric shapes such as spherical surface and paraboloid. The schematic diagram of arched invisibility cloak simulating ground reflection and the preparation process of metasurface stealth cloak are presented in Fig. 16a [140]. The metasurface with periodic metal block resin structure is fabricated by combining SLA technology with metal sputtering technology, which can achieve the air like characteristics without reflecting and refracting light [141]. Accura 60 was fabricated into cubic plastic array by SLA, then 50  $\mu\text{m}$  copper was sputtered and embedded into the PSU cover layer [141]. This kind of metal mesh can obtain low scattering amplitude by adjusting the node frequency of scattering channel, and realize the self-invisibility of microwave band, which can be used to make perfect antenna cloak (Fig. 16b) [141].

A wide-band invisibility cloak working from 0.3 to 0.6 THz can be made by PuSL. The subwavelength hole structure is designed based on the principle of transform optics to extrude the plane refractive index to achieve stealth. 3D solid model slices were projected onto the surface of 1,6-hexanediol diacrylate (HDDA). After UV curing layer by layer, isopropanol was used to remove the residual in the hole. The experimental results show that the cloak can well hide the geometric and spectral characteristics of  $\alpha$ -lactose monohydrate absorber. The experimental results of fabrication of terahertz stealth cloak and hidden absorber are shown in Fig. 16c [142]. By using direct laser writing lithography technology, it is possible to make a 3D stealth carpet cloak working at 700 nm. The local effective refractive index of polymer wood pile photonic crystal can be adjusted by changing the local volume filling rate to achieve stealth. The stealth cloak is independent of the polarization state of the incident light and is suitable for the wide band of 600–3000 nm. The true color reflection optical micrographs of the three-dimensional reference structure (upper part) and three-dimensional stealth structure (lower part) are shown in Fig. 16d. It can be seen that the concave convex fringe is well concealed [143]. Meta atoms in sub wavelength scale can form an ultra-thin invisibility cloak for visible light. The resonant elements composed of Au-MgF<sub>2</sub>-Au layer by layer can achieve specific light polarization by compensating the phase deviation and hide 3D objects of arbitrary shape. The invisibility cloak can not only be extended to the macro size to hide the visible objects, but also be used to hide the objects with obvious edges and sharp features. The working principle of a metasurface skin cloak, metasurface design and full-wave simulation results for the metasurface skin cloak are shown in Fig. 16e [144].

### 5.2. 3D printing of metasurface for laser beam modulation

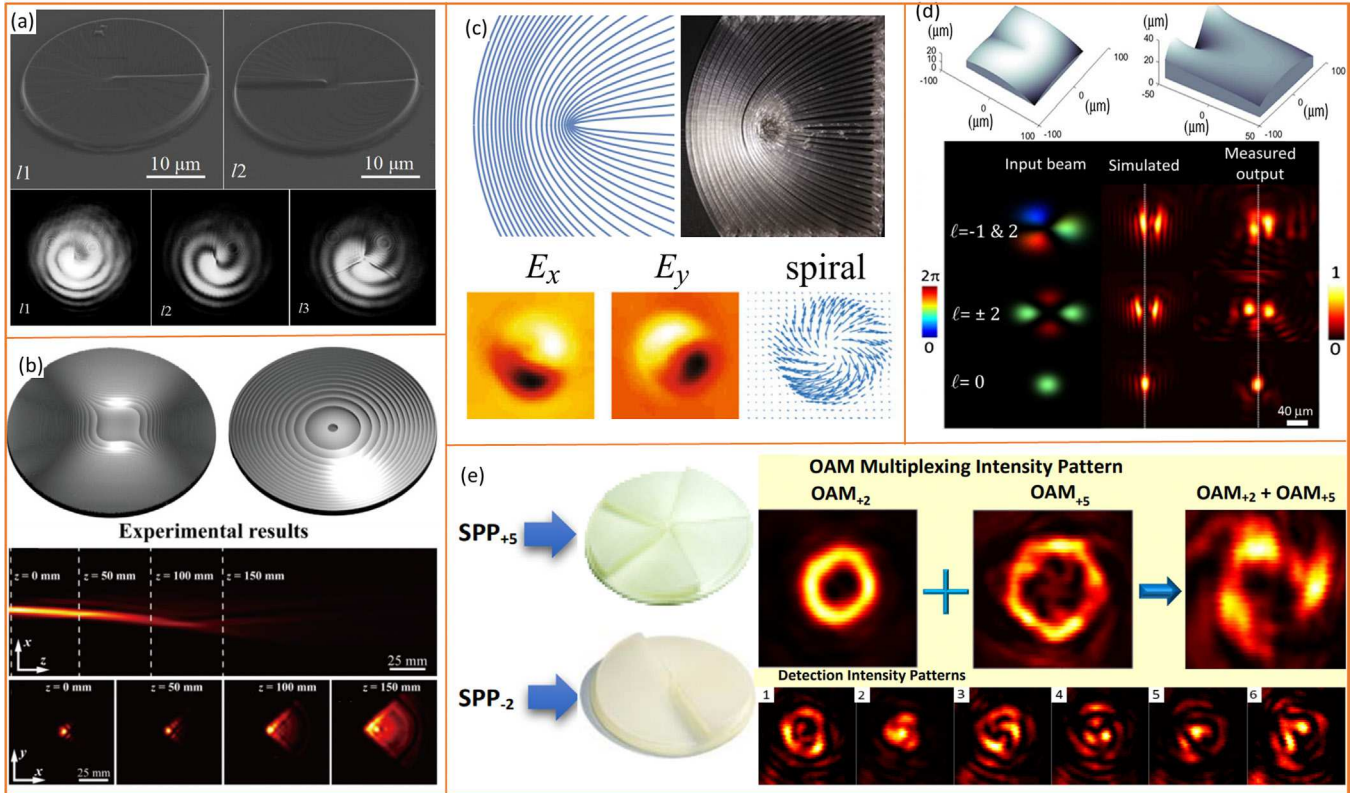
The optical wavefront processing capability of sub wavelength spatial resolution of metamaterials can generate structured beams with special phase or polarization singularity with high accuracy. Vortex beam is a kind of structured beam with spiral distribution of phase wavefront and orbit angular momentum. It has a wide range of applications in particle control, optical communication, rotating body detection, biomedicine and other fields. Phase plate is a common method to generate vortex beam. Due to the high resolution of 3D printing technology, the preparation of high quality and high precision phase plate becomes easier. A spiral phase plate with 40  $\mu\text{m}$  diameter



**Fig. 16.** 3D printing of metasurface for cloak. (a) Schematic diagram of arched invisibility cloak and preparation process of metasurface stealth cloak; Copyright from Ref. [140]. (b) Fabrication process of stealth hypersurface and far field radiation pattern at 10.4 GHz; Copyright from Ref. [141]. (c) Fabrication of terahertz stealth cloak and experimental results of hidden absorber; Copyright from ref. [142]. (d) Comparison of micrographs of reference structure and stealth structure under 700 nm illumination; Copyright from Ref. [143]. (e) Working principle of a metasurface skin cloak, metasurface design and full-wave simulation results for the metasurface skin cloak; Copyright from Ref. [144].

and 50 nm step height can be printed on the fused silica substrate Using TPP in a few minutes [145]. Due to fast writing speed and high resolution, the 3D printed plate makes the conversion of Gaussian laser beam

to vortex beam efficient and convenient. The SEM images of helical phase plates and interference of a vortex beam with a spherical wave for spiral phase plates (SPPs) with different topological charges are shown



**Fig. 17.** 3D printing of metasurface for laser adjustment. (a) SEM images of helical phase plates and interference of a vortex beam with a spherical wave for SPPs with different topological charges; Copyright from Ref. [145]. (b) Height profile of diffractive element, simulation (upper part) and experimental (lower part) results of the finite-energy accelerating THz airy beam; Copyright from Ref. [146]. (c) Theoretical model of q-plate and 3D printing of q-plate entity and transverse amplitude measurements with THz-TDI; Copyright from Ref. [147]. (d) Design of theoretical multiplexer/demultiplexer for conversion and correction elements, schematic design and results of the optical setup for testing the vortex multiplexer; Copyright from Ref. [148]. (e) Schematic diagram of 3D printing spiral phase plate and experiment results of OAM multiplexing; Copyright from Ref. [149].



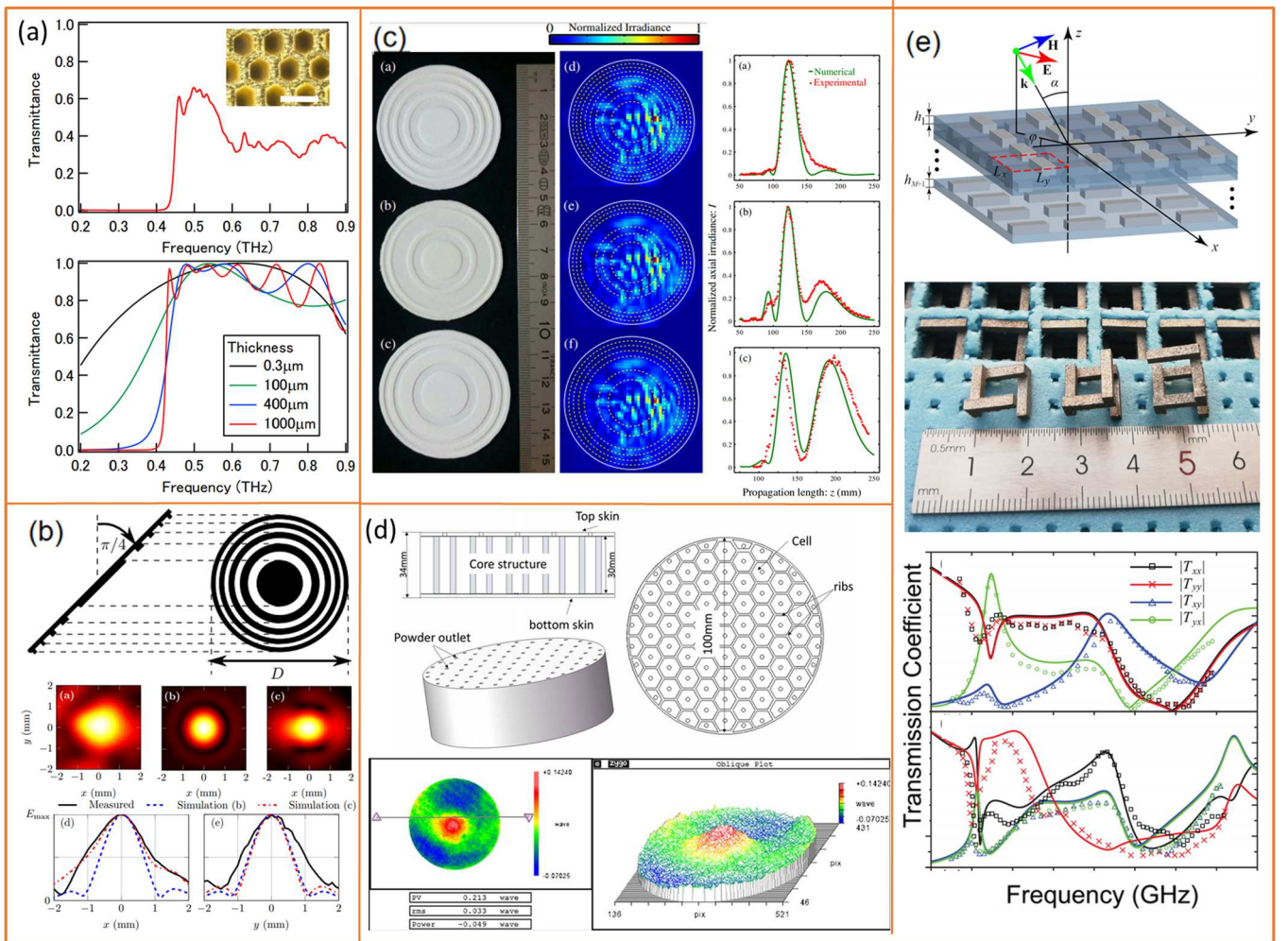
in Fig. 17a [145]. Besides, 3D printing technology is used to make the rigid opaque material into diffractive element. The additional cubic phase difference is introduced into the incident Gaussian beam while the photon loss is reduced, which is used to generate a non-diffractive Airy beam. For example, the height profile of the diffractive element, simulation (upper part) and experimental (lower part) results of the finite-energy accelerating THz airy beam are shown in Fig. 17b [146]. In addition to introducing special phase, 3D printed continuous q-plate can be used to generate cylindrical vector beams with non-uniform transverse polarization patterns [147]. Polystyrene was deposited layer by layer along the optical axis streamline by the melt deposition method, which printed out the soft and continuous track structures. In this method, the optical q-plates were fabricated at a lower cost to generate complex structured vector beams, which was convenient for the study of special physical phenomena in singular optics. The theoretical model of the q-board, the 3D printed q-board entity and transverse amplitude measurements with terahertz time-domain imaging (THz-TDI) are shown in Fig. 17c [147].

Meanwhile, the orbit angular momentum of the vortex beam provides a new degree of freedom. Through the design of the phase plate microstructure, the orbital angular momentum (OAM) of the vortex beam can be reused and demultiplexed, which can greatly improve the communication capacity and transmission rate of the communication

system. The micro eddy current mode separator made of negative photoresist by using TPP technology can combine or separate the OAM state of vortex beam. In TPP process, photosensitive materials are polymerized through nonlinear two-photon absorption mechanism to achieve arbitrary shape printing. The finished products can reach micrometer scale and can be directly integrated into the optical system, opening up the way for the application of vortex beam as information carrier in the field of communication [148]. A theoretical multiplexing/demultiplexing design for the conversion and correction elements, schematic design and results of the optical setup for testing the vortex multiplexer are shown in Fig. 17d [148]. The spiral phase plate manufactured by 3D printing technology can also be used for multiplexing and demultiplexing of different OAM modes [149]. The helical phase plate is made of polypropylene material, of which the absorption loss is negligible, and the crosstalk between OAM mode and unexpected mode is less than  $-11$  dB [149]. This technology can make full use of terahertz gap and expand the range of free optical communication. A schematic diagram of a 3D printed spiral phase plate and experiment results of OAM multiplexing are shown in Fig. 17e [149].

### 5.3. 3D printing of metasurface for optical field manipulation

Metamaterials have different electromagnetic characteristics from



**Fig. 18.** 3D printing of metasurface for optical field manipulation. (a) Radiation transmission spectra of metamaterials with different thickness and schematic diagram of hexagonal hole array metamaterial; Copyright from Ref. [150]. (b) 3D printed reflective zone plate and field distribution in focal plane of reflected beam at 530 GHz; Copyright from Ref. [151]. (c) Experimental models of 3D printed THz diffractive lenses and results of axial PSF measurements; Copyright from Ref. [51]. (d) Digital model of aluminum alloy mirror and surface accuracy of the 3D printed Al alloy mirror; Copyright from Ref. [152]. (e) 3D printed metal spiral structures and the simulated cross-polarization transmission of linearly polarized waves based on the 3D printed metasurfaces; Copyright from Ref. [153].



traditional natural materials. Through the design of resonance unit structures, the equivalent electromagnetic parameters of metamaterials can be effectively controlled in a specific frequency band. Coding the required phase profile to the metasurface can optimize the functions of traditional optical devices, such as filters, waveband plates, lenses, mirrors, polarizers, etc., and realize the manipulation of optical field with high precision and resolutions. Besides, 3D printed optical metamaterials can provide a variety of functions to replace the combination of multiple traditional optical devices.

For example, the hexagonal hole array metasurfaces printed by SLA can be used as high pass filters with high cut-off frequency, and the cut-off frequency is controlled by changing the hole size [150]. In the manufacturing process, acrylic resin was cured by using a nano laser beam, and a thin metal layer was electrodeposited on the cured parts [150]. This 3D printing technology enables the fabrication of planar structures on the function of components with high resolution [150]. The radiation transmission spectrum of different thickness metamaterials and the schematic diagram of hexagonal hole array metamaterials are shown in Fig. 18a [150]. The terahertz reflective waveband plate made with titanium alloy powders using SLM printing process has a reflection efficiency of more than 90% at 530 GHz. This 3D printing technology is suitable for the fabrication of a variety of metal materials with good conductivity and not easy to oxidize. Due to the high-resolution fabrication capability, the surface roughness was improved so that the photon loss was reduced and the reflectivity was improved [151]. The 3D printed reflective zone plate and the field distribution of the focal plane of the reflected beam are shown in Fig. 18b [151]. The diffractive lens made of polyamide powder by using SLM can be applied for focusing and imaging in terahertz band, and further produce the unique phenomenon of focal length expansion and double focus.

3D printing technology not only provides a rapid and economical scheme for making complex lenses, but also improves the diffraction efficiency of multilayer diffractive lenses with high resolution. For example, Fresnel lens, fractal lens and Fibonacci lens were fabricated by using 3D printing approach (Fig. 18c) [51]. The 3D printed THz diffractive lenses showed the result of axial PSF measurements which can be predicted by using numerical model [51]. A light aluminum alloy mirror with uniform and stable structures was made by SLM and replication technology. The superposition characteristic of 3D printing not only reduced the mass without sacrificing the rigidity of the mirror, but also reduces the processing time of complex parts greatly. The resin replication technology further improved the surface roughness, of which the product can reach 2 nm while ensuring surface accuracy. Moreover, the optimization of processing parameters improved the product performance and also reduced the cost of materials and time. The design of mirror and the surface accuracy of the 3D printed Al alloy mirror are shown in Fig. 18d [152]. By using SLM technology, the cobalt chromium alloy was made into a chiral super surface composed of a square spiral array, which can be used for arbitrary polarization conversion and separation. Different functions can be realized by designing the spiral microstructures with different geometries. For example, even number of spirals was used for asymmetric transmission in dual band, and odd number of spirals provided the same polarization conversion in any polarization direction. The resolution of SLM printing approach reached tens of microns so that 3D printed metal structures with complex geometries and high-precision can be used for terahertz wave processing. The schematic diagram of the metal spiral structures with different numbers and simulated cross-polarization transmission of linearly polarized waves are shown in Fig. 18e [153].

#### 5.4. Summary and outlook

Optical metamaterials have unique electromagnetic properties and exhibit super strong capability to control the light. From the regulation of classical light field to the field of quantum optics, metamaterials

become a promising new material that are widely used in industry, military and civil. 3D printing technology shows advantages in the manufacturing of complex structures and multi types of materials. The high processing precision of 3D printing is beneficial to the design of microstructure of metamaterials, and the expansion of the action frequency band can be realized while improving the device performance. The materials and 3D printing methods used for the fabrication of cloak, optical laser adjustment, and optical field adjustment are summarized in Fig. 19. 3D printing provides convenience for the development of flexible and scalable optical metamaterials. However, there are still some issues and challenges in 3D printing of optical metamaterials. For example, there are certain restrictions on the selection of materials in 3D printing of optical metamaterial, and it is still difficult to realize synchronous manufacturing of structures using multiple types of materials. Due to the material limitation, 3D printed optical metasurfaces are lack of strength and easy to damage which will directly affect the phase control of metamaterials. 3D printing technology is not as good as the relatively mature etching process in machining accuracy and has insufficient advantages in the fabrication of nanoscale microstructures.

The ability of metamaterials to freely control classical light on the sub wavelength scale has been explored. Although the role of metamaterials in quantum optics is still relatively unknown due to the loss characteristics of many sub wavelength components, quantum multiphoton interference and state reconstruction using the metasurfaces composed of nano resonators has been realized in 2018 [154], and quantum entanglement of spin and orbital angular momentum of photons using a dielectric metasurface composed of anisotropic nano antennas were achieved in the same year [155]. Since then, the research on metamaterials in quantum optics has been carried out gradually. Currently, due to the lack of processing accuracy and material properties, 3D printing technology has not been applied to the manufacturing of metamaterials in the field of quantum optics. The laboratory researches haven't given full play to the advantages of 3D printing technology, such as geometry complexity, low cost and rapid prototyping. With the development of metamaterial design theory and the maturity of 3D printing processing technology, the preparation of optical metamaterials will span from the micro field to the macro field, from the classical optical field to the quantum optical field. The applicable spectral range will be further expanded, and more supernatural and unconventional characteristics will be obtained.

## 6. Conclusion and perspectives

3D printing shows many excellent performances on the fabrication of optics components with structures which traditional manufacturing cannot achieve. For example, compared to the traditional manufacturing of optical waveguide, which mainly include high temperature and hazardous hot-draw processes, micromachining workflows, hand assembly and draw tower, 3D printing can produce this optical component in one step, and it also can be used to build THz waveguides with more accurate resolution in a repeatable way. Many different materials, including optical glass, crystal, polymers, metal and some special materials, have been used to fabricate optical devices using 3D printing technologies [89]. 3D printing processes such as FDM, SLM/S, TPP, DLW, DLP, and SLA, demonstrate the suitability and characteristics of building different optical materials [89]. Currently, many commercially available 3D printers based on different manufacturing principles and a large selection of materials with excellent performance can be used to produce optical devices with specific properties. Selection of 3D printing techniques depends on the raw materials, processing speed and resolution, cost of time and materials, and optical performance requirements of final products [31]. 3D printed optical devices show versatile applications in imaging, sensing, coloring and displaying and the status of 3D printed optical devices is shown in Fig. 20. In term of imaging, 3D printed optics involve cross-scale manufacturing of optical materials with resolution freely switching

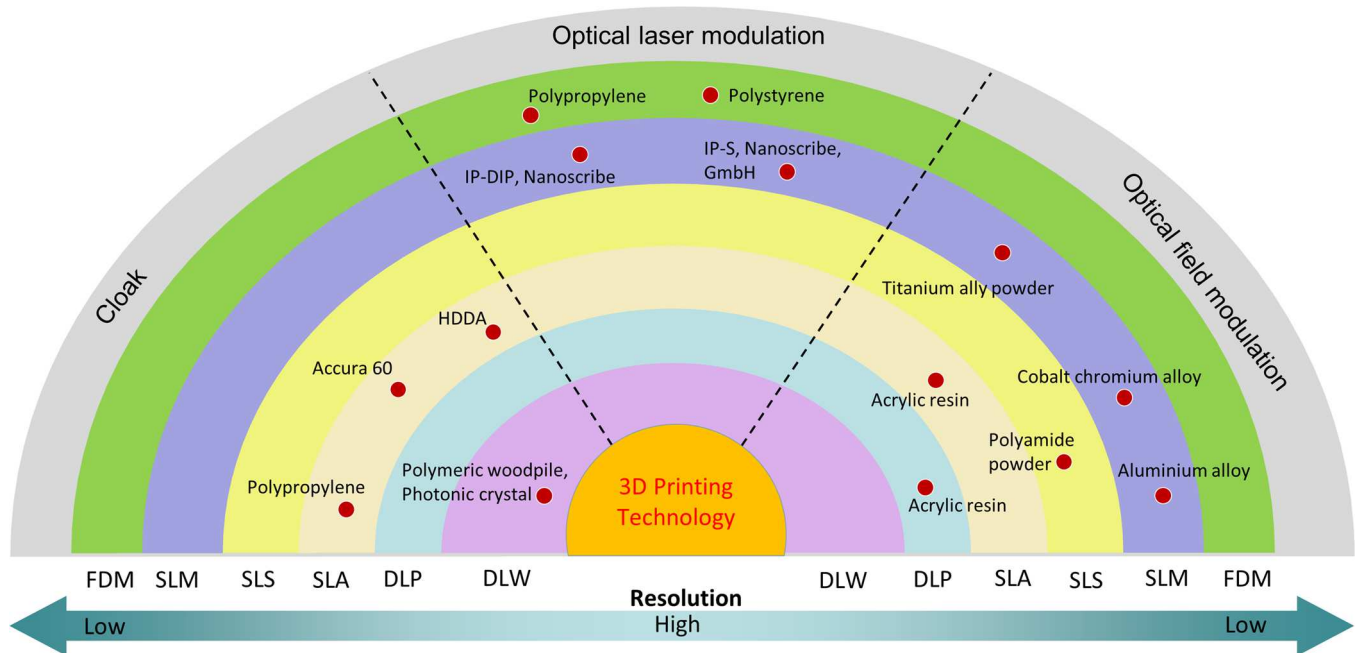


Fig. 19. Schematic diagram showing the materials and 3D printing methods used for cloak, optical laser adjustment, and optical field adjustment.

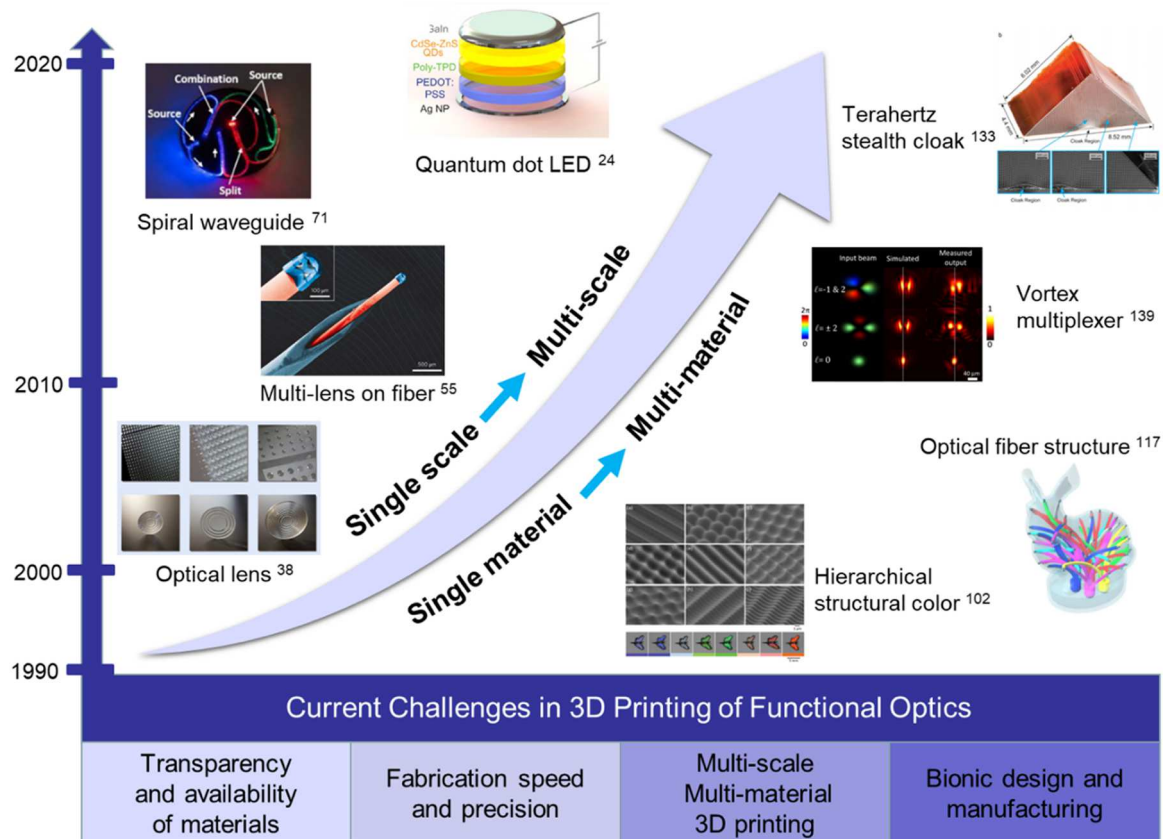


Fig. 20. The technological trends of 3D printing of functional optics in the past thirty years.

from nanoscale to macroscale [89]. The 3D printed optoelectronic devices for sensing are LEDs, photodetector waveguides, LD, and SCs, and their working capability shows a promising application prospect in different fields. The structural color can be achieved by designing the nanoscale and microscale bioinspired structured and 3D printing

provide capability to reproduce such hierarchical structures using crystal-based materials. Besides, 3D printed optical fibers have widely used for developing functional devices for imaging, sending, coloring and displaying. Optical metamaterials attract a lot of research interests and lead to unique applications because of their special ability of light



manipulation.

3D printing has the advantages such as high fabrication speed, high-resolution, large-area manufacturing, less material consumption, accurate replication assisted by computer modeling, and it greatly reduces the cost for optics manufacturing. 3D printing can be applied to the fabrication of any shape surface such as spherical surface, paraboloid, etc., which brings new opportunities in the development of optical devices. Benefiting from 3D printing of optical components, application in structural color, art, beam splitting, combiner circuits, optical encoding radiance of light, and light manipulation for display are investigated. Optimizing structure design and improving fabrication accuracy, the application scope of 3D printed optics has been extended from visible light band to microwave band. However, limitations and drawbacks are also existed in 3D printing of optical functional structures and materials. The current challenges in the field of 3D printing of functional optics are listed in Fig. 20. Specifically, the material is a major aspect holding the development of 3D printing of functional optics for different purposes. For examples, the transparency of materials is a major issue of 3D printed optical lens, and the lack of available material options is slowing down the research progress for optoelectronics and metamaterials. Most of 3D printing processes are developed for rapid prototype and it is hard to be extended for mass production. Another major obstacle is that 3D printing is developed with the focusing of single scale fabrication and current commercial 3D printers are hard to fabricate multiscale structures, which determines the functionality of optical components. Meanwhile, there exists a tradeoff between the fabrication efficiency and resolution. Thus, a lot of developments still are required in the development of 3D printing technologies based on new principles (Fig. 21).

Investigating new materials and structures and developing novel 3D printing processes will lead us to drive the 3D printing of optics forward (Fig. 21). First of all, the introduction of multi-materials and multi-scales structures into optical components design has a positive synergistic effect on the performance of printed optical devices. Multi-scale and multi-material 3D printing process should be developed to address the challenges in the field of 3D printing of optical components. Besides, one potential direction is to make more innovations of optical devices using 4D printing process, through which 3D printed components can transform and assemble in a programmable way. 4D printing not only increases the manufacturing efficiency, but also open opportunities for

manufacturing optical components that are difficult to assemble using other approached. In addition, eco manufacturing of optics is also a topic remaining to explore especially when sustainable development is extremely important for the daily life in the future. New 3D printing should be developed to facilitate the production of optical parts by using recyclable, renewable, naturally degradable and non-toxic materials.

Biomimetic 3D printing of optics is also a promising research field. Biological materials in nature exhibit specific optical properties due to their unique structures and material system, which can create, shape, and manipulate light [89,156]. By studying the mechanism of natural optical structures and material system, new types of optical devices with excellent performance can be developed based on bionic design using 3D printing, which demonstrate its capability to fabricate complex and multiscale structures over traditional manufacturing approaches. Besides, current status of 3D printing optics is remaining in research stage, and how to transfer the accomplishment of research outcomes into repeatable industrial productions using low-cost materials is an issue to be solved. The integration of advanced optical materials and cutting-edge 3D printing technologies provides researchers with unprecedented opportunities to overcome obstacles in manufacturing functional optics. The manipulation of programmable material helps to produce optical devices with different properties to meet needs under specific occasions, which expands the scope of 3D printing of functional optics.

The development of 3D printing, as a new and promising manufacturing method, will be pushed the application of advanced optical devices into a new generation. Therefore, it is reasonable to prospect that more and more applications of additive manufacturing will appear in the fabrication of optical devices. For example, multiscale hybrid lens can be developed with photocurable resin by using photon-based lithography [157]. Quantum optics and smart optical interaction devices will be major research direction in the 3D printing of optics. Moreover, functional components such as lens, waveguide, LED, photonics, and SCs, will open new opportunities for develop advanced optical devices for various applications, including aerospace, biomedical engineering, computational imaging, energy harvest, camouflage [158–161].

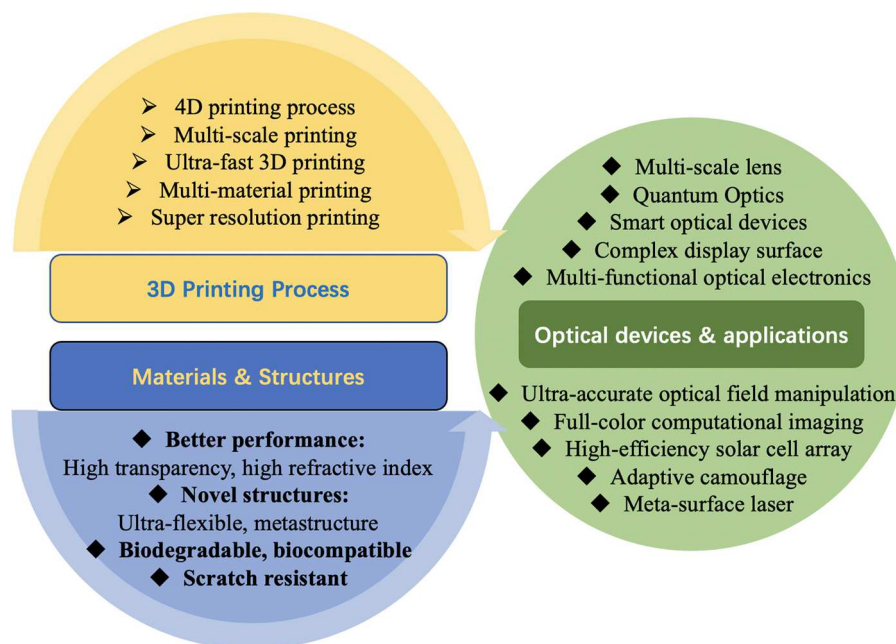


Fig. 21. Integration of new materials and structures, and novel 3D printing processes to enable innovations in optical applications in the future.

## CRedit authorship contribution statement

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## Declaration of Competing Interest

The authors declare no conflict of interests.

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