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Engineering 3D Printed Structures Towards Electrochemically Driven Green Ammonia Synthesis: A Perspective

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Broadening scope of 3D printing technology is recently identified as a potential strategy to mitigate concerns in the light of rising energy crisis and environmental imbalances. The importance of ammonia as a hydrogen carrier is well known and, in the context of 3D printing, designing and fabrication of electrode substrates for ammonia synthesis from nitrate sources will present a twofold advantage toward addressing the energy crisis and also limiting the harmful effect of excessive nitrate from the environment. Studies in the direction of employing 3D printed catalysts or reactors for ammonia production have been rarely reported. Thus, in this perspective article, the possibilities of engineering several 3D printed electrocatalysts for nitrate reduction to ammonia via various techniques are discussed and experimental demonstrations to substantiate the potential of 3D printed electrocatalysts toward ammonia production are provided, for the first time. In addition, postfabrication treatments, modification, and patterned coating of 3D printed substrates using active materials are also discussed along with the possibilities of fabricating catalysts for ammonia synthesis via nitrogen reduction reaction. Certain limitations and possible solutions of this printing technology for ammonia production are discussed along with the future outlook. Such timely discussions will be interesting for researchers and scientists for enhancing further possibilities toward broadening this field and toward other catalytic applications.

1. Introduction

The consistent decline in the availability of fossil fuels along with a rapidly growing population has resulted in a severe energy crisis in most parts of the world today. Several efforts have been carried out by the global scientific community to derive renewable and sustainable energy sources to meet these growing demands.[1–4] The synthesis of ammonia at an industrial scale is considered to be one of the most impactful discoveries of the last century[5] and its importance is manifold with applications in agricultural sectors, pharmaceuticals, textiles, refrigeration, and so on. Being a "green" hydrogen-rich molecule, ammonia is known to be an important next-generation energy carrier due to its high hydrogen content (17.65 wt%) and high gravimetric energy density (3 kWh kg^{-1}), which assists in convenient storage and transportation along with clean emissions.[6–11] Hence, its production requires critical attention, especially for combatting the increasing energy shortage. Owing to the environmental concerns, and high set-up cost for ammonia production via traditional techniques such as the Haber–Bosch process, researchers are now focusing on simple, efficient, and alternative approaches for ammonia synthesis.

Interestingly, studies focusing on nitrate ions have recently gained momentum as a new area of research where they are known to be a potential source for ammonia production. The electrochemical reduction of nitrate (NO_3^-) into ammonia (NH_3), abbreviated as NRA, involves an eight-electron and nine-proton transfer reaction proceeding through multiple reaction pathways/intermediate steps.[12,13] NRA has a reaction potential lower than hydrogen evolution reaction (HER). Furthermore, HER can be an interfering and competitive process during NRA, where electrons can be consumed for hydrogen generation, which can significantly limit the Faradaic efficiency (FE) and selectivity of the reaction system. Hence, the fabrication of catalysts becomes a key step in addressing the challenges associated with NRA, by limiting the N≡N bond formation and competitive HER, aiding selective reduction, and delivering appreciable FE necessary for practical applications. Although several fabrication

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techniques for catalysts have already been reported,[14–17] the demand for newer alternative strategies is increasing.

From the fabrication point of view, traditional formative manufacturing techniques such as injection moulding, and subtractive manufacturing techniques such as drilling, cutting, and milling, although practiced, have several limitations.[18,19] For instance, complexity associated in device and electrode fabrication, along with time consumption and high cost, has slowed the pace toward fabricating state-of-the-art catalysts. Also, poor selectivity, stability, activity, and mass transfer limitations associated with the catalysts limit their usage for catalytic applications directly. Thus, the need for simpler fabrication approaches that can easily modulate the internal structure, and print complex geometries, has increased dramatically. Furthermore, the complexity associated with traditional techniques, along with high fabrication time, the need for skilled users, excessive resource wastage, and the need for advanced operational facilities for material fabrication has led to further distress.

Advancements like 3D printing technology (known as “additive manufacturing” technique) have revolutionized the material fabrication technique, accounting for its rapid prototyping ability, and flexibility in designing and printing.[20–23] In addition, this innovative technique has the potential to deliver structures with myriad geometries, better rigidity, tunable porosity, and size, thereby mitigating the multiple limitations associated with conventional fabrication techniques. Modifying designs using computer-assisted design (CAD) software is relatively simple; therefore, materials can be easily formulated and examined on the basis of targeted products and experimental conditions. Nanostructuring of these 3D printed structures in the micrometer (µm) resolution can induce porosity and enhance the surface area, delivering nanometric features that can efficiently escalate and favor the catalytic reaction.[23–25] Engineering 3D printed structures can result in varied geometric morphologies, enhancing the chances of fabricating active catalyst structures for ammonia production.

Other advantages such as its user-friendly nature, rapid and flexible customization, and possibility to formulate and fabricate complex structures using different catalytic materials, make 3D printing a highly desirable technology for NRA. Also, this would be a breakthrough in the design of materials that can be easily integrated into an electrolyzer, with a consequent easiness in scalability and manufacturing. In other words, the flexible nature of 3D printing technology favors rapid material production, facilitating the easy optimization of designs to obtain higher yields.

In short, this perspective article discusses the scope of devising 3D printed materials with enhanced activity, selectivity, and considerable yield for ammonia production. This accounts for the fact that proper formulation, engineering, and postfabrication treatments of the 3D printed substrates could render active sites capable of performing NRA, and consequently improve ammonia production. Further, we discuss various strategies for designing 3D printed electrocatalysts, an overview of the catalytic reaction mechanisms, experimentation using 3D printed electrocatalysts toward ammonia production as a proof of concept, key challenges, and a future outlook of this field. The above discussion is anticipated to provide researchers working in this area with relevant ideas on designing newer electrode materials for ammonia synthesis by exploiting the possible benefits of 3D printing technology.

2. Nutshell on 3D Printing Technology

A bottom-up technique, 3D printing classified under the category of automated manufacturing processes that has the potential to fabricate desired 3D objects by depositing active material in a layer-by-layer manner.[21,22,26] Right from its inception in the 1980s, this field of study has made remarkable progress in terms of providing complete autonomy for designing and printing customized products.[27,28] Fundamental advantages of this technology emanate from its features like immediate prototyping ability, scalability, repeatability, flexibility in structural design, the capacity of manufacturing complex designs, and minimal waste generation.[19,22] The technology today has come a long way from its initial usage of generating prototypes to a full-fledged 3D printing industry based across regions. The principles of 3D printing techniques have evolved with time based on the precursor materials used, setup cost, and targeted applications. The diverse prospects associated with 3D printing make it a reliable technique for fabricating various industrial tools and its popularity can be measured in terms of its shrinking cost, increasing purchase rates, and its application has broadened to multiple domains such food,[29] biosensing,[27] biomedical,[25,30] health emergency,[22] electrochemistry,[20,23,31–33] and beyond. Interestingly, today it is also expanding to educational[34] and domestic circles.

The printing process begins with modeling 3D structures using CAD 3D modeling software, a 3D scanner, or photogrammetry.[22,23] After successful modeling of the design (**Figure 1**A), it is converted to stereolithography file format (STL), which is the standard format file, followed by slicing using another software. Postslicing, the final output is obtained in the form of a G-code file that contains geometrical information of the modeled design, commands, extrusion and bed temperature details, number and density of layers, and so on (Figure 1B). The G-code file can be later transferred to the 3D printer for final printing. While printing, the 2D layers of active/precursor material are aligned on top of each other sequentially, resulting in the desired 3D structure (Figure 1C). 3D printing techniques and precursor materials, such as metal filaments/powders, thermoplastics, carbon based filaments, composites, and ceramics, offer multiple possibilities for a diverse range of applications. Certain techniques associated with the technology are discussed below since a proper understanding of these printing strategies is indeed necessary for designing application-specific devices/electrodes for targeted applications.[20,35,36]

2.1. Extrusion-Based Printing

Fused deposition modeling (FDM) or “fused filament fabrication” (FFF) involves the extrusion of active filaments down the printer nozzle to obtain a rigid 3D printed structure as shown in **Figure 2**A.[25,31] This printing technique is in high demand owing to its low cost and flexibility in using different materials. Each filament has its specific extrusion temperature capable of melting desired filaments down the printer

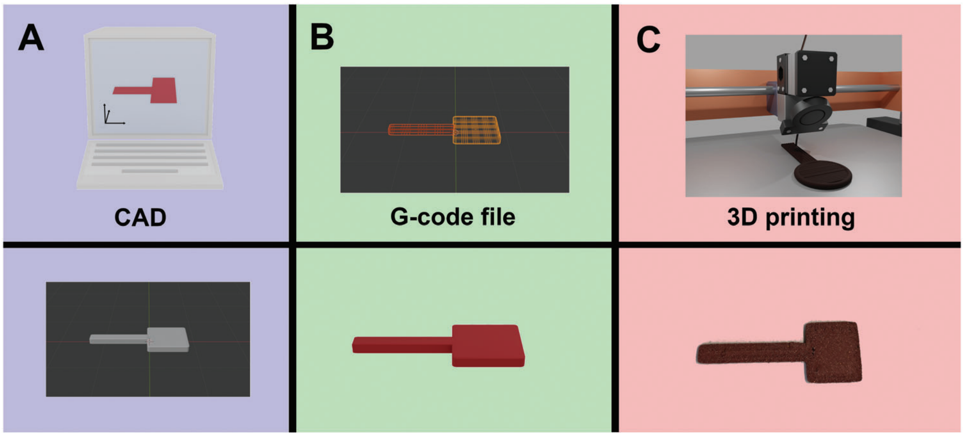


Figure 1. Schematic representations of steps involved in designing and fabrication of 3D structures. A) designing, B) slicing of modeled structure, and C) 3D printing.

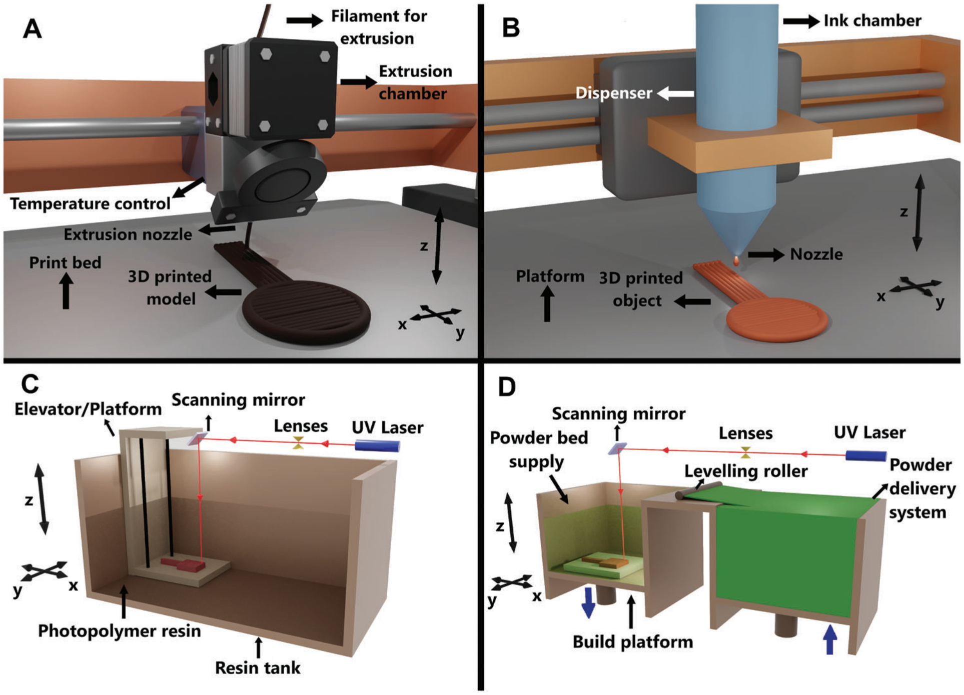


Figure 2. Schematic representations of 3D printing techniques: A) fused deposition modeling, B) direct ink writing, C) stereolithography, and D) selective laser sintering.

nozzle to the print bed platform. The precursor material includes graphene/polylactic acid (PLA) filaments (also known as “black magic”),[25] carbon-black/PLA (protopasta), metal/PLA filaments[37,38] (where metal = copper [Cu], bronze, stainless steel [SS], titanium [Ti], iron [Fe], aluminum [Al], etc.), PLA, acrylonitrile butadiene styrene (ABS), customized filaments, and so on. The directly printed materials are often subjected to post-fabrication protocols to make them conductive electrode/support for desired applications. Interestingly, studies on 3D printed graphene/PLA filament[31] and metal/PLA filaments[37] have been reported recently, as ideal electrode substrate for catalytic applications.

Furthermore, another interesting extrusion-based technique commonly used is direct ink writing (DIW, Figure 2B) where liquid-phase “ink” is dispensed out of the nozzle and deposited on the underlying printed layers to fabricate 3D structures.[39,40] Typically, the inks are electrochemically active materials of interest in suspension or solution form. Ink formulation is a key aspect of this printing technique, where electroactive materials along with additives, binders, solvents, and so on, are optimized based on their rheological properties in order to develop an ideal ink capable of extruding down the nozzle. This printing technology has expanded in terms of printing various materials[41] that are difficult to practically realize using FDM techniques, thus improving its scope for wider applications. Low cost, easy operation, and highly functional products are other advantages of this technology.[18]

2.2. Photopolymerization

Developed in the 1980s, this technique involves the selective curing of liquid photopolymer (resin) sequentially using a specific light source to fabricate active structures. This technique can be further categorized into stereolithography (SLA, Figure 2C)[42] and digital light processing, where in the former, a thin film of photopolymer resin is solidified using UV light to obtain a 3D printed structure while the latter uses a digital light source.[43] Good accuracy and resolution, versatility, multicolor, and multimaterial printing are added advantages of this technique.[18,19]

2.3. Powder Bed Fusion

Selective laser sintering (SLS, Figure 2D)[22,44] uses thermal energy or high-powered lasers to sinter finely powdered material together to procure a final solid structure. This method is highly advantageous as it can function without any external aid, has high accuracy, and constitutes a wide range of materials facilitating the easy production of complex structures. However, its operation requires better expertise and is also expensive in terms of equipment and maintenance costs.

Selective laser melting (SLM), on the other hand, uses precursor materials like metal powders, which are heated until the melting point is achieved.[42,44] Upon heating, the metal powder particles become fused to procure the 3D printed structure , often a conductive metal or metal alloy. Electron beam melting (EBM) is yet another quick 3D printing technique, where a computer-controlled electron gun is used to fabricate 3D structures from active metal powder in high vacuum conditions.[19,45] Precious metals and alloys are active materials employed for printing via this technique. Low cost, faster printing with high build speed, and reduced waste generation are some notable advantages of this technique.[18]

In short, the above techniques can effectively aid in the design and fabrication of 3D substrates for a broad spectrum of applications. Furthermore, these 3D printed structures, upon appropriate tailoring or postprinting treatments,[46,47] can serve as conductive catalyst substrates and/or catalyst support for electrocatalytic applications. It is, however, the user's choice regarding the type of material and printing technique that will be paramount in designing substrates. Apart from that, further advancements in this technology can be advantageous in the designing and fabrication of reactor vessels, along with multiple components in an electrolyzer cell. Thus, research in this direction can make this technology efficient in devising a complete electrochemical setup by itself, thus reducing the production cost significantly. In the following sections, multiple approaches toward designing 3D printed substrates for ammonia production will be discussed.

2.4. 3D Printing versus Conventional Techniques

3D printing differs from the traditional manufacturing technique such as "subtractive manufacturing," where, in the case of the latter, the expected final structures are carved out of a bulk material via drilling, milling, sawing, broaching, and so on.[18,19,23] The excess waste generated during preparation, immense time consumption involved in designing complex structure, the requirement of extensive human effort, expensive instrumental setups, and the inability to alter the volumetric density of the building material are a few of the drawbacks associated with subtractive manufacturing.[22] Debates on the efficiency of 3D printing and conventional techniques are ongoing. However, more than a replacement of established conventional techniques, 3D printing expects to enhance the existing ones for various applications. However, in the case of 3D printed substrates for catalytic applications, this technology has an upper hand over other techniques, especially due to its ability to fabricate custom-made catalysts with versatile structures, different shapes, and geometry of the 3D printed electrodes, subjected to the experimental condition.[20,23] For the NRA application, 3D printing can be an advantageous option to fabricate the required 3D printed electrodes, especially to design a substrate using active materials, already known for ammonia production. Such possible prototyping and modifications in 3D printing technology make it more advanced than other traditional printing techniques. 3D printing industries are also expected to witness a massive hike in designing and printing complete electrolyzer cells or catalytic reactors soon. The precursor materials employed are expected to possess high chemical resistance toward the electrolytes often used for electrolysis, making this technology highly promising for designing reactor vessels. However, other advanced printing techniques, such as SLA, SLS, SLM, and so on, are expected to be efficient technologies for fabricating better reactors for ammonia production as well. Thus, by mitigating the issues of intensive energy or labor involved in traditional techniques, 3D printing can serve as an alternative that is capable of simultaneously 3D printing an electrolyzer cell comprising both active electrocatalysts and a reactor vessel. Finally, it is also worth highlighting the advantages of 3D printing in the field of electrolyzer development in terms of less time consumption and ease of iteration of different cell designs for prototype optimization.

In general, prototype cell development processes involve a cycle of steps such as design, built, and testing in real conditions to evaluate performance and to identify the limitations and modify the subsequent designs until an optimized electrolyzer is obtained according to the requirements of the system under study. The entire process can be enhanced through the use of 3D printing technology as prototyping and simulation are simpler and more automated, allowing an optimal construction of devices in a smaller number of iterations. In other words, it can bypass the excessive time taken for optimization.

2.5. Summarized 3D Printing Techniques

For a better understanding and appropriate technique selection, 3D printing techniques (discussed so far), associated precursor

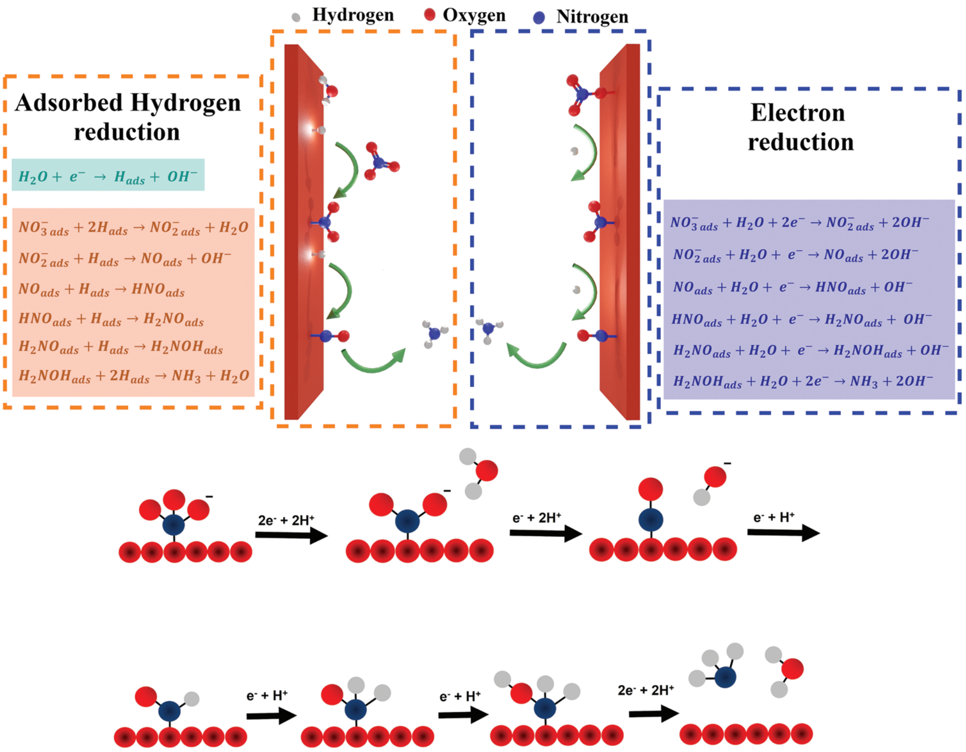


Figure 3. Representation of the reaction mechanism proposed for NRA. Top: The two main mechanisms that explain this reaction taking place at the surface of a cathode electrode, namely, the adsorbed hydrogen reduction (left) and the electron reduction (right). The reaction mechanism has been simplified to understand better. Bottom: Schematic of the step-by-step reaction mechanism (electron reduction) with a ball-type structure. Adapted with permission.[68] Copyright 2021, Royal Society of Chemistry.

materials, advantages, and limitations associated with each technique are presented in Table 1.

3. Insights toward NRA and Benchmarking Protocol

3.1. Significance of NRA

Haber–Bosch is a very well-established method known for large-scale ammonia production,[55,56] but is an energy-intensive process that involves considerable emission of CO_2 and harsh operating conditions. The limitations of this method invite immediate and alternative solutions for ammonia synthesis. One such strategy involves the electrochemical nitrogen reduction reaction (NRR) which operates under mild conditions compared to the Haber–Bosch.[57–60] However, the significantly high energy consumed during the breakage of N≡N , along with the competitive HER, low FE, and selectivity, has compelled researchers to come up with newer experimental approaches, although studies on NRR continue on a vast scale. NRA is one such emerging approaches toward ammonia production which is being extensively studied by researchers currently.[13,61–65] Discussions on the advantages of these approaches over conventional techniques are provided in the Introduction. In the present section, we attempt to explain the reported reaction mechanism associated with the NRA. Further examination has revealed that nitrogen (N_2) containing sources such as NO_3^- ions are present in abundance as major water contaminants, especially in surface-to-ground-level water bodies.[66,67] This method, interestingly, bypasses several limitations possessed by previous techniques for ammonia synthesis, and also strategically eradicates the negative effect of nitrate ions in the environment, making it a significant contributor to the energy sector as well.

3.2. Reaction Mechanism

The mechanism of NRA involves a complex eight-electron transfer process that proceeds through a series of complex pathways.[12] Equation (1) explains the mechanism involved in the nitrate reduction reaction and the respective potential procured with respect to standard hydrogen electrode (SHE)

$$NO_3^- + 9H^+ + 8e^- \rightarrow NH_3 + 3H_2O, E^0 = -0.12 \text{ V vs SHE} \qquad (1)$$

The mechanism of nitrate electroreduction[69–74] proceeds via direct electrocatalytic reduction, which includes two main pathways. The first one is regulated by the active adsorbed hydrogen atom (H_{ads}), called hydrogen adsorption reduction, and the second one comprises the electron reduction from the cathode, known as the electron reduction pathway. These two main pathways are illustrated in **Figure 3**, where the equations of both electrochemical processes are listed.[68] In the H_{ads} mediated pathway (Figure 3, top left), the water molecule is reductively adsorbed on the electrode surface (H_{ads}). Furthermore, nitrate is reduced directly into NH_3 by H_{ads} species through a step-by-step

Table 1. Summary of 3D printing techniques for devising 3D structures for catalytic applications.

3D printing technique	Precursor materials	Layer thickness	Advantages	Disadvantages	Refs.
FDM (Solid based)	Carbon black/PLA, Graphene/PLA, Carbon black/ABS, Graphene/ABS, PLA, ABS Thermoplastic filaments, etc.	50–300 µm	• Cheap, scalable, rapid, and easy prototyping • Easy maintenance, controllable extrusion conditions and nonlaser technique • Multiple postfabrication approaches for enhancing printed surface • (E.g., solvent activation, chemical activation, electrochemical activation, enzymatic, etc.) • Ideal substrate for functionalizing and patterned coating approaches to modify electrode surface • Fabrication of electrochemical cells and reaction wares	• Unoptimized extrusion temperature can result in extruder clogging and bad printing • Time-consuming functionalization and modification approaches • Active materials restricted to filament form • Exposure to highly corrosive aqueous electrolytes can degrade the polymer counterparts (e.g., PLA)	[19,42,48,49]
	Metal/ PLA: Cu/PLA, Ti/PLA, Fe/PLA, stainless steel, etc.	50–300 µm	• Direct fabrication of metal substrates, a possible replacement to costly conventional metal fabrication techniques • Robust, low cost, higher thermal conductivity, and active electrocatalytic surfaces • Resilience to bending • Tunable porosity and properties upon subjection to ideal postfabrication treatments (e.g., sintering)	• High sintering temperature and time-consuming optimization conditions • Solvent-based activation techniques not ideal for polymer removal	[50,37]
	Multi-material printing: (composites of Metal/PLA, Graphene/PLA filaments, PLA, etc.)	50–300 µm	• Combining multimaterial features to enhance the material property • Possibilities of obtaining alloy like structures • Great possibilities for automatizing the design and preparation of multiple components for electrolyzer device	• Complex integration of multiple filaments in the printing protocol • Complex postfabrication protocols • Size limitations • Unoptimized conditions increase chances of nozzle clogging	[19,51]
	Customized FDM printing (2D materials filaments, nanomaterial/polymers composites, etc.)	50–300 µm	• High chance of customization of materials • Tunable properties and reduces the possibilities of foreign impurities • Application-specific devices/catalyst with loading subjected to user's need	• Time consuming • Tedious optimization procedures	[19,52]
DIW (Solid based)	Conductive extrudable inks (nanomaterials, glass, metals, etc.) obeying ideal rheological property	50–300 µm	• Low cost, simple, easy processibility, and varied choices • Tunable composition with multimaterial fabrication facility	• Restacking of active material • Unoptimized rheology aid in clogging and incomplete prints • Poor mechanical properties and low resolution	[18,20,53]
SLA (liquid based)	Photopolymer-based materials	1–50 µm	• Easy, quick, and fine printing with accuracy and good resolution • No need for support material	• Time-consuming protocols • Expensive precursors and lack of conductive materials • Much more complex integration for electrode fabrication	[19,42]
SLS (Powder based)	Metals, ceramics, theromoplastics, low temperature metal alloys	20–150 µm	• Laser-based technique with high accuracy and broad range of material availability • No need for additional support material	• High cost of instrumentation • Time consuming and limited scalability • Poor mechanical properties and surface finishing	[18,19,42]
SLM (Powder based)	Metal and/or metal alloy powders (stainless steel, Ti-based, Ag-based, Cu-based)	20–150 µm	• Highly conductive 3D structures • Decreased electrolyte resistance • Highly desirable for material modification	• Limited precursor availability • Costly instrumentation setup • Time consuming	[19,42,54]

mechanism using a variety of intermediates such as $NO_2^-{}_{ads}$, NO_{ads}, N_{ads}, NH_{ads}, NH_{2ads}, and so on.[68]

On the other hand, in the electron reduction pathway (Figure 3, top right), a similar mechanism occurs without the intermediation of H_{ads}, but the direct cathodic reduction on the electrode surface.[68] Schematic representation of the electron transfer mechanism taking place during the electron reduction pathway is given in Figure 3, bottom. Also, during this reaction pathway, two intermediate N_{ads} recombine to form the most stable N_2. Based on theoretical calculations, the migration barrier of N_{ads} (0.75 eV) is found to be higher than that of H_{ads} (0.10 eV). This fact, along with the less feasibility of N–N bond formation over the N–H bond, enhances the possibility of ammonia formation over the catalyst surface by the H_{ads}. In short, the H_{ads}-mediated pathway could greatly enhance ammonia production via the adsorption of H on the electrode surface. In the electron-mediated pathway, NO_3^- is initially reduced into NO_2^- on the electrode surface and then reduced into NO_{ads}. This intermediate can further result in the formation of either N_2 or NH_3 via multiple complex intermediates such as N_2O_{ads}, HNO_{ads}, H_2NO_{ads}, or NH_2OH_{ads}, wherein NH_3 is procured as a final product. In both cases, the most possible stable products are N_2 and NH_3. However, their prevalence is mainly based on the electrolytic conditions as well as the electrode material selected. For this reason, the careful and rational selection of electrocatalysts should be done in order to favor the mechanism toward NH_3 formation over N_2. In addition, although HER is usually perceived as a competing reaction, its total suppression could hinder ammonia production because H_{ads} is relevant for the reaction to proceed. Therefore, catalyst materials exhibiting balanced H and NO_3^- adsorption capabilities are desirable.

3.3. Experimentation and Quantification

To understand and further compare the performance of a catalyst toward ammonia production, a suitable benchmarking protocol should be followed. As a general approach, the first step consists of conducting an electrolytic experiment followed by quantifying the products generated during an electrolytic experiment. Thus, the classical method to carry out NRA experiments is via amperometry electrolytic experiments in specific experimental cells. Typically, at a laboratory scale, two-compartment H-type three-electrodes cells are employed. The electrocatalyst fabricated (here 3D printed electrodes) serves as a working electrode on the cathodic side along with the Ag/AgCl reference electrode while platinum mesh or wire acts as a counter electrode assembled at the anodic side.

Postelectrolysis, the quantification of products is carried out, where in general, the most common products determined in the reaction are NH_3 and nitrite (NO_2^-).[75] In addition, NO_3^- content is also determined to track the ability of the electrocatalyst to effectively reduce nitrate. Techniques other than UV–vis spectroscopy have also been proposed in the literature to carry out these quantifications.[76] However, the colorimetric technique has gained considerable popularity owing to its ease of usage, low cost, higher accessibility for instrumentation, and accuracy.

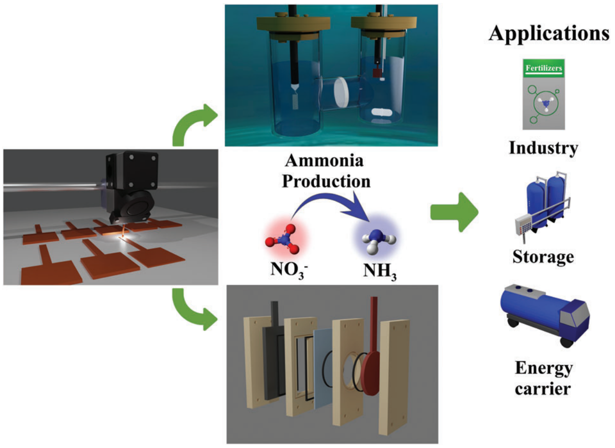
Ammonia is quantified using indophenol blue method, where its presence is confirmed via quantification of a blue complex that results in a slightly green solution with maximum absorbance at the wavelength of 655 nm.[17] Nitrite, on the other hand, is determined by another colorimetric assay where the addition of appropriate reagents results in the formation of a complex red-colored compound measured for its absorbance at 540 nm.[75,76] These compounds are determined to further calculate FE, considering the charge measured during the electrolytic experiment. FE, being a very important parameter to differentiate between several catalytic materials, is frequently used to benchmark electrocatalysts in this field. In addition, selectivity is also an important parameter in the screening of electrocatalysts and evaluating the performance of a material toward ammonia production. Measuring the nitrate concentration is necessary to calculate selectivity. Similar to the quantification approach adopted in ammonia and nitrite, nitrate concentration is measured using a colorimetric method using appropriate reagents, and the absorbance of nitrate is directly measured at 220 nm (subtracting double of absorbance at 275 nm previously).[75] All these methods are used to obtain the important parameters for understanding the role of the catalyst and, ultimately, provide a rational strategy to unequivocally select the best catalytic material to enhance NRA.

4. Scope of 3D Printing Technology for Ammonia Production

3D printing technology has garnered significant recognition in recent years for its multidimensional possibilities, and escalating scientific advancement toward electrocatalytic applications.[20,24,31,32,77,78] However, 3D printed electrodes—an ever-expanding domain with great possibilities—have been surprisingly overlooked for ammonia production although they have been well explored for HER,[31,79] oxygen evolution reaction (OER),[80,81] carbon dioxide reduction reactions (CO_2RR),[19,32] and CO_2 capture.[19] In short, the primary objective of this section is to understand the feasibility of the available 3D printing technology to fabricate 3D printed structures for NRA efficiently. Owing to its immense multidisciplinary aspects, 3D printing technology can flourish in both industry and academia in the near future, for diverse applications (**Scheme 1**).

Geometry optimization is a very crucial parameter for fabricating ideal substrates as they can both facilitate as well as hinder the evolution and detachment of gaseous products from the electrode surface.[19,82] For instance, a lack of proper geometric optimization or poor design of the substrates can accumulate gaseous products over the electrode surface, resulting in the passivation of the active electrode and a significant drop in the catalytic response. Interestingly, 3D printing technology can be beneficial for resolving the aforementioned concerns and is expected to be promising for the fabrication of active functional electrocatalysts with better accuracy and enhanced performance.

Figure 4 shows 3D printed electrodes/devices of varying configurations employed for electrochemical applications.[51,84] These differing complex structures/shapes can be mesh shaped, basket shaped, ribbon shaped, square shaped, circular electrodes with void shapes and varying sizes, etc. Hence, similar adoption and strict optimization can aid in fabricating 3D printed electrocatalysts for NRA, thereby mitigating the limitations faced in fabrication of active catalysts to an extent. Porosity and surface area of 3D structures are also critical aspects for ammonia production.



Scheme 1. Multidimensional applications of 3D printed structures toward ammonia production.

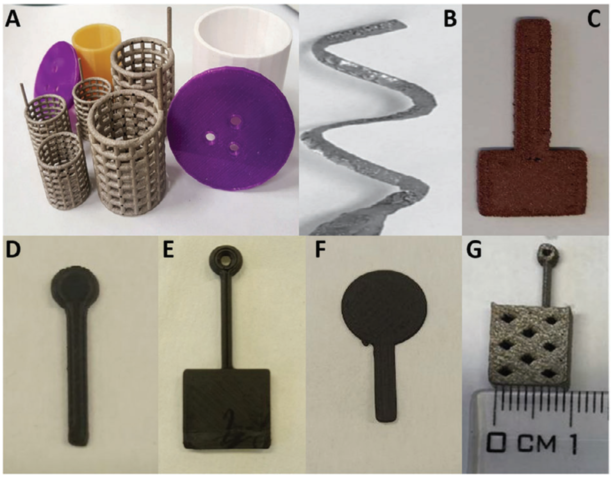


Figure 4. 3D printed electrodes and electrochemical cells of various size and geometry. A) Selective laser melting 3D printed stainless steel gauze-shaped and fused deposition modeling 3D printed polylactic acid based electrochemical cells. Reproduced with permission.[83] Copyright 2017, Wiley-VCH. B) Helical-shaped 3D printed steel electrode. Reproduced with permission.[84] Copyright 2015, Wiley-VCH. C) Square-shaped 3D printed copper electrode. D–F) 3D carbon electrodes of various shape and size. C–F) Adapted with permission under the term of CC-BY license.[19] Copyright 2023, The Authors, Advanced Materials Interfaces published by Wiley-VCH. G) Square shaped electrode. Adapted with permission.[85] Copyright 2019, Wiley-VCH.

The advancements in technology can render enhanced surface area for ammonia production via techniques such as sintering, solvent activation, chemical activation, and patterning, a detailed evaluation of which shall be provided in the subsequent sections.

Electrochemical studies on 3D printed electrodes in various electrolyte systems are available in the literature.[25,86,24] Although the degradation of polymers such as PLA in acidic and alkaline electrolytes is known, a timely improvement in the fabrication of newer metal/polymer and carbon/polymer composites may help to overcome this. Masking 3D printed substrates to mitigate degradation toward harsh electrolyte conditions could be other possible strategies.[19] Employing customized filament fabrication techniques or other metal 3D printing techniques can serve as an immediate solution to this. However, with progress in the technology, this is expected to be used in designing functional electrocatalysts and reactors among others. Furthermore, the following sections and critical discussions provide a broader understanding of the feasibility of 3D printing technology for ammonia production.

4.1. Fused Deposition Modeling

Extrusion-based FDM printing is considered one of the fundamental strategies for 3D printing electrodes/devices. In the FDM technique, active materials, typically filaments, are extruded out of the hot end of the nozzle to obtain a 3D printed structure (detailed in Section 2).[25] At laboratory scale, Original Prusa i3 MK3S+ 3D printer with a nozzle thickness of 0.4/0.6 mm is employed, which can extrude various filaments of carbon/polymer, metal/polymer, and customized 2D material filaments, via FDM technique (**Figure 5**A). The choice of filaments is often application-specific and undergoes specific postprinting treatments to improve the properties of the printed structures. Although several established works using 3D printed electrode substrates via the FDM technique for various electrocatalytic applications have been reported,[20,31,87] ammonia production using 3D printed electrodes is a relatively unexplored domain.

In FDM, the filament materials constitute insulating polymer components along with conductive active fillers. Postprinting, the 3D printed substrates are further subjected to certain modification techniques to remove the nonconductive PLA/ABS polymer components and eventually expose more catalytically active sites over the electrode surface.[33,88] In addition, sputtering, coatings, and patterning can result in modifying the electrode surfaces for desired catalytic applications as explained in detail in Section 5.

4.1.1. 3D Printed Carbon/Polymer Electrodes

Carbon materials are interesting catalytic materials owing to their good electrical conductivity, high surface area, and chemical stability. Interestingly, modifications[89–91] via heteroatom doping, size, morphology and vacancy engineering, crystal facet regulation, and so on can also render carbon materials active for catalytic applications as well. Multiple studies have been put forth regarding modifications and surface engineering strategies over carbon-based substrates for efficient ammonia production.[92,93] These studies show that suitably modified carbon/graphene substrates are ideal for ammonia production and the scope of availing carbon/graphene filaments in the context of 3D printing ensures a huge advancement in the field of 3D printing technology for ammonia production. In short, fabricating 3D printed carbon-based macro/microstructures using carbon-based filaments presents new possibilities in devising electrocatalysts and/or substrates for catalytic applications. Graphene/PLA filament (Figure 5B)[33,94] and carbon-black/PLA (Figure 5C) are two types of commercial 3D printable filament material that are used for printing carbon electrode substrates. Several works have demonstrated the possibility of easy modification of these activated 3D printed carbon surfaces for enhanced catalytic

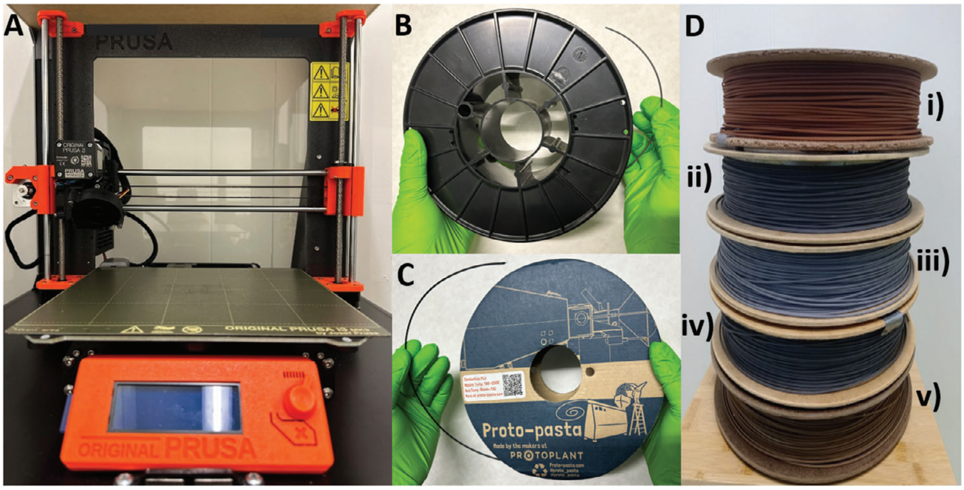


Figure 5. A) Prusa FDM 3D printer capable of extruding filaments to 3D structures. B) Spool of graphene/PLA filament. C) Spool of carbon black/PLA filament. D) Commercial 3D printable filaments of i) copper, ii) titanium, iii) aluminum, iv) stainless steel, and v) bronze.

properties.[25,85] Speculating that although direct 3D printed carbon electrodes may not deliver very high performance like the conventionally well-known catalyst, they can serve as good substrate material for ammonia production.

For instance, in a study by our group, 3D printed carbon substrates were evaluated for NRA.[95] The two filament substrates of 0D carbon black (Protopasta), and 1D carbon nanotubes (graphene/PLA) were evaluated systematically. **Figure 6**A shows linear sweep voltammetry (LSV) profile of 0D carbon black and 1D carbon nanotubes in electrolyte solution of Na_2SO_4 (with and without nitrate), conducted at scan rate of 5 mV s^{-1}. It was observed that 0D was inactive, while 1D exhibited nitrate reduction ability, upon preliminary analysis. Second, electrolysis measurements of the 3D printed carbon 1D catalyst at multiple potentials were done, and the quantitative measurements revealed that the electrocatalysts showed an increasing yield rate of from 6.8 to 364.5 µg h^{-1} cm^{-2} and more than 50% FE at potentials beyond −1.21 V versus RHE (Figure 6B). Cyclic stability assessments at −1.21 V showed a roughly constant performance of 3D printed 1D carbon catalyst in terms of both FE and yield rate (Figure 6C), thereby aiding in devising a cost-effective 3D printed carbon catalyst for NRA application. Furthermore, the role of metal oxide impurities (TiO_2 and Fe_3O_4), carbon defects (basal plane, edge plane), and active sites in 3D printed 1D carbon catalyst was further elucidated in the study. The studies affirmed that a synergistic effect of intrinsic surface features of defective carbon nanotubes and metallic impurities can enhance the NRA performance (Figure 6D). Because commercially procured carbon filaments may have varying inherent impurities (TiO_2 and Fe_3O_4) that could influence catalytic activities, the researchers have further employed uniform deposition of manganese oxides (MnOx) over 3D printed carbon substrates via atomic layer deposition (ALD) technique to procure functionalized carbon frameworks. LSV was initially employed for a preliminary analysis, wherein the ALD-coated layer exhibited a better nitrate reduction ability over the pristine 3D carbon substrate (Figure 6E). Quantification of products postelectrolysis shows that the yield rate (435.9 µg h^{-1} cm^{-2} at −1.21 V; Figure 6F) and FE (64.8% at −1.21 V; Figure 6G) of ALD-coated 3D carbon substrate (300 cycles) catalyst showed a clear dominance over the pristine 3D printed carbon substrate. Furthermore, it was observed that the FE and yield progressively increased with increasing ALD cycles (Figure 6H), thus displaying the potential of ALD-coated MnOx layers to modify the surface chemistry of 3D printed carbon frameworks for catalytic applications such as NRA.

Thus, it can be assured that these commercially available or customized carbon substrates will be a benchmark for the 3D printing industry, specifically for ammonia production. Multiple studies recommend the modification of 3D printed electrodes via electrodeposition[25] and patterned coating of active material[96] in order to achieve better performance. This is explained in Section 5 with a major focus on ammonia production. Therefore, exploiting 3D printed carbon surfaces via appropriate modification techniques and optimization can make them ideal electrocatalysts for ammonia production and open up further application possibilities.

4.1.2. 3D Printed Metal/Polymer Electrodes

With the progress in technology, newer, cost-effective, and scalable techniques with high build speed have also been devised to fabricate 3D printed metal structures.[19] For instance, FDM can be used to extrude metal/PLA filaments, which is also a possible replacement for SLA/SLM. However, there is still a long way to go. The 3D printing hubs have given immense possibility to procure various metal/polymer filaments of Cu, Ti, Al, SS, and bronze, leaving users with extensive choices for fabricating application-specific catalysts (Figure 5D).

Cu/PLA: Among the FDM printable metal/polymer filaments, Cu/PLA is a well-known commercial filament used for 3D printing Cu substrates.[37,38] Interestingly, from the catalysis point of view and previous reports, among transition metals, Cu (CuO or Cu_2O) is considered to be a highly desirable material for ammonia production owing to its high catalytic activity, selectivity, and high FE. Also, the fact that Cu 3D printed metal electrodes have

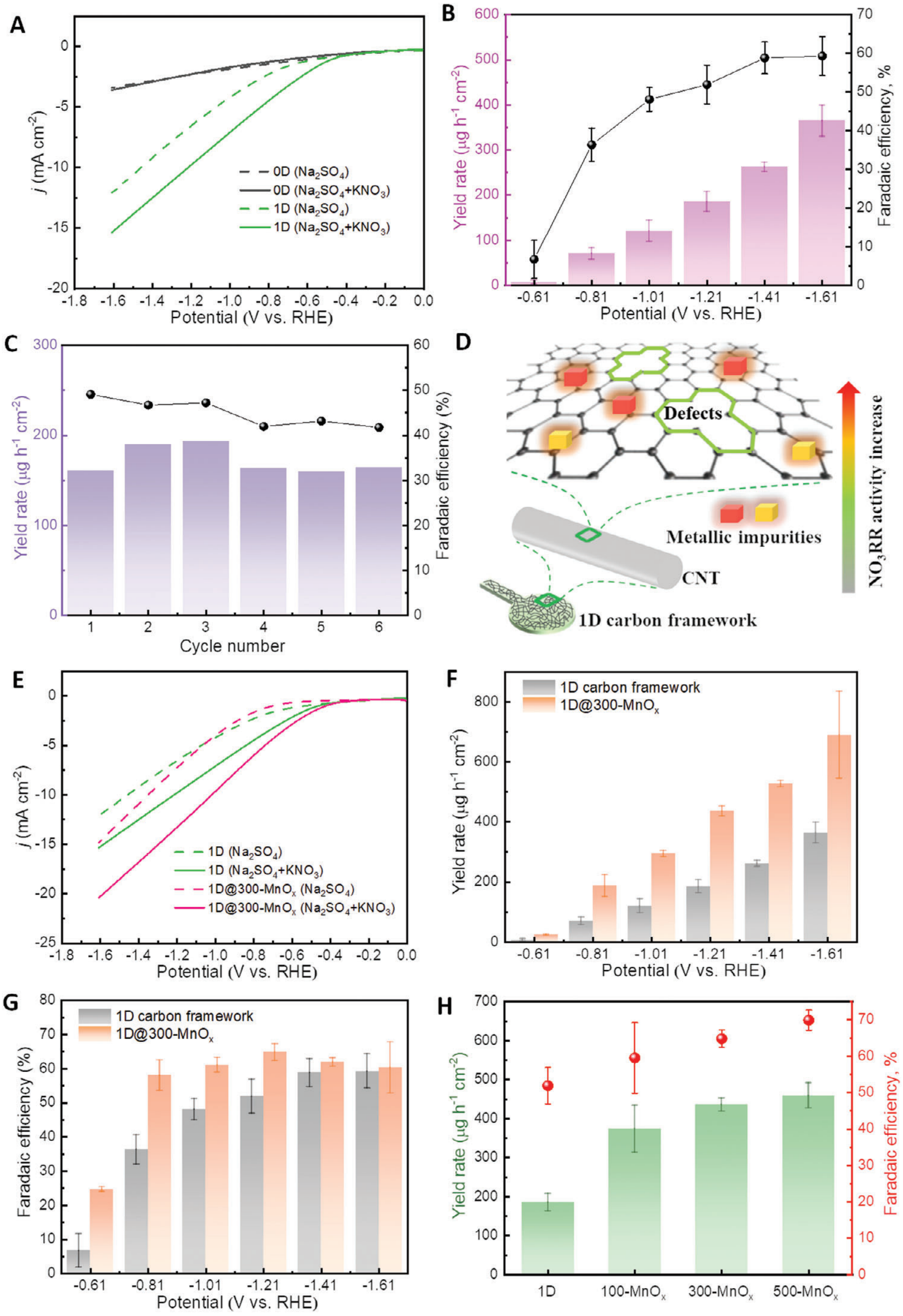


Figure 6. A) LSV profile of 0D and 1D 3D-printed carbon substrates in 0.5 м Na_2SO_4 electrolyte and 0.1 м KNO_3/0.5 м Na_2SO_4 mixed electrolyte. B) NH_3 yield rate and FE of 3D printed 1D carbon framework at multiple potentials. C) Durability assessments of tests of 3D printed 1D carbon framework at −1.21 V. D) Schematic representation of enhanced activity of 1D 3D-printed carbon framework. Electrochemical performance of 1D carbon framework and MnO_x ALD-coated 1D carbon framework: E) LSV curve, F) yield rate, G) FE, and H) effect of varying ALD-coated MnOx thickness over 1D carbon framework for NRA activity. A–H) Reproduced with permission.[95] Copyright 2023, Elsevier.

been studied as catalysts for energy conversion applications[37] substantiates the high possibilities of their use as electrocatalysts for ammonia production as well. Cu as a precursor material is also known to be cheap and nontoxic along with exhibiting good electrochemical activity toward reduction reactions, high sensitivity, and lower overpotential for reductive electron transfer.[38] In Cu/PLA metal filaments, Cu fillers provide good strength and high conductivity to the printed electrodes while PLA ensures structural integrity to filaments both before and after printing.

However, postprinting treatment of these 3D printed metal electrodes is conducted to improve the conductivity of electrodes for enhanced catalytic activity. For instance, sintering 3D printed Cu electrodes increases the contact between Cu metal particles to eventually realize a conductive Cu metal electrocatalyst.[38] This approach can also aid in controlling the morphology of the metal electrode substrate. For instance, in a recent study, 3D printed Cu electrodes were sintered at various temperatures, and their elemental states at different temperatures were examined using X-ray photoelectron spectroscopy (XPS).[38] From such observations, it is expected that researchers proceeding toward electrocatalyst fabrication would need to optimize the sintering conditions because variations in conditions such as temperature could modulate the composition of the Cu in printed electrodes. Indeed, such optimization can provide a viable strategy to fabricate and activate 3D printed metal electrodes that could be integrated into electrolyzers for enhanced NRA. Overall, research focusing on these metal 3D printed parts for ammonia production would be highly beneficial for the 3D metal printing industries and future electrochemical applications.

Ti/PLA: Transition metals such as Ti are interesting, owing to its cost-effectiveness, robustness, abundant availability, and being a poor HER catalyst. In addition, its electrochemical potential stability window is quite large, making Ti highly selective for nitrate anion reduction. In a study by Jaramillo and co-workers,[97] electrolyte engineering was carried out using Ti electrodes for the efficient NRA. The effect of various electrochemical conditions on selectivity and electrochemical activity at Ti cathode for ammonia production was examined using this study. The catalyst was successful in delivering 82% FE (−1 V vs RHE) and a partial current density to ammonia was also recorded at around −22 mA cm^{-2} (nitrate concentration of 0.4 м; pH ≈ 0.77). Today, 3D printing technology allows the advanced facility of 3D printing Ti electrodes via FDM using Ti/PLA filaments. Commercial filaments for extrusion are available from sources like The Virtual Foundry. Employing postfabrication strategies such as sintering would result in the successful elimination of the possible nonconductive PLA from 3D printed Ti/PLA structures. This approach can result in constituting more than 90% Ti metal counterpart, making them suitable prototypes for catalysis such as NRA. Tuning the geometry, size, and porosity of 3D Ti printed structures can avail easy access to fabricate active Ti catalysts for NRA.

Fe/PLA: Fe-based catalytically active centers are long known to be capable of ammonia production, such as in the Haber–Bosch process.[98] In a very recent study by Wu et al.,[17] Fe single atom catalyst was used for NRA and showcased interesting results. In the context of 3D printing, we find that this technology gives the possibility of fabricating 3D printed Fe substrates via extrusion-based printing of Fe/PLA filaments[99] at around 185–195 °C and bed temperature of around 50 °C. The possibility for rapid prototyping of electrodes with varying geometry, porosity, and employing specific activation techniques to these printed platforms can make the 3D printed Fe substrates active for NRA applications.

4.1.3. Experimental Demonstration

To validate the possibility of ammonia production via 3D printed electrodes, an experimental demonstration is carried out by authors with their expertise in 3D printing devices/electrodes and ammonia electrocatalysis. A detailed study on 3D printed Cu electrodes for NRA is beyond the scope of this article, as the authors expect to show only a working model in this new domain, as no studies have been reported in this field, to date.

Original Prusa i3 MK3S+ 3D printer (**Figure 7**A), with a nozzle thickness of 0.6 mm (nozzle temperature [T_{nozzle}] = 230 °C, print bed temperature [T_{bed}] = 60 °C) was employed for 3D printing of Cu/PLA filaments. Commercial Cu/PLA filament (Figure 7B) was procured from the Virtual Foundry, USA, which was used for 3D printing Cu electrocatalyst substrates via FDM (Figure 7C). Sintering of the 3D printed Cu/PLA electrode substrate was further carried out at following temperature ramp: 0–300 °C at 5 °C min^{-1}; 300–1010 °C at 3 °C min^{-1}, 1010–1060 °C at 1 °C min^{-1}. Finally, the Cu electrodes were held at 1060 °C for 60 min and the oven was allowed to cool down to room temperature (Figure 7D). This protocol was carried out to reduce the nonconductive PLA counterpart in printed structures and eventually expose more conductive Cu active sites. Postactivation, the 3D printed electrodes were employed for NRA and quantification studies (Figure 7E).

Initially, the electrocatalytic activity of the 3D printed Cu electrodes toward NRA was evaluated using the LSV technique. The experiment was carried out in a three-electrode setup wherein, a 3D printed Cu electrode served as the working electrode, Ag/AgCl as the reference electrode, and platinum as the counter electrode. The LSV was performed in 1 м KOH electrolyte systems both with and without NO_3^- at a scan rate of 20 mV s^{-1}. Analysis of the LSV curves revealed that the 3D printed Cu electrode was successful in reducing nitrate ions in the electrolyte at low onset potential.

Furthermore, the electrocatalysts displayed a very high current density in electrolyte systems containing NO_3^- (j_{max} = 56 mA cm^{-2}), while the catalyst delivered high onset potential and low current density in electrolyte solutions without NO_3^- (**Figure 8**A). Hence, from the preliminary analysis, it becomes well evident that 3D printing Cu electrode substrate and subsequent activation treatment results in devising newer conductive active substrate for NRA applications. Further, NRA experimentation was performed on 3D printed electrocatalysts in an H-type cell at −0.92 V versus RHE. This is done to evaluate if the 3D printed electrocatalysts are ideal for delivering FE of a reasonable amount upon electrolysis. The electrolysis experiment was carried out for 1 h at room temperature with continuous magnetic stirring at 100 rpm.

Postelectrolysis, the analyte samples from the cathodic side were taken and quantified for ammonia as shown in Figure 8B, using the standard colorimetric method. Interestingly, the electrocatalysts delivered about more than 85% of FE and high yield rate. Thus, this experimental demonstration validates the

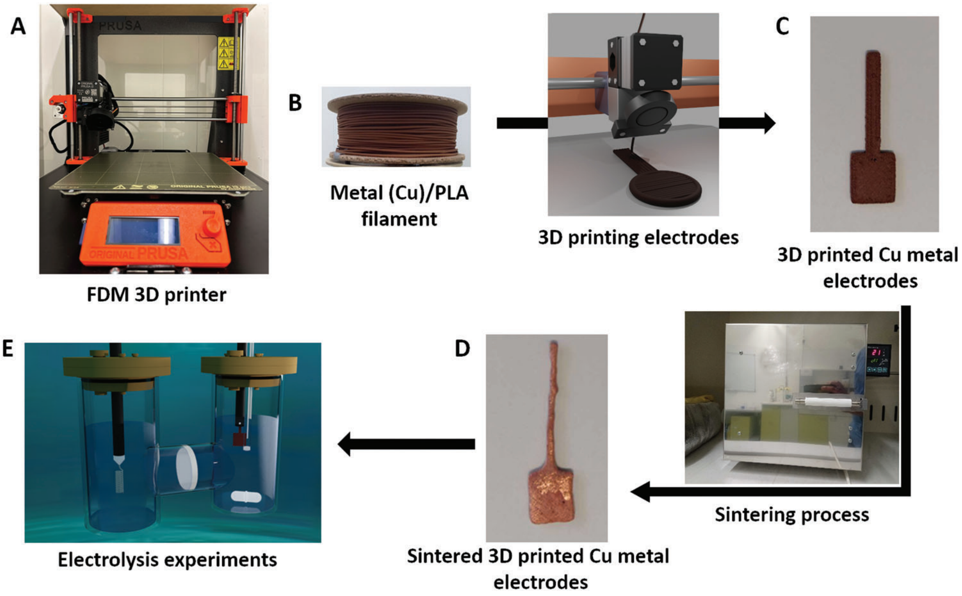


Figure 7. Schematic representation of designing and fabrication of 3D printed Cu electrocatalysts for ammonia production.

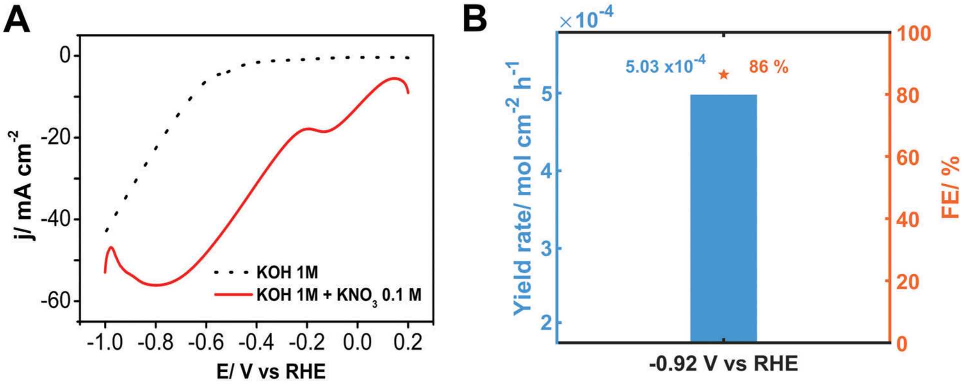


Figure 8. A) LSV profile of 3D printed Cu metal electrode. B) Calculated FE and yield rate.

potential of 3D printing technology toward ammonia production. Engineering of these catalysts and ideal optimization conditions can deliver FE and yield, beyond the one reported above. Furthermore, researchers and scientists are expected to explore the possibilities of this technology to fabricate multiple other electrocatalysts for ammonia production in the near future.

4.1.4. Customized Filament Fabrication

Besides commercially available carbon and metal-based filaments, the advanced research today provides the possibility of on-demand filament fabrication using various active materials, 2D materials, and nanomaterial composites, based on the user's choice.[19] For instance, in a recent work published by our group, filaments of 2D material were fabricated using a slurry containing MoS_2, graphite, activated charcoal, and multiwalled carbon nanotubes.[52] The slurry prepared from the above mixture was dried at room temperature and fed into a filament extruder (Felfil Evo, Italy, **Figure 9**A) to obtain MoS_2/C/PLA filament. The resultant filament was successfully FDM 3D printed to electrodes, activated using optimized technique and further studied for electrochemical applications. Thus, advancements in 3D printing technology have given users the freedom to create their own 3D printable filaments of 2D transition metal dichalcogenides (TMDs).

TMDs such as MoS_2[100,101] with suitable modifications, are found to be ideal for ammonia conversion as well. Thus, the aforementioned observation gives a clear pathway to fabricate MoS_2/carbon filaments that are either modified or engineered, and later 3D printed and activated to fabricate a 3D printed MoS_2 electrocatalysts for NRA.

Literature also shows that TMDs other than MoS_2 are also being noticeably used as catalysts for ammonia production. Hence, appropriate optimizations and the adaptation of previous studies can result in designing and fabricating various 3D printed substrates/ catalysts other than MoS_2.[102] Since filament fabrication using graphene and TMDs is already shown to be successful, we expect that this approach can be expanded toward designing several similar electrocatalysts using other active materials such as MXenes[103] MAX phases,[104] MOFs,[105] COFs, other layered materials,[106] and so on. Such customized fabrication of

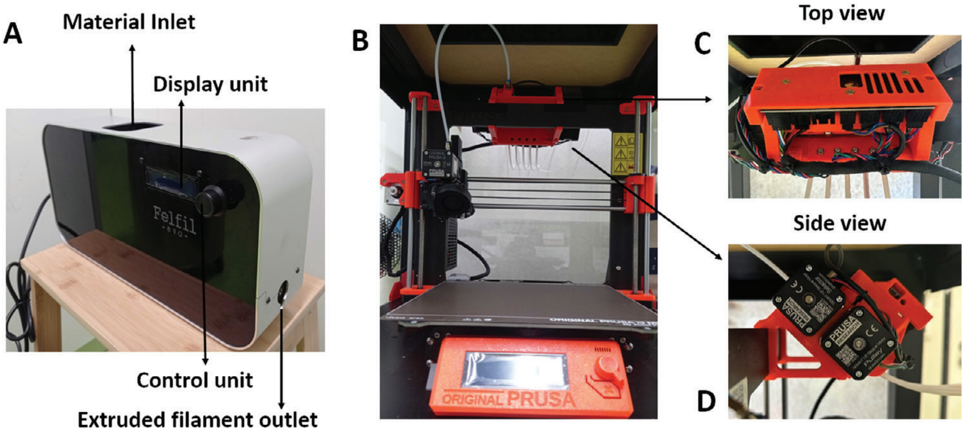


Figure 9. A) Filament fabricator offering customizable filaments. B) Multimaterial FDM 3D printer and components. (A) and (B) Adapted with permission under the term of CC-BY license.[19] Copyright 2023, The Authors, Advanced Materials Interfaces published by Wiley-VCH. C) and D) Printer components from different perspective.

filaments with the desired composition is expected to provide a huge advancement in the preparation of electrode materials for ammonia production. Also, it would truly be a landmark case if such customized filaments can be used for practical applications and provide users with extensive choices.

Furthermore, fabricating filaments using metal particles and polymers is highly beneficial in achieving active 3D printed substrates for various applications via FDM. For instance, in an article by Hwang et al., Cu and Fe particles were mixed with ABS thermoplastic to fabricate corresponding metal/polymer composite filaments.[107] Based on the loading of metal particles in the fabricated filaments (i.e., Cu/ABS and Fe/ABS), tensile strength and thermal conductivity were analyzed along with the optimization of parameters such as temperature and fill density. The investigation showcases the importance of both metals and polymers in filaments for enhancing conductivity and structural integrity, respectively. However, postfabrication approaches can resolve the conductivity issues without compromising the property of the active metal based material. Proper optimization of composition will lead to the fabrication of an ideal 3D printed metal substrate, which in turn can serve as an active electrocatalyst for NRA.

4.1.5. Multimaterial Printing and Catalytic Reactors

Multimaterial (MM) FDM 3D printing is another interesting printing technique that allows the users to sequentially extrude multiple filaments of entirely different compositions simultaneously (Figure 9B–D).[51,108,109] This can be considered a major revolution in the field of 3D printing, as earlier 3D printers were capable of extruding only one filament at a time. MM FDM 3D printing can be interesting for a wide range of applications, especially for catalysis, anticipating a synergistic effect of materials in these 3D printed hybrid electrode systems. Studies on Cu–Ni alloys for enhanced ammonia production are already reported.[16] Also, there are reports available on using metal polymer filaments of Ni for FDM printing.[110] Thus, in the context of 3D printing by taking advantage of the filaments of both active materials, an alloy of 3D printed Cu–Ni hybrid catalyst can be fabricated using the MM FDM printing technique to procure 3D printed bifunctional catalysts. Furthermore, subjecting these 3D printed hybrid systems toward post-fabrication treatments is speculated to enhance the performance of the fabricated catalyst. Such 3D printed hybrid electrode systems can be highly innovative for catalytic applications such as NRA.

3D printing technology finds wide applications not only in the designing and fabrication of catalytic material for various energy applications[23,24,111] such as water splitting,[112] CO_2 reduction,[32,113] and artificial photosynthesis,[114] but also in the fabrication of electrolyzers[51] (electrolytic cells) that can be used for practical applications. Components of an electrolyzer device include electrodes and current collectors based on the intended application. Advancements in 3D printing technology have enhanced the prospects of this industry, especially with more precursor materials being added continuously to print hubs. Also, significant advancements are taking place in the integration of both insulating and conducting parts into the electrolyzers. In other words, the possibilities of manufacturing the casing and internal components of electrolyzers with complex shapes and architecture are infinite using 3D printing approach such as MM FDM.

As a general approach, the electrocatalysts developed are extensively tested in a standard three-electrode cell. However, the behavior of the electrocatalyst in terms of efficiency and stability is completely different when transferred to an electrolyzer (two-electrode cell) under real conditions. For this reason, the testing of developed electrocatalysts under actual working conditions is mandatory. In principle, MM FDM technology offers a promising breakthrough in cell design due to decentralized manufacturing, and customization possibilities for designing cost-effective and highly complex structures with minimal waste generation during the manufacturing process.

Thus, over time, this technology is expected to advance toward designing a complete electrolyzer cell that requires less labor, is cost-effective, efficient, and ideal for catalytic applications such as NRA. However, one of the drawbacks that need to be addressed is the integrity of the cell under operation. Owing to the layer-by-layer based printing technology, there is a possibility of liquid leakage with the consequent change in experimental conditions, making it difficult for direct application in the reactor design. However, these limitations are expected to be addressed by researchers over time. Nevertheless, at the onset, it appears to be a very beneficial technique due to its ease of usage and multiple possibilities in the designing and testing of new cell configurations in short time periods.

4.2. Direct Ink Writing

Designing 3D printed substrates using all types of precursor materials may not be feasible with the FDM-based technique; hence, there is a need for better and improved alternatives such as DIW. DIW is a well-known 3D printing technique that works on the principle of extruding a formulated ink dispersion of the active material out of the nozzle to obtain a final 3D printed structure.[22,40] This printing technique permits the user to 3D print any desirable material as long as the formulated precursor inks follow rheological behavior that is ideal for extrusion. Shear thinning and the viscoelastic properties of the ink also help retain the shape and continue to provide sufficient fluidity, and interlayer adhesion, resulting in an ideal 3D printed electrocatalyst. 2D materials, such as graphene,[115] TMDs,[101] and MXenes[116,117] with modifications and improvements, are known to serve as ideal catalysts/support material for ammonia production.

Like 2D materials, the scope of single-atom catalysts (SAC)[119] is also advancing in recent times, especially in the light of catalytic applications. SAC constitute isolated single metal atoms (active sites), anchored by support materials, with cost-effective, tunable catalytic sites, and high catalytic selectivity being added advantages. Complex wet chemistry synthesis approaches and costly precursors aggravate the overall cost of fabrication of SAC. Accounting for these critical material fabrication aspects, in a recent study, 3D printed SAC was proposed by Xie et al.,[118] to fabricate cost-effective target materials and mitigating the complexity associated with the wet chemistry process. Transition metal precursors along with natural polymers such as gelatin and gelatin methacryloyl (GelMA) was employed to formulate the extrudable ink for fabrication of 3D printed SAC catalysts. Postprinting, the sample was freeze-dried, followed by pyrolysis of dried samples to anchor active metal atoms onto the gelatin/GelMA-derived carbon. Employing the above synthesis approach, the researchers were successful to procure isolated Fe sites with Fe(acac)$_3$ (Tris(acetylacetonato)iron(III)) serving as Fe single atom precursor. The synthesis was also extended to other metal acetylacetonates, such as Pt(acac)$_2$, Ni(acac)$_2$, Zn(acac)$_2$, Co(acac)$_2$, Cu(acac)$_2$, and multiple others to procure PtSAC, NiSAC, ZnSAC, CoSAC, and CuSAC, respectively. In addition, the research provides an experimental demonstration of these 3D printed Fe SACs (Fe3DSAC) for NRA as an approach to exhibit the potential of this technology toward fabrication of active electrocatalysts. The electrochemical performance was evaluated in an Ar-saturated 0.10 M KOH aqueous solution with 10×10^{-3} M NO_3^-. It was observed that Fe3DSAC showed a higher ammonia production over 3D carbon material. Also, the yield for Fe3DSAC at −0.6 V versus RHE was procured around ≈4.55 µmol cm^{-2} h^{-1} which was about 7.5 times the value procured from 3D carbon. The SAC also displayed a high activity and stability during the NRA process. Furthermore, electrocatalytic performance of other metal sites was evaluated by changing the central elements and spatial geometries of 3D printed SACs. In principle, the technique has opened up enormous possibilities for fabricating large-scale commercial production of SACs for a sustainable production of fuels and chemicals and a broad spectrum of other applications.

3D printable inks of 2D materials for DIW[120,121] have gained attention for designing electrodes; however, using such electrodes for ammonia production remains unexplored. For instance, there are reports on DIW of 3D MXene substrates,[122] yet employing these 3D printed substrates as electrocatalysts for NRA has hitherto not been subject to experimentation. Technically, MXene dispersions are prepared in both aqueous and non-aqueous systems, provided that the rheological properties are optimized prior to 3D printing. Understanding the fluidic properties is an important task because the lack of proper optimizations can lead to deviation in the ink flow and result in bad printing.

In addition, there are a couple of studies on Cu-modified MXene that have emerged recently for NRA, wherein in one of the works by Li et al., Cu molecular catalyst (copper phthalocyanine, CuPc) was anchored to the $Ti_3C_2T_x$ MXene surface to obtain a CuPc@MXene catalyst. The catalyst delivered very high ammonia selectivity of 94.0% and a nitrate conversion rate of 90.5%.[123] The above works expand the possibilities of modification of MXene surfaces using various other transition metals for ammonia production. Using this approach, similar MXene slurries can be formulated for the DIW of 3D printed MXene electrocatalysts for NRA. Also, 3D printing of MOF-based catalysts was recently reported via DIW using aqueous Fe-based MOF/silicon carbide composite inks[124] enhancing its possibility as an electrocatalyst for NRA. In short, formulating slurries of 2D material composites or nanoparticles will be interesting for DIW as the extrusion of such composite materials may be more challenging via the FDM approach. However, fabricating multicomponent 3D printed substrates using 2D materials will be a good foundation for ambitious projects in the future, especially for NRA.

3D printed Cu substrate for NRA via FDM is already discussed in the previous section. Interestingly, metallic micro- or nanoparticles that are sintered at high temperatures are found to serve as dispersions for DIW. For example, in a study by Lim et al.,[125] Cu particles were mixed with Pluronic F127 to obtain a self-standing ink that was 3D printed successfully. This was followed by postprinting treatments to deliver efficient and conductive substrates. Taking advantage of the principle adopted in fabricating Cu electrodes via DIW, the possibility of 3D printing other metal nano/microparticles beyond Cu can be explored. Noticeably, the 3D printed electrode material prepared via DIW may also need to be treated using additional methods to activate and expose their catalytically active surfaces as in the case of FDM. Furthermore, gold- (Au)[126] and silver- (Ag)[127] based electrodes were also studied for NRA. Fabricating 3D printed structures using these active materials via DIW can enable robust and conductive platforms for catalytic applications as in a study reported by Zhu et al.[128] In short, the above work can be referred to and/or adapted for designing 3D printed substrates of Ag, Au, multiple alloy composites, and so on. Thus, designing

3D printed electrocatalysts using a wide variety of materials via DIW for ammonia production shall be a novel venture that guarantees wide-scale application in the future.

4.3. Other Printing Approaches

Metal 3D printing technology provides a rapid prototyping platform to fabricate robust and conductive 3D metal electrode substrates.[84,129,130] Integrating the design flexibility rendered by 3D printing technology with the mechanical properties of respective metals to fabricate electrocatalysts, substrates, and reactors are interesting material fabrication approaches. In previous sections, the ability of metal FDM 3D printing was discussed as a potential possibility of the recent advancements to design metal 3D printed catalysts. However, multiple other 3D printing technologies[19,54,131] are conventionally known for designing robust, conductive, and active metal 3D printed catalysts, and catalytic reactors. In principle, in this technology of 3D printing, high power laser sources are typically used for binding the powdered metal particles and then systematically printed to procure the final conductive 3D printed structures. Among these, SLS and SLM are the potential techniques that can be employed in designing 3D structures with the help of metal powders or metal-based precursor materials.

SLS-based metal 3D printing technology has been recently used by a group of researchers to fabricate self-catalytic reactors (SCR) for CO_2RR applications using various active metal components of Fe, cobalt (Co), and Ni.[77] Hence, understanding the potential of 3D printing technology for the fabrication of metal 3D printed parts is regarded to be highly promising for devising active 3D printed substrates for NRA applications. SLM 3D printing techniques have also been employed to fabricate 3D printed conductive electrode substrates, where the precursor materials are either metal or metal alloys of Cu, Ti, Al, and so on.

3D printed metal electrodes can be printed efficiently using both SLM and direct metal laser sintering (DMLS) techniques, where metal powder particles are sintered using a laser source and fused in an inert gas-filled chamber.[132] During the process, metal powder is added over the sintered layer and the above procedure is repeated until the final component is printed based on the predesigned 3D modeled data file. While only a single metal powder is used with the SLM technique, multiple metal alloys with varying melting points are used to 3D print structures using DMLS. This approach can be used to 3D print metal substrates using single or multiple metallic components that would render the user the ability to design electrodes with different compositions and customize an electrocatalyst for ammonia production. The list of precursor materials available for metal 3D printing ranges from Cu, Ni, Ti, Al, etc., and their alloys, to precious metals such as Au, Ag, and metal powders. Based on discussions carried out in this paper, it can be observed that these metal precursors can be 3D printed as active materials toward NRA. However, we do not expect the alloy to be efficient by default for ammonia production but anticipate that metal printing via SLS, SLM, EBM, and DMLS will be advantageous in fabricating electrode materials with excellent mechanical and conductive properties, making it ideal for NRA. In short, improvements, modifications, and optimizations of these 3D printed alloy parts over time will allow the user to devise an active electrocatalyst for large-scale applications.

5. Postfabrication Treatments and Modification

3D printed electrocatalysts/substrates can be considered a forerunner to next-generation energy applications in terms of devising electrode materials that are scalable and can be easily extended toward large-scale production. FDM 3D printing of graphene/PLA and metal/PLA filaments are well known for the fabrication of catalyst/substrate for a broad spectrum of applications. Although PLA in these substrates provides structural integrity to the printed structure, the conductivity of substrates is severely hampered by these nonconductive polymer counterparts. Thus, postfabrication approaches are introduced to limit the amount of polymers in the printed structures, with the objective of increasing the conductivity of the printed substrates, especially for catalysis applications.[20,47,94] Solvent,[31] thermal,[88] electrochemical,[46] enzyme activation,[133] among others, are some of the techniques employed to get rid of nonconductive PLA in carbon substrates or customized substrates.

In a broader context, especially for the FDM technique, solvent activation using DMF,[25,31] acetone,[94] $NaBH_4$,[49] and NaOH,[134] are commonly employed for activating carbon/polymer, graphene/polymer electrode substrates, with several other solvents being studied periodically. Electrochemical treatment is another possible strategy that has been suggested by researchers to improve the conductivity of 3D printed substrates. In a study by Browne et al.,[86] an interesting approach of material enhancement was proposed via sequential solvent activation of graphene/PLA electrodes in DMF, followed by electrochemical activation in phosphate-buffer solution, resulting in 3D printed electrodes with enhanced performance. These catalytic carbon surfaces can also be modified or surface-engineered with metal nanoparticles to fabricate electrocatalysts that are efficient for ammonia production.

Sintering is another strategy employed for metal/PLA electrodes,[37] such as Cu/PLA and Fe/PLA, wherein exposure of 3D printed substrates to high temperature can result in the removal of nonconductive PLA counterparts, delivering metal substrates with enhanced and exposed metal active sites.[37,38]

Modification of 3D printed substrates using appropriate strategies can render to electrocatalysts for various catalytic applications.[135] Electrodeposition,[25] ALD,[85] patterned coating techniques,[31,96] functionalization of active molecular materials, and so on, are a few among a host of other techniques known to fabricate active 3D printed structures for ammonia production.

Electrodeposition is a well-known and widely adopted technique employed to deposit a layer of active material from a corresponding precursor metal salt solution over the activated 3D printed substrates (**Figure 10**A). This approach can be used to electroplate 3D printed structures with a Cu and Ni layer,[25] or any similar salt of transition metal[81,136] provided they are active metal centers for ammonia production. Cu and Ni are well known as active electrocatalysts for ammonia production. Thus, techniques such as chronoamperometry can be employed using a Cu- and/or Ni-based salt solution at defined time intervals for the electrodeposition of Cu/Ni over carbon[25] or metal substrates.[83] TMDs like MoS_2 and WS_2 are promising materials

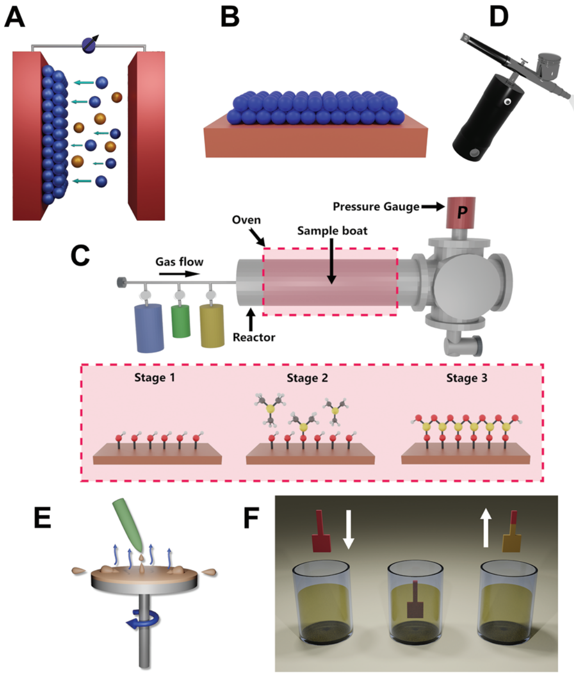


Figure 10. Modification of 3D printed electrocatalysts via A) electrodeposition, B,C) ALD, D) spray-coating, E) spin-coating, and F) dip-coating.

for ammonia production. Because electrodeposition of these materials is already reported,[137] we assume that these modified 3D printed electrocatalysts could be highly efficient for NRA as well.

Furthermore, techniques such as ALD deliver a feasible, homogeneous (Figure 10B), and conformal deposition of active layers, sequentially without compromising the 3D topography. A stepwise demonstration is given in Figure 10C. These are advanced deposition techniques with high reproducibility that are ideal for depositing material of tunable thickness over complex structures such as 3D printed electrodes.[138] For instance, in a study, 2D materials such as MoS_2 are shown to be coated efficiently over 3D printed titanium electrodes for catalytic applications.[50] This technique is ideal for depositing active material over carbon-based substrates as well.[138] Although limitations from electrodeposition can be mitigated by adopting better techniques such as ALD, they are expensive and require expert guidance, especially during coating over 3D printed electrodes. ALD also has a wide range of metal/metal oxide precursor materials that can be explored for obtaining a better electrode surface, ideal for NRA.

Patterned coatings of active material dispersions over 3D printed substrates are an interesting, rapid, and cost-effective electrode modification approach to devise electrocatalysts. This approach has attracted significant attention in recent years due to the low complexity of the instrumentation and minimal complications involved in ink formulation.[31,139] Techniques such as spray-coating (Figure 10D),[96] spin-coating (Figure 10E), and dip-coating[31] are commonly known approaches to fabricate substrates that are cheaper and less toxic, enabling successful coating over the desired 3D printed substrates. These techniques give users the freedom to develop a wide range of 3D printed material catalysts by patterning 2D materials, their composites, nanoparticles, metal oxides, and so on, to be active for ammonia production. For instance, in a study, MoS_2 was spray-coated over 3D printed carbon-based (graphene/PLA) electrode surfaces, and evaluated for HER.[96] The approach aided in abundant and ideal coverage of electrode surfaces by MoS_2 sheets. Furthermore, in another interesting study from our groups, dip-coating (Figure 10F) of 2D materials such as MXenes and TMDs of MoS_2, $MoSe_2$, WS_2, and WSe_2, were coated over DMF-activated 3D printed graphene/ PLA electrode.[31] Postdrying, the electrode was evaluated for HER application in 0.5 M H_2SO_4 electrolyte solution, showcasing improved electrocatalytic activity of 3D electrode substrate. Thus, techniques such as dip-coating can be employed as a facile and cost-effective approach of electrode modification over conventional techniques.

Sputtering an active material can also be highly beneficial for designing 3D printed electrocatalysts. For instance, in a study, NRA was carried out over modified Au electrodes.[126] Modifications via sputtering of Au on 3D printed carbon electrodes and post-treatments also have been reported to improve the surface properties of electrode substrates. This can be extended to Ag or similar transition metals, which could be ideally sputtered over 3D printed electrode surfaces to fabricate newer electrodes for NRA. Thus, there is an immense possibility of improving the substrate surface for NRA in multiple ways. The major task lies in deciding the ideal modification approach for each catalytic material followed by its optimization. Hence, the 3D printing of active material substrates is expected to show high possibilities for the design of ideal electrocatalysts that are efficient, active, and highly selective for NRA.

6. 3D Printed Substrates for Nitrogen Reduction Reaction

Haber–Bosch process is the conventionally well-known industrial process for ammonia production. Owing to the limitations of this technique, as mentioned in the previous section, there have been constant efforts among researchers for finding alternatives. Among them, electrochemical NRR for ammonia production[59,140,141] has gained massive scientific interest in the recent past. NRR continues to be a well investigated domain, although recent studies consider NRA to be more efficient than NRR. Thus, a discussion on the possibilities of designing 3D printed electrocatalysts for NRR can be interesting to the researchers working in this area. NRR offers the possibility for large-scale applications owing to the abundant availability of nitrogen source in the atmosphere.[140,142,143] In addition, the clean and sustainable mode of NH_3 production with less energy-intensive working conditions and low or even zero CO_2 emissions makes this technique unique and preferable over the Haber–Bosch process.

Thus, the fundamental focus would be on developing ideal electrocatalysts with high activity and stability that can efficiently carry out ammonia synthesis under ambient conditions. Furthermore, it must also be capable of mitigating selectivity toward HER and favor ammonia production. 3D printed electrocatalysts for NRR are also relatively new and unexplored like NRA. The mechanism can be procured from the literature as detailing is beyond the scope of the article.[59,144,145] Although several catalysts for NRR, and the possibility of fabricating catalysts using these active materials via 3D printing are both well known, the interdisciplinary domains of 3D printing electrocatalysts for ammonia synthesis via NRR are still not explored well. In the following discussion, we focus on developing a bridge between existing reports on the possible active materials known for NRR and the feasibility of using these materials toward fabrication of 3D printed electrodes/devices via various techniques.

6.1. Carbon Substrates

Advantages of carbon substrates are very well discussed in Section 4.1.1 along with several reports on carbon/graphene substrates for NRR applications.[146,147] For instance, Zhang et al.[93] put forth a detailed discussion on multiple defect engineering strategies over carbon-based substrates for efficient ammonia production. Also, Majumder et al.[148] discuss the possibility of modifying graphene electrocatalysts for enhanced ammonia production from nitrogen. Therefore, adapting the possibilities of using carbon material from the above works into the realm of 3D printing technology can lead to the fabrication of 3D printed carbon substrates via FDM (black magic/protopasta/customized carbon-based filaments, etc.) for ammonia synthesis.

6.2. Metal Electrocatalysts

Cu,[149] Ti,[150] Ni,[151] Au,[152] and Ag[153] have been explored for NRR application as well. In the domain of 3D printing, employing the respective metal/PLA filaments of corresponding active material (Cu, Ti, Ni, etc.) and/or modification of 3D printed substrates via sputtering (Ag, Au), electrodeposition (Ag, Au, Ni, Cu, etc.), coatings of active material (Ni, Cu, etc.) over substrates, would help in designing ideal and efficient 3D printed electrocatalysts. In principle, this approach would help in designing 3D printed electrocatalysts for NRR applications at a large scale, in minimal time, and cost-effective manner. Advancements in 3D printing technology, such as customized filament fabrication (Section 4.1.4), MM 3D printing techniques (Section 4.1.5), and other known 3D printing techniques, would also help in designing ideal electrocatalysts for ammonia production via nitrogen reduction. The postfabrication techniques and electrode modifications discussed in Section 5 are also advantageous for the fabrication of conductive 3D printed electrodes with high selectivity and efficiency for NRR, as well as for high-yield ammonia production.

Furthermore, molybdenum (Mo) and Fe are considered to be theoretically feasible electrocatalysts for NRR. In a work by Zeng et al.,[154] nitrogen-doped MoS_2 nanoflowers were studied as electrocatalysts under ambient conditions. It was observed that the catalyst delivered high FE (9.14%) at −0.3 V versus RHE in 0.1 M Na_2SO_4 and provided NH_3 yield of 69.82 μg h^{-1} mg_{cat}^{-1}. In our previous discussion about the FDM 3D printing technique, the work on MoS_2 3D printed substrates conducted by our group was mentioned.[52] The possibility of modifying these electrode surfaces via nitrogen doping or similar method is also known to be technically feasible. Thus, we propose the possibility of designing nitrogen-doped 3D printed MoS_2 substrates via extrusion-based technique that are speculated to be ideal for NRR.

6.3. 2D Materials

Studies on combining 2D materials to fabricate electrocatalysts for ammonia production are known to be relatively new, one among them being the recent studies on loading 1T′-MoS_2 with Ti_3C_2 MXene.[155] The possibility of ideal ink formulation via DIW can also result in developing 3D printed MoS_2/MXene electrocatalysts for desired catalytic applications such as for NRR. These novel approaches of designing self-standing, robust, and active 3D printed electrocatalyst substrates can bring an impactful improvement in this field.

Though the major part of this article focuses on the possibility of utilizing 3D printed electrodes for NRA, we also claim that the technique of 3D printing electrocatalysts has not been hitherto introduced to NRR as well. Thus, a large possibility exists for designing electrocatalysts for NRR via several other techniques, given the fact that 3D printing shows enormous prospects of fabricating substrates similar to the ones that have been already reported for NRR. Also, the mechanism shared by these two reactions (NRA and NRR) to give the same product (ammonia) has a big difference, and their adaptability to serve as a catalyst via 3D printing technology is subject to repeated improvement, considering the geometry, porosity, and size with respect to the experimental conditions, systematic optimization, and tuning/optimizing the postfabrication approaches. However, considering the reports on the limitations of NRR over NRA, the major focus was shifted to 3D printing electrodes for NRA. Nevertheless, there is still scope for improvement in designing electrocatalysts of active material using FDM, DIW, SLA, or SLM among others for NRR.

7. Challenges and Solutions

The prospect of 3D printed substrates for NRA is relatively new and, thus, the expected uptake in this area can be a bit slow; however, once the abilities of this technology toward NRA are fully realized, it will represent a promising leap in the design of electrodes/devices. FDM-based electrode and device fabrication using graphene/PLA, carbon black/PLA, carbon black/ABS, customized 2D material/PLA, and so on, are well known. However, extruded 3D printed structures may not be ideal for direct catalysis applications owing to the presence of nonconductive constituents (PLA, ABS, etc.), requiring postfabrication treatments.[47,94] Although several techniques have been proposed,[19,20] very strict optimization measures are recommended because overexposure to postfabrication treatments such as solvents, and physical and/or chemical treatments can result in excess loss of polymer from printed parts. This eventually affects the strength of 3D printed structures, resulting in the weakening and breakage of the printed structures. Nevertheless, an initial exploration of this technique for the fabrication of 3D printed catalyst can be relatively time-consuming, where the user will initially need to fabricate multiple prototypes with varied compositions of active material, fillers, polymers, additives, and so on (e.g., customized filaments). Optimization also extends to the filament extrusion quality, extrusion temperature, and reproducibility. Postoptimization of the ideal filament composition can aid in employing these 3D printed structures as electrocatalysts for NRA applications.

Temperature is another vital factor for the extrusion of filaments, wherein the extrusion temperature will vary from filament to filament. Sometimes high temperatures can result in the oxidation of metal nanoparticles or filament composites, affecting the conductivity severely. A possible remedy would be to design a special chamber that would be capable of providing inert atmospheric conditions via constant purging of Ar/N_2 gas during printing.[19] In addition, sintering 3D printed metal electrodes such as Cu/PLA, Fe/PLA, and Ti/PLA, at elevated/unoptimized temperatures can result in the degradation or deformed shape of the printed electrodes. This could be mitigated by using covering materials and molds that help to preserve the shape of the electrode post thermal treatment. As a feasible strategy, experiments like thermogravimetric analysis could be initially employed to track the degradation of polymers from the printed structure. With such systematic understanding, the user can easily optimize the required temperature for activating the printed electrode substrate without losing the shape of the printed structures. DIW using certain active materials can result in clogging of the nozzle; however, the rheological properties of inks should be constantly assessed for better printability. Proper optimization of ink fluidity can also prevent bad printing or incomplete printed structures.

Electrode modification via various techniques was discussed in detail in the previous section. However, certain challenges are also associated with the modification of the electrocatalyst surface using conventional techniques, which has to be taken care of for efficient catalyst fabrication. For instance, although electrodeposition techniques are cheap, quick, and provide a wide range of choices for metal or metal oxides, the semiuniform deposition of material over the 3D printed structure can serve as a major limitation to this technique.[19] The techniques employed for electrodeposition are expected to be well optimized, prior to its coating over fabricated 3D electrode material.

Every technique has its pros and cons. Therefore, finding the ideal technique based on the experimental setup/targeted applications has to be carefully executed to fabricate ideal electrocatalysts/reactors/devices for applications such as ammonia production. Strategies to improve ammonia production have evolved over time and have come a long way from conventional techniques like Haber–Bosch and NRR to recent ones like NRA. Designing ideal electrocatalysts or catalytic reactors has been the primary goal of all these techniques, where the catalyst exhibits high activity, selectivity, efficiency, and stability during the reaction. 3D printing for ammonia production is a relatively new approach toward designing electrodes or electrolyzers; therefore, it is guaranteed to take a considerable amount of time and research to develop effective strategies for fabricating efficient catalysts for NRA.

8. Conclusion and Future Perspective

Catalysts can play a significant role in resolving several ongoing crises arising due to the declining availability of fossil fuels and the exhaustion of resources with the increasing population. The conversion of nitrate into ammonia has unfolded the scope of an alternative sustainable pathway for ammonia synthesis and, thus, the design of ideal electrocatalysts for this process has become a major task. This perspective article discusses how 3D printing technology can be an asset in the fabrication and engineering of 3D printed electrodes that serve as active electrocatalysts for ammonia production. Several precursors materials have emerged in recent years that can be extruded/sintered/formulated successfully to procure 3D printed electrodes and devices. These precursors include carbon materials, 2D materials (graphene, MXene, TMDs, MOFs, etc.), metal/metal oxides, nano/microparticles, and many more. Interestingly, 3D printing techniques today provide the flexibility of printing self-supported catalyst substrates, SACs, for catalysis and possibly resolve several issues encountered by traditional printing techniques. We summarize that although several active materials are reportedly known to be ideal for ammonia production, 3D printing technology confers the freedom to 3D-print these active materials for catalytic applications like NRA. The technology of 3D printing was developed four decades ago; however, it has taken a considerable length of time to expand and flourish as a domain across multiple industries and sciences. This technique today has become exponentially cheaper as the cost of printers, precursor materials, and other accessories consistently declines. Although 3D printing electrodes for catalytic applications are primarily studied as a proof-of-concept, over time this technology is expected to potentially expand to large-scale manufacturing terrains, using structures that are less expensive and with large outputs. This process of escalating from small-scale laboratory operations to a large-scale industrial setup can be challenging and requires critical and creative resolutions in its design.

3D printing is known to have great potential in terms of designing reactors for catalytic systems as it holds a dual advantage of having a catalyst component as well as the ability to moderate the flow of reactants. This article, however, has focused on using 3D printing technology for the fabrication of functional catalysts, catalytic reactors, and similar systems for ammonia production. Significant advancements have been witnessed in recent years in fabricating 3D printed devices, with a major focus on catalysis applications. Thus, the fabrication of active electrocatalysts that could be integrated into the electrolytic system, along with the manufacturing of both framework and internal part of the electrolyzer, can be considered to be significant advancements in the field of NRA. This would also be an impactful technology in the future for diversifying ammonia production. In short, with ammonia production being a vital application, further advancements are expected in this direction and 3D printing would be a breakthrough in designing novel electrocatalyst structures that are more cost-effective, energy-efficient, and also mitigate the environmental concerns.

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Conflict of Interest

The authors declare no conflict of interest.

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