catalysts

Review

Catalytic Materials by 3D Printing: A Mini Review

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Abstract: Catalytic processes are the dominant driving force in the chemical industry, proper design and fabrication of three-dimensional (3D) catalysts monoliths helps to keep the active species from scattering in the reaction flow, improve high mass loading, expose abundant active catalytic sites and even realize turbulent gas flow, greatly improving the catalytic performance. Three-dimensional printing technology, also known as additive manufacturing, provides free design and accurate fabrication of complex 3D structures in an efficient and economic way. This disruptive technology brings light to optimizing and promoting the development of existing catalysts. In this mini review, we firstly introduce various printing techniques which are applicable for fabricating catalysts. Then, the recent developments in 3D printing catalysts are scrutinized. Finally, challenges and possible research directions in this field are proposed, with the expectation of providing guidance for the promotion of 3D printed catalysts.

Keywords: 3D printing; catalysts; 3D framework; structure design

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1. Introduction

Since its emergence in the 1980s, [1] three-dimensional (3D) printing technology, also known as additive manufacturing, has attracted much attention owing to its ability to fabricate 3D intricate structures rapidly [2–4]. This technique constructs 3D structures via a layer-by-layer process, which is controlled by digital model files. Theoretically, any varisized 3D structure from the nanoscale to meter-scale can be realized by 3D printing technology through the control of computer-added modeling [4,5], ignoring the high demands of resolution of equipment and development of printable materials. This promising technology brings new insights into the fields of mechanical engineering, biological [6,7], medical [8], electronic, etc., and in recent years, it has gradually penetrated into energy storage and conversion [9–12].

Catalytic processes are the key for various energy storage and conversion technologies such as fuel cells [13–15], metal-oxygen batteries [16–18], CO_2 reduction [19–21], etc., since the application of catalysis makes these processes easier toward target products [22–24]. When serving in certain systems, in case of being scattered, catalyst powders must be interconnected and shaped into common contactors or tightly loaded onto the surface of scaffolds. Traditional processing techniques such as wet-jet spraying for granules and pelletization under pressure limit the dynamic properties of catalysts, while the extrusion process limit the free design of the complex structure. The application of 3D printing technology endows free design and fabrication of complex porous structures including periodic or gradient structure [25–27], high loading of active species with thoroughly exposed active sites can be easily realized. In some cases, proper structure design will change the gas flow from layer to turbulent mode, greatly improving the catalytic efficiency. Further, combined with selective post-treatments, hybrid catalytic properties can be achieved [28]. Thus, 3D printing technology shows great potential in the catalytic area with the promise of unleashing the maximum potential of the existing catalysts, and optimizing their mass transfer, pressure drop, and reactivity.

In this review, we will briefly introduce various 3D printing techniques suitable for catalysts' printing and their working mechanisms. The recent developments of 3D printing catalysts focusing on monolithic catalysts and catalysts' supports in various catalytic systems are scrutinized. Finally, challenges and perspectives in this field are proposed.

2. Printing Strategies for Catalysts

As a disruptive manufacturing technology, 3D printing can be mainly categorized into material extrusion-based, vat photopolymerization-based and powder-based techniques according to their printing mechanisms, and each of these categories includes several specific techniques. Among them, direct ink writing (DIW), fused deposition modeling (FDM), stereolithography (SLA), digital light processing (DLP), selective laser melting (SLM), and selective laser sintering (SLS) techniques have been reported for constructing catalysts. In this section, we will briefly introduce these 3D printing technologies for catalysts.

2.1. Material Extrusion

Material extrusion 3D printing techniques, mainly including direct ink writing (DIW) and fused deposition modeling (FDM), are quite traditional and easy to operate. Objective materials can be directly made into inks or filaments, after extrusion from nozzles, the designed structure can be obtained.

2.1.1. Direct Ink Writing (DIW)

DIW printing technique fabricates structures by continuously extruding rheological inks from the nozzle with the help of air pressure. The motion of the nozzle and platform can be controlled by computer-added design software [29–31]. With the layer-by-layer deposition of extruded inks, the 3D structure can be realized (Figure 1a). A wide range of materials can be printed by DIW, refs. [32–34]; that is one of the most important reasons why DIW becomes the most widely applied printing technique for catalysts, but the preparation of functional inks is quite important and challenging. To ensure the inks flow smoothly from the nozzle and then maintain the structure during the solidification process after deposition, the rheological properties of inks need to be adjusted [35]. Thus, various additives are added to the slurry to produce high-performance printable inks, which makes the exploration of high-quality functional inks a hot research topic.

2.1.2. Fused Deposition Modeling (FDM)

Similar to DIW, the FDM technique also builds 3D products by extruding materials through a nozzle and depositing them onto the platform, and the structure fabrication is realized by the movement of the nozzle and platform. The difference is that the extrusion materials are thermoplastic filaments, which need to be heated to a semi-molten state at the tip of the nozzle for extrusion, and then quickly solidified after their extrusion and deposition on the platform [36,37] (Figure 1b). Materials suitable for FDM are very limited, to make printable filaments, a large amount of thermoplastic materials are required. But it is easier to produce printable filaments than printable inks, which is the merit of the FDM technique. If we would like to print catalysts by FDM, catalyst particles can be embedded into the thermoplastic matrix to produce catalysts containing printable filaments, or the active species can be post-loaded on the surface of printed 3D supports.

These two techniques have been widely applied in extended fields, the printing quality of the products mainly depends on the properties of feedstocks (inks or filaments). In most cases, to make printable feedstocks, electrochemical inert additives are necessary, thus we must balance the printability and electroactivity [38]. As well, extruded products usually suffer from relatively poor accuracy.

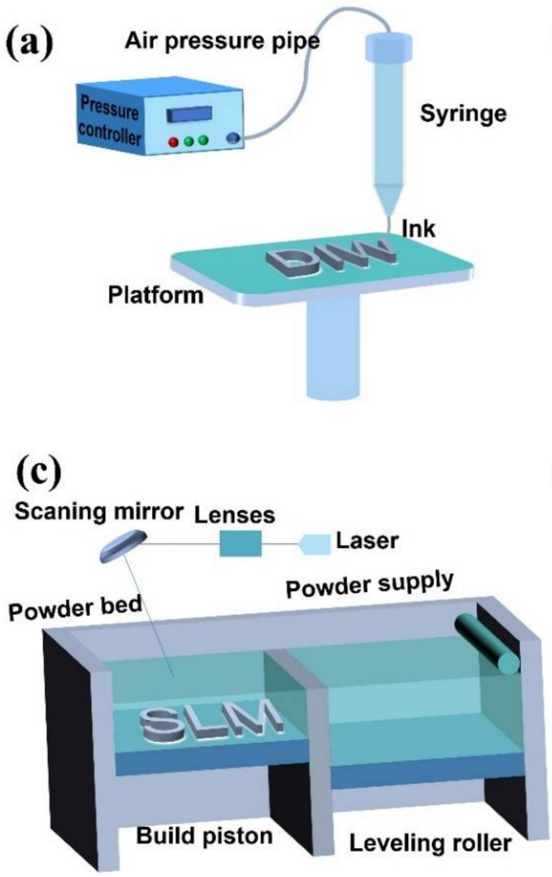

Figure 1. Schematic diagrams for (**a**) DIW, (**b**) FDM, (**c**) SLM and (**d**) SLA 3D printing strategies.

2.2. Vat Photopolymerization

Vat photopolymerization is a kind of light-based 3D printing technique. Three-dimensional structures are built via polymerization of photosensitive resin which is precisely controlled by a certain light source. By this technique, the designed structure can be rapidly prototyped with high accuracy. But for the printing of catalysts, it also needs to disperse catalysts particles into resin for the printing process.

2.2.1. Stereolithography (SLA)

SLA is a typical vat photopolymerization-based printing strategy, when the liquid light-curing resin in the tank is hit by the moving light spot, it solidified quickly. After the designed slice is constructed with the hit of focused light spot point by point, the platform descends and the printing of the next layer starts (Figure 1d). The whole process is also instructed by a computer, and a designed structure with high resolution can be rapidly constructed by SLA [39,40].

2.2.2. Digital Light Processing (DLP)

The working mechanism of DLP is much similar to that of SLA, but instead of dependence on moving light spots, a high-resolution digital optical processor is equipped, and it can directly print the designed pattern of a single layer [41,42]. As a result, the printing speed is improved.

2.3. Powder-Based Strategy

2.3.1. Selective Laser Melting (SLM)

SLM is generally applied to construct the metallic structure. During the printing process, metal powders are completely melted by high-energy laser irradiation and then solidified quickly (Figure 1c). With the instruction of a computer, the designed structure can be fabricated by repeating the melting and solidifying process layer by layer [25,43].

2.3.2. Selective Laser Sintering (SLS)

In a typical SLS process, particles with a lower melting point are previously added, with the irradiation of the laser, these added particles are partially or completely melted and serve as binders, aiding the formation of 3D structure [44,45].

3. 3D Printing for Catalysts

Similar to the 3D printing processes in other fields, the preparation of feedstocks containing active species is the pivotal step [46–48]. To make catalysts printable, proper solvents and/or various additives are necessary for preparing satisfying feedstocks, and in some cases, post-treatments are required for the formation of final products. While for 3D printing catalysts, it is unique in that we must make efforts to maintain the structure of the catalyst particles during ink formulation, since the active species may decompose if they react with other ink components such as binders, plasticizers, or solvents. Besides, the maintenance of physiochemical properties of active particles such as surface area and pore structure must be under consideration. In a word, we must try to hold the active sites of the catalyst particles during inks formulation and printing processes. For practical application, mechanical properties and thermal stability of the 3D scaffolds are also important parameters.

3.1. 3D Printing of Monolithic Catalysts

DIW is generally applied for the printing of monolithic catalysts, since various catalytic materials such as molecular sieve carbon materials, and metal catalysts can be directly printed into the designed integrated structure by adding these active species into printable inks. Further, 3D printing technology also enables free doping by simply adding the doping sources into the printing paste, of course, the phase and concentration of dopants can be freely adjusted [49].

Thus, a series of related works have been reported. For instance, Liu's group [50] reported 3D printed porous carbon with controllable structure and tailorable pores, which was applied as metal-free catalysts (Figure 2). By designing and constructing a 3D carbon framework with various meso/macro pores, the catalytic performance for benzyl alcohol conversion was enhanced while maintaining high benzaldehyde selectivity.

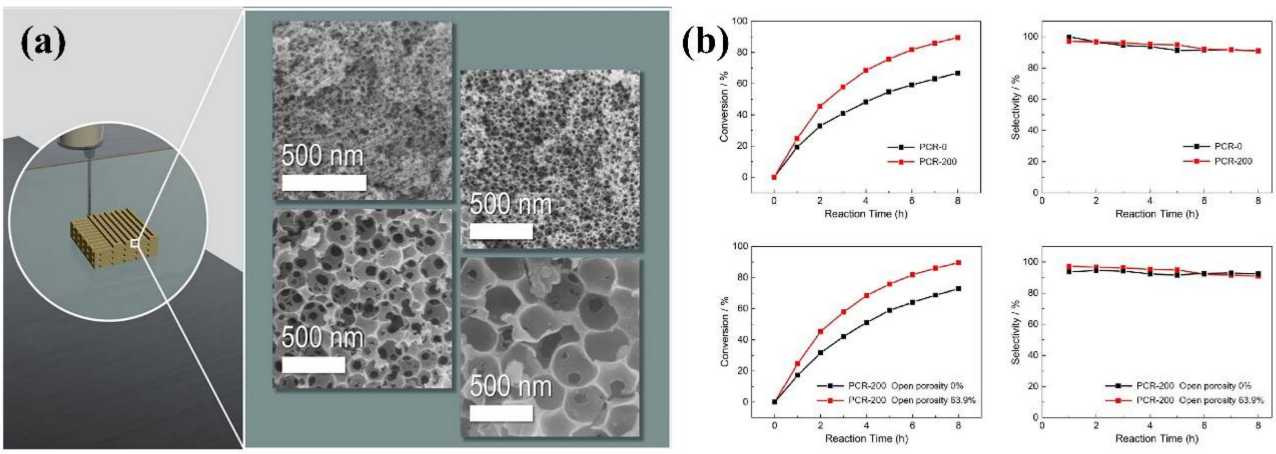

Figure 2. (**a**) Schematic and SEM images of 3D printed porous carbon and (**b**) their catalytic performance [50]. Reproduced with permission from ref. (Zhou et al., 2020) Copyright, 2020, Elsevier BV.

Beale and coworkers demonstrated good catalytic performance of 3D printed Ni/Al_2O_3-based catalysts for CO_2 methanation, and this was also realized by the DIW technique [51]. Precursor materials that involve catalyst preparation play an important role in design of the 3D catalytic structures. Some authors indicate the usage of the impregnation method using nickel nitrate salts onto alumina powders allowing to control mixture percentages, followed by calcination at elevated temperatures to transform the mixed powders into Ni/γ-Al_2O_3 material. Though catalytic particles are dominant in the final performance, mechanical properties are also important in the whole catalytic process. Thus, bentonite and alumina-based binders were introduced into the ink. The obtained 3D printed Octolyst catalyst showed the best performance.

In terms of improving the catalytic performance, despite structure design, binders and other additives for ink preparation also play important roles. But to make extrudable inks and maintain the designed structure after extrusion, the rheology of the inks needs to be adjusted. In most cases, electrochemical inert rheological modifiers such as clays are introduced to ensure the inks are printable. While the existence of these additional modifiers will negatively affect the catalytic performance. Chin and coworkers developed a modifier-free printable UiO-66 ink, where the UiO-66 MOF composites can serve as rheological modifiers themselves [52]. Then the facile construction of excellent 3D printed UiO-66 composite catalysts for hydrolysis was realized.

3.2. 3D Printing of Porous Supports Followed by Post Loading

To complement the limitation of the direct printing of monolithic catalysts, which is mainly caused by the negative influence of necessary additives and solvents during the inks preparation, loading of active catalysts onto 3D porous supports has been proved to be an effective strategy.

Early in 2004, Stuecker and coworkers fabricated a ceramic lattice with complex internal structure for the supporting of barium manganese hexaaluminate [53]. It was demonstrated that by tailoring the structure of the support into FCC lattice structure, turbulent flow of gases can be achieved and catalytic performance is highly enhanced. Agustín's group also proved the favorable turbulent of gases by fabricating asymmetrical channels within the honeycomb-like supports via 3D printing technology, after loading of Cu/Ceria active phase, the products showed better catalytic performance for preferential CO oxidation in H_2-rich mixtures b [54].

To achieve a high energy density of energy storage and conversion devices, thick electrodes with high activity are expected. But traditional construction of thick electrodes always leads to unsatisfying performance since it is difficult to fully utilize the inner active species. Three-dimensional printing technology provides the possibility to construct electrodes with high mass loading and thoroughly exposed active sites by structure design. Hu's group demonstrated the realization of thick electrodes with high catalytic activity for Li-CO_2 batteries by 3D printing technology [55]. Specifically, the 3D graphene oxide (GO) framework was firstly constructed by DIW, after its reduction in Ar atmosphere and in-situ anchor of Ni nanoparticles, the ultrathick cathode was finally obtained (as shown in Figure 3b). Benefiting from the 3D interconnected structure and uniform distribution of the ultrafine Ni catalytic nanoparticles, the thick electrode delivered low overpotential and high areal capacitance. As well, 3D printed graphene-supported CeZrLa has also been reported to show improved catalytic performance for the conversion of CO_2 [56].

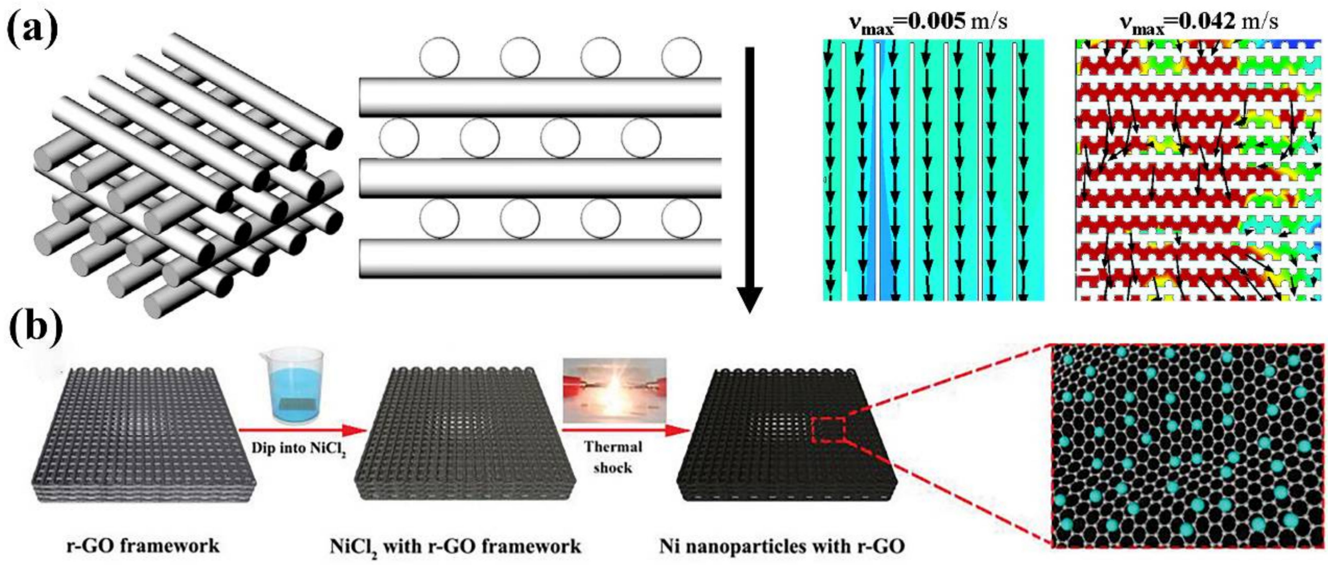

Figure 3. (**a**) Schematic of FCC structure (left) and simulation of velocities (right); [53]. Reproduced with permission from ref. (Stuecker al., 2004) Copyright, 2004, ACS. (**b**) The synthesis process of 3D-printed r-GO framework anchored with Ni nanoparticles [55]. Reproduced with permission from ref. (Qiao et al., 2018) Copyright, 2018, John Wiley and Sons.

Ding's group constructed 3D stainless steel supports with hollow porous cone arrays by SLM, providing a large surface area for the following in-situ growth of active $NiCo_2S_4$ nanoneedles (Figure 4) [57]. The designed 3D printed architecture endows high loading of active electrolytes, the electrochemically active surface area of the 3D electrode was nine times that of the plate structure. Combining with deposited $NiCo_2S_4$ catalyst, this electrode delivered excellent OER performance. By loading Ni/CeO_2-ZrO_2 on 3D stainless-steel honeycomb supports, better heat transfer was realized and the activation time for methane dry reforming was saved.

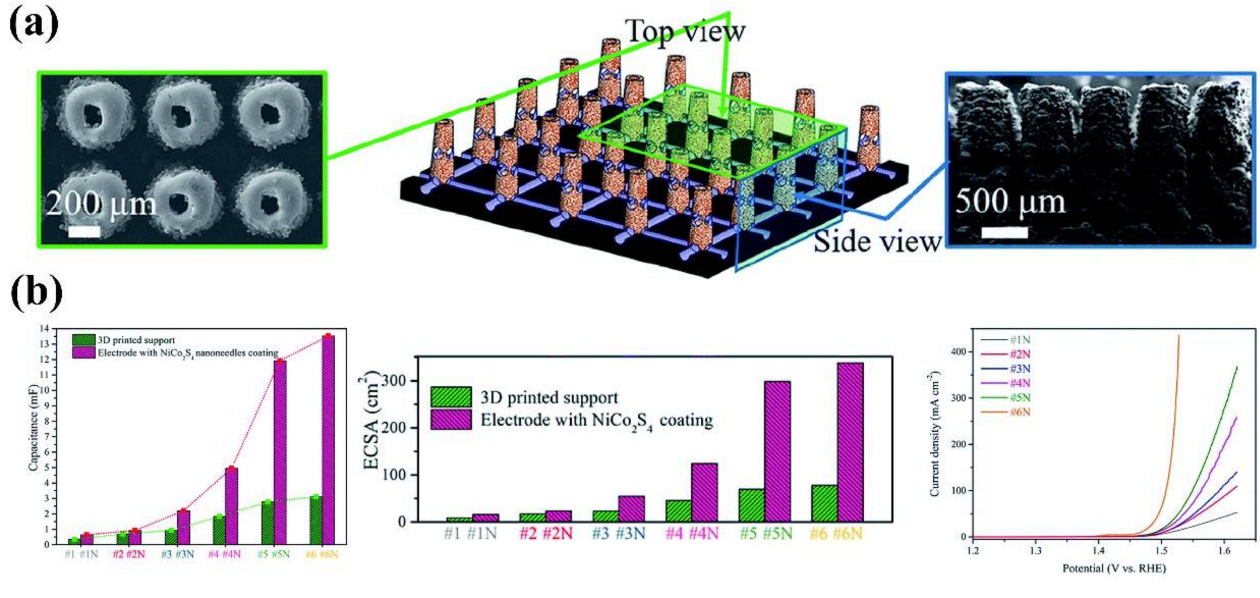

Figure 4. (**a**) Images of 3D stainless steel supported $NiCo_2S_4$ nanoneedles (**b**) and the electrochemical performance [57]. Reproduced with permission from ref. (Chang, 2019) Copyright, 2019, Royal Society of Chemistry.

In addition to the printed supports and post-deposition of catalysts mentioned above, catalyst particles can also be directly integrated with supports. For instance, Alvaro Gil's group introduced Cu source ($Cu(NO_3)_2 \bullet 2.5H_2O$) into the printable paste which mainly contained Al_2O_3 powders [58]. After the 3D printing process, the formed structure was dried and then sintered at a high temperature. Finally, the controllable 3D heterogeneous Cu/Al_2O_3 was fabricated and it exhibited excellent catalytic performance. Jack and co-workers also incorporated electrocatalytic 2D-$MoSe_2$ and Super-P into polylactic acid (PLA) bulk when preparing filaments, after the extruding process, the catalytic electrodes for water splitting were directly fabricated, with no need for any post-treatment. To balance the printability and catalytic activity, the authors also adjusted the contents of additives to obtain optimized fabrication parameters [38]. With the similar idea, Vidales. et al. mixed photocatalytic TiO_2 powders with the granulated polymer during the filaments-making process, to ensure homogeneous distribution of TiO_2, dispersing agents were added. Then the 3D photocatalysts were obtained by FDM technology. Owing to their low density, these 3D printed products can float on the surface of the water and serve as photocatalysts to remove contaminants in wastewater [59].

While in practical cases, the incorporation of active species with the supports' matrix may greatly affect the catalytic performance, especially for polymetric monoliths. Bueno-Lopez's group fabricated 3D polymeric monoliths to support CuO/CeO_2 catalysts [60]. To strongly anchor the active particles onto the polymetric supports, they tried to add inorganic materials into the printable feedstocks, and then chemically attack the printed supports with various liquid phases before or during the incorporation (dip-coating) process. By this method, high mass loading and favorable anchoring of CuO/CeO_2 catalysts were achieved, as a result, this product exhibited good performance for preferential oxidation of CO.

3.3. Combination of 3D Printing Technique with Dealloying Process

Pursuit of the catalysts or their supports with large surface area, low density, good mechanical properties, excellent catalytic performance, and smooth mass transport proposed the demands of fabricating hierarchical structures with pore sizes ranging from nano- to micro-scale. With the 3D printing technique, the porous structure can be easily realized, but for nanopores, their construction by other strategies will be much easier and more economical than by 3D printing equipment with much higher resolution. Dealloying is a classical method to build nanopores, which selectively remove the sacrificing elements by electrochemical reaction and leave pores for objective products. The combination of these two technologies shows great promise in fabricating complex hierarchical structures.

Takeshi's group demonstrated hierarchical nanoporous copper as a high-efficient catalyst for methanol oxidation (Figure 5) [61]. The researchers printed a 3D Cu-Mn scaffold using Cu-Mn alloy powders by SLM, then they immersed the 3D printed architectures into $(NH_4)_2SO_4$ aqueous solution to remove Mn, after this dealloying process, a hierarchical nanoporous Cu catalyst was obtained. Owing to the well-designed architecture with nano- to micro-scale pores, active catalytic sites were thoroughly exposed and the limitation of mass transport was reduced, the 3D Cu catalysts exhibited noticeable catalytic performance for methanol oxidation.

3D printing technology shows great potential in various fields, and it also brings light to high-performance catalysts. However, the research on 3D printing catalysts is still in its infant stage. The recent works on 3D printed catalysts are summarized and listed in Table 1.

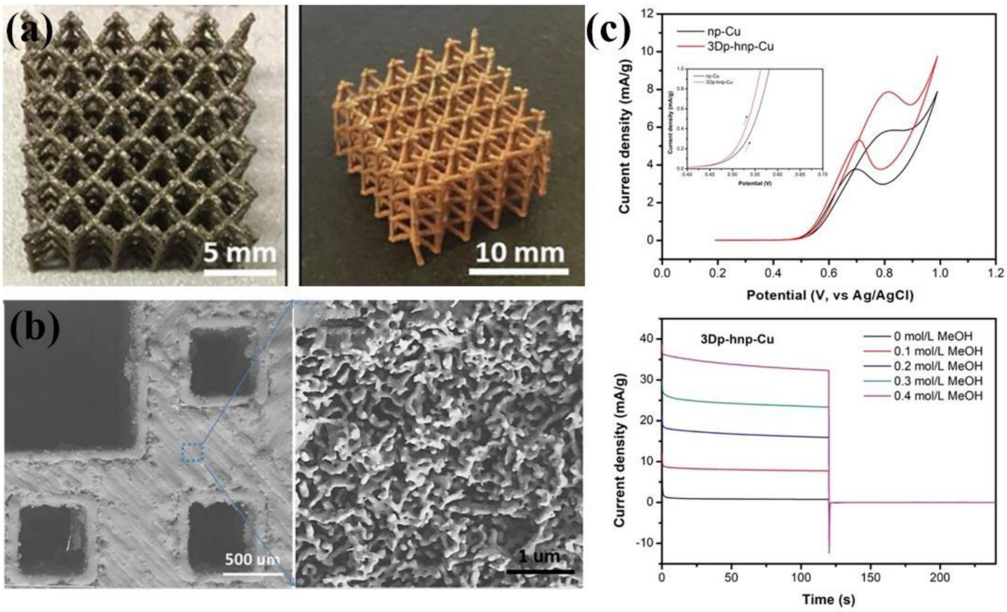

Figure 5. (**a**) Digital images of 3D Cu-Mn scaffold (left) and dealloyed 3D Cu scaffold, (**b**) SEM images, and (**c**) catalytic performance of 3D hierarchical Cu catalyst [61]. Reproduced with permission from ref. (Zhang, 2019) Copyright, 2019, John Wiley and Sons.

Table 1. Summary of 3D printed catalysts.

Printing Technology	Printed Parts	Dominated Catalysts	Reaction Target/Application	Advantages	Ref.
DIW	Catalyst precursor	Cu/Al_2O_3	Ullmann reactions	Excellent catalytic performance, no leaching contamination	[58]
DIW	Silica support	CuAAC, PCCCRs, and MMCRs	multicatalytic multicomponent reactions (MMCRs)	Stable, can be reused >10 times, allows individual recycling	[62]
DIW	Catalyst monolith	Au	methanol oxidation	Markedly improves mass transport and reaction rates for both liquids and gases	[63]
DIW	Catalyst monolith	HZSM-5 and HY	n-hexane cracking reaction	More stable activity, higher selectivity	[64]
DIW	GO framework	Ni/r-GO	Li-CO2 battery	Thick electrodes with high catalytic activity	[55]
SLM	3D supports	$NiCo_2S_4$	OER	Dramatic improvements in electrochemical performance	[57]
SLA	3D supports and catalysts precursor	CuO/CeO_2	Preferential Oxidation of CO	Good catalytic activity, stability, and reusability	[60]
FDM	Catalyst monolith	TiO_2	wastewater treatment	Floating photocatalyst	[59]
DIW	Catalyst monolith	UiO-66	catalytic breakdown of methyl-paraoxon	Mechanically stable, highly porous	[52]
SLM	Catalyst monolith	Cu	methanol oxidation	Promoted mass transport, enhanced catalytic properties	[61]
DIW	Catalyst monolith	porous carbon	selective oxidation of benzyl alcohol	A high conversion with high benzaldehyde selectivity	[50]

4. Conclusions and Perspectives

3D printing technology has promoted the developments of various fields since it disruptively subverts the traditional manufacturing processes. People just design 3D patterns on the computer and then the designed structure can be precisely fabricated with the instruction of computers or built-in software. This disruptive technology also brings new insights into exploring advanced catalysts. By constructing a hierarchical porous structure, high loading of catalysts can be realized, and the most important is that the abundant active catalytic sites can be thoroughly exposed for electrochemical reactions. For some gas phase catalytic processes, a unique structure design can help to realize turbulent gas flow, which is of great significance in promoting the reaction. In spite of the merits of currently reported 3D printed catalysts, the following issues need to be addressed to keep their promises in comprehensively optimizing catalysts' performance:

1. Not all the existing catalysts can be printed by current 3D printing techniques. Though most of the materials can be printed by DIW, electrochemical inert additives are added to the inks to ensure the printability, which negatively influences the catalytic performance. What is worse, their contact with other additives or even the solvents will change the surface structure of catalyst particles and reduce their performance. Thus the preparation process of printable functional inks needs to be optimized, or new printing technology should be developed for expanded applicability.
2. There's a lack of deep understanding of the relationship between structure and performance. It takes much time to try various structures fabrication and then unearth the best performance and explore the influence of law. Combination with simulation will help to solve this problem and provide guidance for catalysts' design and fabrication.

Though 3D printed catalysts are still in their infant stage, the achievements reported previously have demonstrated the great potential of 3D printing technology in the field of catalysts. The development of printing technology is ongoing with the easier operation, higher resolution, and broader applicability, and many efforts are contributed to exploring catalysts with optimized performance. We do believe the current challenges will be well addressed and 3D printing technology will bring new insight into promoting the development of catalysts.

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