

Chemistry from 3D printed objects

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Abstract | 3D printing technology has started to take hold as an enabling tool for scientific advancement. Born from the marriage of computer-aided design and additive manufacturing, 3D printing was originally intended to generate prototypes for inspection before their full industrial production. As this field has matured, its reach into other applications has expanded, accelerated by its ability to generate 3D objects with complex geometries. Chemists and chemical engineers have begun to take advantage of these capabilities in their own research. Certainly, the most prominent examples of this adoption have been the design and use of 3D printed reaction containers and flow devices. The focus of this Review, however, is on 3D printed objects, the chemical reactivities of which are of primary interest. These types of objects have been designed and used in catalytic, mechanical, electronic, analytical and biological applications. Underlying this research are the efforts to add chemical functionality to standard printing materials, which are often inert. This Review details the different ways in which chemical reactivity is endowed on printed objects, the types of chemical functionality that have been explored in the various printing materials and the reactions that are facilitated by the final printed object. Finally, the Review discusses new avenues for the development and further sophistication of generating chemically active, 3D printed objects.

Initiator

A chemical needed to initiate polymerization. In some instances, initiators do this by generating radicals under mild conditions.

Photosensitizer

Upon absorbing light, a photosensitizer can cause a change to a nearby chemical. In some instances, photosensitizers are used to generate radicals on initiators.

The first 3D printing process was developed by Hideo Kodama in the early 1980s¹ (FIG. 1a). He was able to generate a complete 3D object from 2D cross sections, successively formed on top of one another, using photo-hardening polymers and UV light. Kodama's apparatus consisted of a print bed, which contained a liquid polymer resin (an unsaturated polyester), a crosslinking agent, an initiator and a photosensitizer. A solid structure was produced by either raster-scanning an optical fibre over the print bed or placing a mask over the bed and fully illuminating the exposed surface. The growing object was then lowered into the bed, exposing unset liquid resin, and a new solid layer was formed on top until the object was fully fabricated.

Current 3D printing technologies have advanced, in great part because of computer generation of 3D structures and control over the printing processes^{2–9}. Many modern printing technologies, though, still use the chemical foundation exploited by Kodama to build his device. 3D printing techniques can be sorted into two distinct classifications. The first class includes methods, like Kodama's, in which an object is generated from a reservoir of patternable or polymerizable materials. The second class includes processes in which a material is extruded through a nozzle onto a platform. Horizontal movement of the nozzle and vertical movement of the platform during extrusion defines the final shape of the 3D printed object.

Although 3D printing was initially used by designers to evaluate industrial prototypes, the widespread use and popularity of 3D printing have grown because of the enthusiasm of at-home users. These makers most often use extrusion-based printers, which tend to be the least expensive to own and operate. An entire online community has evolved in which makers share their object designs and provide tips for managing tricky or complicated prints. Not to be left out of the fun, scientists are also finding ways to use 3D printing for their work. Researchers can print supplies for their laboratories^{10,11} (FIG. 1b). In some cases, objects cost less to print than they would to purchase from laboratory supply companies. An added benefit to this approach is that there is no wait time for item orders to be processed and shipped. Scientists have also designed objects that fill a very specific niche for which there are no commercially available products¹². Finally, there are many examples of 3D printed replicas that scientists use to visualize their research. 3D printed organisms, organs and chemical structures (both large and small) can be used to educate and engage non-specialists as well as facilitating deeper understanding and insights from the scientists who study them.

Chemists and chemical engineers have begun to move past printing replicas to printing objects that facilitate research in new and interesting ways. Custom reaction vessels have been generated in an attempt to

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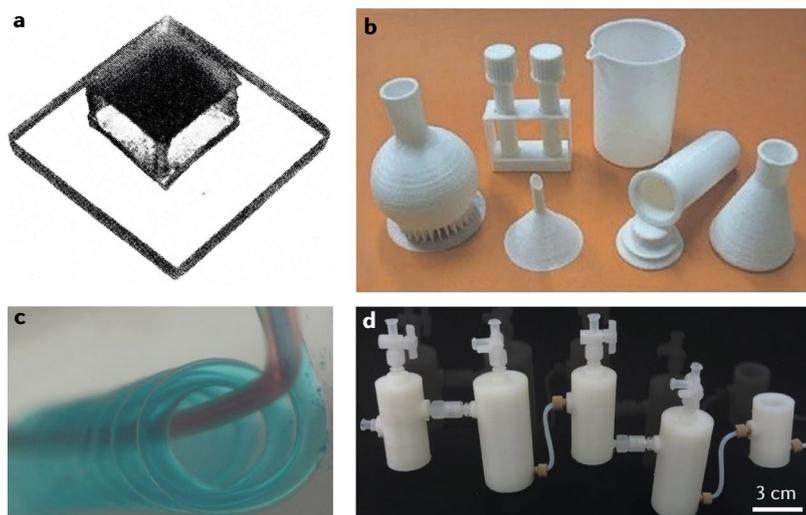


Fig. 1 | Examples of 3D printed objects. **a** | One of the original pieces printed by Kodama in the early 1980s¹. **b** | Typical laboratory supplies generated with a 3D printer¹¹. **c** | A 3D printed fluidic device²³. **d** | 3D printed 'reactionware' for performing a multistep, organic synthesis and purification²⁸. Part **a** is reproduced with permission from REF.¹, AIP Publishing. Part **b** is reproduced from REF.¹¹, Springer Nature Limited. Part **c** is reproduced with permission from REF.²³, Wiley-VCH. Part **d** is adapted with permission from REF.²⁸, AAAS.

study and optimize reaction conditions and product yields^{6–8,12,13}. One example of this type of work includes the preparation of flow reactors^{14–23} (FIG. 1c). These types of devices can exhibit flow circuitry designed to accommodate specific reaction kinetics (precise reaction times) and thermodynamics (safely facilitating highly exothermic reactions). Flow reactors can also accommodate multicomponent reactions in which each component is added at a specific time point during the reaction. Perhaps most relevant to the capabilities of 3D printing are reactors that employ mixing chambers with unique geometries, which might otherwise be difficult or impossible to generate^{24–27}. Along with flow devices, larger reaction vessels have also been printed^{12,28–31}. In one example of this type of 'reactionware', Cronin and colleagues generated a connected network of containers that facilitated the synthesis of baclofen (a muscle relaxant)²⁸ (FIG. 1d). Their printed container facilitated three reactions along with several extractions, filtrations and isolation steps required to generate intermediates and final product.

In the above examples, the reaction containers necessitate the printing material to be chemically resistant. Although these printed devices facilitate chemistry, the materials from which they are made are not actively involved in the chemistry of the reactions. There has been a growth in the number of studies in which scientists produce printed objects that are chemically active. In this Review, we focus on ways in which chemical functionality can be added to 3D printing materials and highlight areas where we feel these materials can make an impact on future research efforts. Specific equipment and materials are identified in this Review in order to describe the experimental procedure adequately. Such identification is not intended to imply endorsement by the National Institute of Standards and Technology, nor

is it intended to imply that the materials or equipment identified are necessarily the best available.

Printing processes

There are a number of relevant publications that fully detail the different styles of 3D printing, instrumentation, their material requirements, post-printing processing steps and capabilities^{2–8}. Here, we describe some of these aspects mainly to highlight how the maintenance or addition of chemical reactivity can be facilitated (FIG. 2).

FIGURE 2 shows the types of materials from which a 3D printed object can derive reactivity. Polymers are the basis for nearly all 3D printing processes. Relevant functionalities are found in both the polymer backbone and side chains^{32,33}, which can be used as they are or altered after printing. Nanoparticles and microparticles have also imbued printed objects with reactivity^{31,34,35}. Particles can be used as the primary component of a 3D printing paste³⁵, included as a secondary component to the printing material³⁴ or incorporated onto the surface of an already printed object³¹. Platelet-shaped particles and high-aspect ratio particles have been primarily used to alter the mechanical properties of the printing material³⁶ but can also facilitate interesting chemistry, which is the case for montmorillonite K10 and its ability to catalyse a number of organic transformations³¹. 2D materials (such as graphene and graphene oxide), normally incorporated before printing, have been used as rheological modifiers to enable printing and for their specific reactivities^{37,38}. Metal organic frameworks (MOFs) and zeolite particles, valued for their high internal surface areas, are incorporated before printing or synthesized on the surface of a printed object^{32,39–41}.

In this Review, we explore the different printing techniques and commonly used materials that enable novel chemistry from 3D printed objects (FIGS 3,4). We detail the ways in which these materials can be modified and the interesting chemical processes they facilitate. The cost of purchasing a 3D printer or the difficulty in producing modified printing materials may be an entry barrier to this field. However, many companies now sell customer-defined objects printed from a variety of materials, providing a solution for those that are curious but do not want to incur some of the cost or effort required.

Fused deposition modelling

In fused deposition modelling (FDM), a thermoplastic filament is fed through a nozzle that is heated above the glass transition temperature of the polymer^{42,43}. The polymer flows through the nozzle and solidifies after being deposited on the print bed. FDM printers are the most commonly used by hobbyists. A number of commercially available polymer filaments in a variety of colours with a variety of mechanical and electronic properties can be used for FDM. The most typically used filaments are composed of acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA). Other FDM plastics include high-impact polystyrene (HIPS), polyvinyl alcohol (PVA), polypropylene (PP), polyethylene terephthalate (PET), polyethylene terephthalate glycol (PETG), polycarbonate (PC), polycaprolactone (PCL), polyethylene co-trimethylene terephthalate (PETT) and nylon.

Printing paste

A viscous fluid made from particles suspended in a solvent.

Thermoplastic filament

A polymer that displays malleability at higher temperatures and is a solid at lower temperatures. For the purposes of fused deposition modelling 3D printing, a thermoplastic must be able to extrude through a nozzle at elevated temperatures.

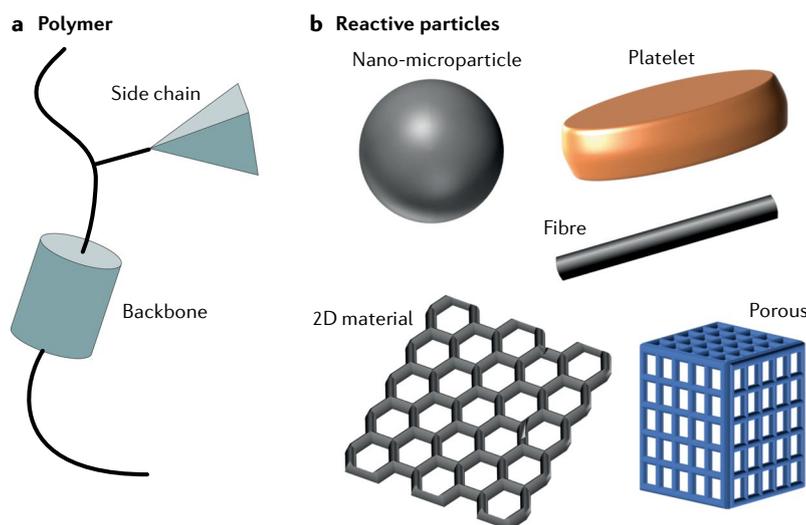


Fig. 2 | Additives that imbue chemical reactivity in 3D printed objects. **a** | Polymers in 3D printing materials can have reactive side chain or backbone functional groups. **b** | Different types of particle can be added to 3D printing materials to facilitate chemical reactivity in printed objects. These particles include platelets, nanoparticles, microparticles, fibres, 2D materials and porous particles such as metal organic framework and zeolitic materials.

There are very few easily accessible functional groups on these polymers; the nitrile groups on the ABS side chains, the hydroxyl groups on PVA and the ester backbone of PLA are the rare examples (FIG. 3a).

ABS is a staple in injection-moulded consumer products. As such, there are a number of commercially available coating technologies that treat ABS for use in different applications^{44,45}. These processes have yet to be explored as a way to tailor the reactivity of 3D printed ABS objects. Additionally, the organic reactions for transforming nitriles are also well known but have not been adapted for modifying 3D printed objects⁴⁶. Both of these approaches offer pathways for imbuing ABS objects with chemical reactivity.

PLA has also been used to generate objects for research purposes. For example, the incubation of PLA-based biological scaffolds in aqueous systems results in the hydrolysis of the ester bond of the polymer⁴⁷. As discussed below, this hydrolytic reactivity plays an important role in the success of the scaffold, as it supports cell growth and tissue development. As with modification of ABS objects, the transformation of esters has yet to be explored as a means to add specific reactive functionalities to PLA.

Several researchers have manufactured their own filaments to print objects for very specific applications. One approach in this direction is to synthesize custom polymers. Boydston and co-workers produced PCL filaments by reacting caprolactone monomers in the presence of caprolactone-modified spiropyran⁴⁸. The resulting polymer was formed into a printable filament using a common extruder. Some researchers have incorporated functionality into their filaments by mixing traditional 3D printing polymers with other materials. Several groups have solvent cast suspensions of inorganic nanoparticles and polymers and generated printable filaments

from the evaporated films^{34,40,41,49}. Despite the ease of this approach, there is a risk of phase separation between the printing polymer and the additive during evaporation. Another approach involves the use of the blending instrumentation regularly employed in the polymer industry. Twin-screw extruders are used to compound dyes and polymers to generate commercially available coloured filaments. Similarly, these instruments can blend a printing polymer with other types of additives. We used this approach to generate ABS–MOF composites³⁹. During this process, we flooded the system with nitrogen to ensure the stability of the organic linkers in the MOF at the high temperatures required for blending. MOF particles have also been grown on printed thermoplastic objects and tested for their ability to remove dye molecules from water^{32,50}. Liu and co-workers have synthesized HKUST-1 (a MOF composed of copper ions and 1,3,5-benzenetricarboxylic acid) on an ABS object³², whereas Zhang and co-workers synthesized the same MOF on a PLA object.⁵⁰

One issue with the use of FDM-based approaches for 3D printing chemically active objects is that the polymers tend to have low porosity. This leaves the surfaces exposed by the object as the best sites for modification if the goal is to produce efficient catalysts. One approach for overcoming this limitation is to generate pores within a 3D printed object. Porogens are materials that have different solubility from the primary structural polymer⁵¹. For composites containing a printable polymer and reactive insert, the choice of porogen must be made such that the initial blending and final solvent treatment do not affect the distribution of the reactive insert in the structural polymer. This approach has been successfully employed to produce a commercially available filament that is composed of a rubber-elastomeric polymer and PLA. Pores are generated by soaking printed objects in water, solubilizing and removing the PLA.

Another issue that arises in FDM printing is that not all thermoplastics print as easily as others. As an example, PLA does not require as many controls on external parameters during printing as ABS. PLA can be printed directly from the heated nozzle onto an unheated platform. ABS, however, contracts as it cools. During printing, this can lead to object warping. We have found that printing on a heated platform in an insulated chamber works best for ABS^{34,39,41}. Issues with printing quality (such as, changes in thermo-physical properties, rheology, warping and others) complicate laboratory-manufactured filaments of pure polymers, polymer blends and polymer composite materials.

Robocasting and direct ink writing

In robocasting or direct ink writing (DIW), an ink (often a gel or paste) is extruded through a syringe onto a platform in a similar manner to the FDM process⁴. The ink is composed of a solvent and either a gelling polymer or paste-producing nanoparticles. Often, these inks are made by mixing multiple components to generate optimal rheological properties⁵². These properties include the ability to be extruded through a syringe needle or tip under an applied pressure and to maintain a given shape after extrusion when no force is being exerted.

Extruder

An instrument that forces a fluid through a nozzle. For the purpose of 3D printing, the fluid can be a thermoplastic (fused deposition modelling), a gel or a paste (robocasting and/or direct ink writing).

Twin-screw extruders

Devices used to homogeneously blend a polymer with another substance. During this blending process, the polymer is heated above its melting or glass transition temperature while two screws, which interpenetrate one another, continuously mix the components.

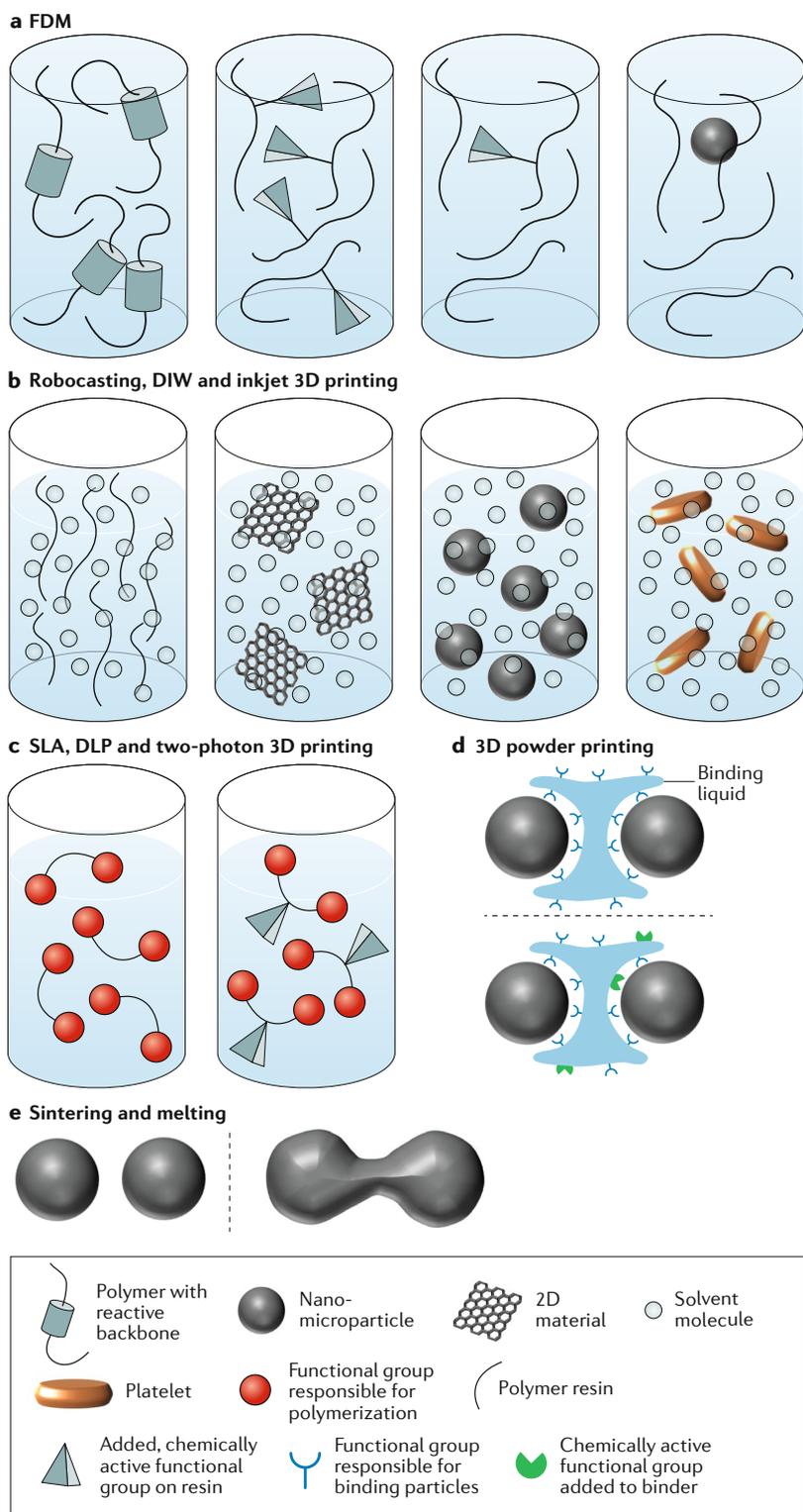


Fig. 3 | Overview of reactive materials that can be used in various 3D printing techniques. **a** | Filaments used in fused deposition modelling (FDM) are made from any polymer composite that can be extruded at high temperatures and quickly solidified upon cooling. Chemical reactivity in FDM materials can come from the primary polymer or from additives (blended polymer, blended nanoparticle or reactive moiety added after the printing process). Care must be used in modifying the filaments before printing, as the high temperatures required for extrusion can degrade some additives. **b** | Robocasting, direct ink writing (DIW) and inkjet 3D printing all use liquid-based inks. Chemically active species can be part of the printed ink or can be added after printing (in the case of robocasting and DIW). **c** | Stereolithography (SLA), digital light processing (DLP) and two-photon 3D printing generate objects through photopolymerization of reactive resins. These resins can incorporate reactive functional groups (orthogonal to the photochemistry) or reactive particles or can be functionalized after printing. **d** | 3D powder printing involves using a printed binder liquid to glue together particles in a powder. The chemical reactivity of these objects can come from the powder or from the deposited ink. **e** | For objects made with metal or ceramic powders, a final sintering step is required that will degrade any organic functionality from the binder liquid. In sintering and melting-based 3D printers, a polymer or metal powder is locally heated to join individual particles into a larger object. The powder can be the basis for the desired chemical reactivity, or the object can be functionalized after the printing process. Metal sintering printers have a higher cost than those that use polymers.

can also be based on inorganic nanoparticles, in which particle–particle interactions (and not particle–solvent or solvent–solvent interactions) dictate rheological properties³⁷. To achieve the high particle concentrations for these inks, it is often necessary to use orbital mixers for blending.

The great benefit of DIW is that inks can be generated on demand. Users have free latitude to include reactive molecules or particles as they see fit. These have included polymers^{55–57}, proteins⁵⁸, graphene³⁸, graphene oxide³⁷, nanoparticles and microparticles (of clays and ceramics^{59,60}, metal oxides³⁵, quantum dots⁶¹, metals^{62,63}, zeolites⁶⁴ and MOFs⁶⁵) (FIG. 3b). The use of metal oxide particles has been especially notable in the production of catalytic 3D printed objects.

The challenge to DIW is that printed objects need to have stability within the environments in which they are to be used. The structures generated with DIW require extra processing steps to achieve the mechanical properties of objects produced by FDM. In most cases, the solvent needs to be carefully removed from the object, usually using gentle heating and lyophilization⁶⁰. Methods to optimize the mechanical properties of these objects vary depending upon the materials used. Some combination of inorganic particles and polymers will generate stability⁶⁶. Some polymer-containing systems can be crosslinked^{67,68}. Metal oxide-based systems can be sintered, although any organic molecules present will be carbonized⁶⁰. In some instances, carbonization can be a feature instead of an issue. Travitzky and co-workers

Hydrogels

Water-based substances with increased viscosity caused by the interaction of macromolecules within the mixture.

There are several procedures that can be used to achieve these results. Similar to FDM, a solid gel can be heated until it exhibits flow and extruded onto a cooled platform. Gelatin-based suspensions can be printed in this manner⁷³. Another approach is to create a solid-like suspension that flows only under periods of shear stress. Inks can be based on hydrogels, in which the polymer forms a web-like solid network within the solvent⁵⁴. Inks

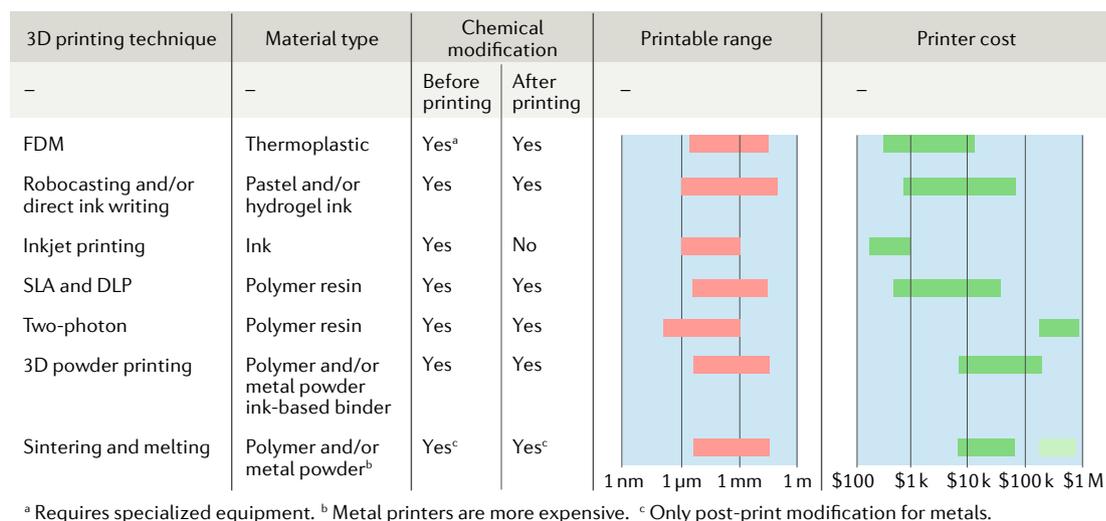


Fig. 4 | **Technical details of different 3D printing approaches.** 3D printing methods to imprint chemical activity to an object are compared. DLP, digital light processing; FDM, fused deposition modelling; SLA, stereolithography.

and Hutmacher and co-workers have generated graphitic structures using DIW with inks that contain starch and by carbonizing the resulting object^{69,70}.

Once a stable object has been generated, there is an array of options for chemical functionalization. Objects can be coated with thin films⁷¹, and molecular components, ranging from molecular transition-metal catalysts⁷² to biologically relevant small molecules and proteins^{73,74}, can be covalently attached.

Inkjet printing

Inkjet printers can manufacture small-scale (micrometres to millimetres) 3D printed objects^{75–78}. In this case, inks are composed of a solvent along with a structure-forming material (FIG. 3). Liu and co-workers, for example, generate their inks from ethanol, acetic acid, hydrochloric acid and structure-forming materials (a triblock co-polymer and metal ions)⁷⁷. Another example of an ink used in this kind of printing from Parkinson and co-workers includes a metal salt in a water–glycol mixture⁷⁸. A general schematic of the inks is shown in FIG. 3b. As opposed to the inks used in DIW, those required for inkjet printing do not need to exhibit thixotropic properties, typical of thick fluids that change their viscosity under an applied force. In fact, these inks are optimized with lower viscosities and fast evaporating solvents. A benefit of using inkjet printing is that it is easy to use multiple inks during the same printing process. Most of the chemically reactive objects produced by inkjet printing so far are new catalytic materials^{6,76–78}. The ability to use multiple ink wells allows for mixing metals and metal oxides at various ratios for testing reactivity. There are other printing technologies that combine inkjet deposition with controlled material curing steps. One example of this is the **PolyJet technology from Stratasys**, which combines inkjet printing and photopolymerization processes (described in the next section) into a single printer. This technology can generate large (with sizes on the order of hundreds of centimetres) and intricate

structures (with features as small as 100 micrometres) from a variety of polymers and polymer composites from inkjet printing processes.

SLA, DLP and two-photon 3D printing

Stereolithography (SLA)^{79–81}, digital light processing (DLP)⁸² and two-photon⁸³ 3D printing use photochemistry to generate solid polymers from a liquid resin (FIG. 3c). SLA and two-photon printers use lasers, whereas DLP uses projected light, structured into a 2D image. DLP tends to generate objects more quickly than SLA, which requires a laser to be raster scanned across the surface of the resin. Continuous light interface production (CLIP), an advanced form of DLP, uses oxygen diffusion to control the polymerization process and speed printing⁸⁴. Two-photon 3D printing polymerizes resin only at the focus of a laser passed through a microscope objective. This process can generate objects with the smallest print resolution (on the order of 100 nm)⁸³ but is limited by the object size and time required for printing.

Resins used in SLA, DLP and two-photon 3D printing are composed of acrylic, epoxy or urethane-based molecules and can be modified both before printing and after printing to achieve the desired chemical functionalities^{85–88}. Resins with designed chemical reactivity orthogonal to the polymerization process can be synthesized and used in the same manner as the commercially available resins. Polyethylene glycol (PEG) dimethyl acrylate resins have been used to generate biocompatible scaffolds^{89,90}. Boydston and colleagues have developed special resins that can generate flexible printed structures⁸⁸. There is no reason why similar modifications that incorporate catalytic functionalities could not be used for the production of chemically reactive objects.

Polymer composites can also be generated during photopolymerization. Carbon, the company that licenses the CLIP technology, generates composites that contain thermoset polymers within the polymerized scaffold. Post-printing heat treatments ultimately dictate the

mechanical properties of the printed object. Gao and colleagues have incorporated nanoscale hydroxyapatite into their printed objects to facilitate the regeneration of bone tissue⁹¹. Hensliegh and co-workers have used SLA processes to produce polymer–graphene oxide composite structures⁸¹. Several groups have used resin curing to produce printed polymer–MOF composites^{92,93}.

3D powder

For 3D powder printing, an inkjet is raster scanned across a bed of powder^{94,95}. The ink solution contains a chemical glue that binds the powder particles together (FIG. 3d). As the object is generated, the platform is lowered, a new layer of powder is added on top, and the next layer of the object is formed through the application of binder ink. A number of polymer powders can be used in this process as can ceramics and metals. The metal and ceramic objects built this way require sintering to achieve full stability. Polymeric objects from these types of printer have been used in a number of medically related applications^{70,96–98}.

Sintering and melting

Laser sintering and laser melting techniques use high-power laser sources, scanned over a bed of powder, to selectively sinter the powders into a solid object or melt the powders, which form a solid object on cooling (FIG. 3e). New layers are added in a similar manner to the 3D powder printing technique. There are laser sintering and melting instruments that are designed for either polymers (polyamide 12 is the most widely used) or metal or ceramic particles^{25,94}.

Chemical reactivity

Chemical functionality can be manifested in a number of ways, and catalytic properties come immediately to mind. In the next sections, we discuss 3D printed catalytic objects but also touch upon other, perhaps subtler, types of chemical reactivity. Molecular recognition and binding, signal transduction and bond lability are all types of chemical functionality that are found and applied in 3D printed objects. We detail examples of these types of chemical properties for applications in catalysis, molecular storage, electronics, signal transduction and tissue culture.

Chemical catalysis

Catalytic objects are ideal targets for researchers using 3D printing^{7–9} (FIG. 5a). The ability to define a printed material gives the researcher control over the reactions that they wish to catalyse. Furthermore, the ability to define object geometry can lead to structures that optimize the flow of reactants through a printed reactor. Because of these capabilities, 3D printing has the potential to increase the efficiencies and decrease the cost for many industrial processes.

One of our goals, when first thinking about generating chemically active 3D printed objects, was to create a printing material that could potentially have a low entry barrier for casual users. ABS and PLA-based FDM filaments seemed to be ideal for this purpose. We solvent cast TiO₂ nanoparticles and ABS from an acetone

suspension³⁴. The resulting TiO₂–ABS composites were formed into filaments, printed and evaluated for photocatalytic activity. The printed objects were capable of degrading a dye when they were in direct sunlight, but they showed no activity when stored in the dark.

Although the approach we proposed offers broad accessibility, the composite polymer–catalyst material is not optimized to efficiently facilitate catalysis. For a reactive object, the exposed surface plays the largest role in supporting catalysis. In our approach, the reactive nanoparticles within the polymer composite are not optimally exposed to the analytes of interest. To this end, some researchers have printed reaction containers using FDM and modified the surfaces of these containers with reactive moieties. Cronin and colleagues printed a set of connected reaction containers with polypropylene^{12,31}. In one chamber, the surface was modified with montmorillonite K10, applied as a paste of acetoxysilicone. In another chamber, the surface was modified with Pd on carbon catalysts, applied in a similar manner. The reactionware facilitated a Diels–Alder reaction (catalysed by the montmorillonite K10) and a reduction (catalysed by the Pd on carbon). In another experiment, the same group modified an object, printed with polypropylene, with silver paint followed by a sputtering of gold. They used these reaction containers to support the electrolysis of water⁹⁹.

Perhaps the most used technique for generating catalytic 3D objects involves the direct print of the catalytic material through DIW or inkjet printing. In both cases, inks are composed of reactive particles suspended in solvent. After printing, the solvent is removed and the object sintered. For the cases in which inkjet printing is used, object formation usually occurs using some sort of non-reactive glass as a substrate. DIW can generate free-standing metal and metal oxide objects that are larger in size than those made using inkjets. Catalytic monoliths have been produced and discussed in detail elsewhere^{7–9}, but we report a few examples below.

Michorczyk and colleagues used a DLP printer to produce a polymer-based template of a catalytic monolith¹⁰⁰. They filled the template with a manganese-doped sodium tungstate paste. Burning off the polymer and sintering the paste, they were left with a monolith structure that contained open channels in which to flow reactants. They tested these catalytic monoliths for the conversion of methane into larger hydrocarbons at 800 °C. Sotelo, Gil and colleagues used DIW to print a catalytic monolith from a copper-doped Al₂O₃ paste⁶². The sintered object was then used to perform a number of copper-catalysed organic transformations. Zhu and co-workers generated a gold monolith with nanoporous features by first printing an ink composed of a polymer and a gold–silver alloy⁶³. Sintering and dealloying processes generated a final gold object, which allowed for fast mass transport and catalysis in the oxidation of methanol to methyl formate. Finally, Gil, Coelho and colleagues used DIW to print silica pastes. After sintering, they used silane chemistry to modify the surface of the monoliths with either a Cu(I)-based or a Pd(II)-based molecular catalyst⁷². Placing both monoliths in a reaction container, they were able to

Sintering

The act of changing a powder into a solid material through application of heat and pressure without completely melting the powder.

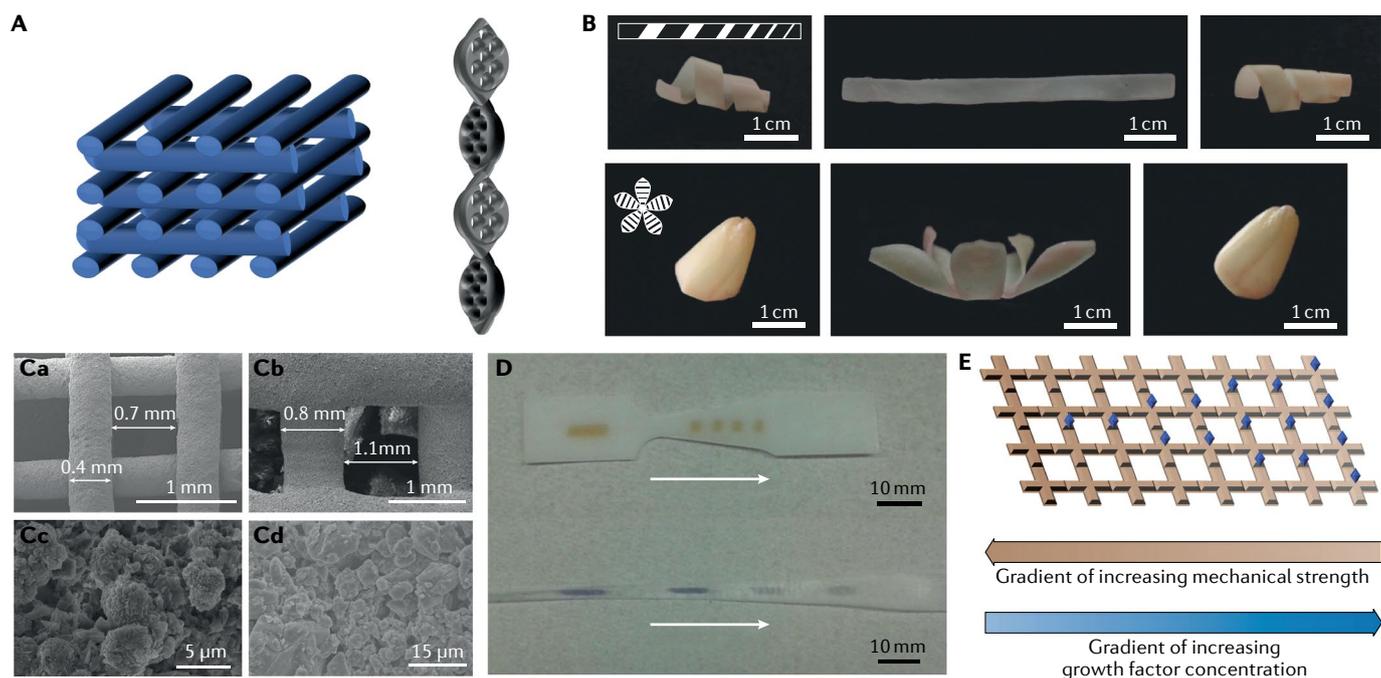


Fig. 5 | Examples of printed object geometries that exploit chemical functionality. **A** | Catalyst architectures (left: woodpile; right: porous helix) increase the exposed surface area of the printed object and induce turbulent flows in reactive devices. **B** | 3D printed objects made of a stimulus-responsive wax-based polymer. These polymers swell according to the duration of their light exposure and were used to print different planar layouts (inserts). Exposing the different parts of the printed layouts (light areas correspond to short exposures, and dark areas correspond to long exposures) leads to complex 3D shapes: a helix (top left) and a tulip flower (bottom left). The objects can be deformed at high temperature (top and bottom centre), but the initial shape can be recovered by cooling (top and bottom right)¹⁰⁷. **C** | 3D printed metal-organic framework material (MOF) monoliths for gas storage. Parts **Ca** and **Cb** show scanning electron microscopy (SEM) images of MOF-74(Ni) monoliths, and parts **Cc** and **Cd** show SEM images of UTSA-16(Co) monoliths⁶⁵. **D** | 3D printed materials for sensing mechanical distortions, before (top) and after (bottom) elongation⁴⁸. **E** | Design targets for tissue engineering featuring gradients of mechanical strength and concentrations of growth factors are shown. Part **B** is adapted with permission from REF.¹⁰⁷, Wiley-VCH. Part **C** is adapted with permission from REF.⁶⁵, ACS. Part **D** is adapted with permission from REF.⁴⁸, ACS.

perform a multicomponent reaction that included a copper-catalysed alkyne–azide cycloaddition and a palladium-catalysed cross coupling.

Catalytic architectures can also be generated using photocuring resins. Yang and co-workers used a bromine-containing photocuring initiator⁸⁵. After the printing process, they used the initiator incorporated within the object as a site for facilitating atomic-transfer radical polymerization. Slowing and colleagues printed objects with resins containing a number of functional groups (carboxylic acids, amines and copper carboxylate) along with the vinyl groups necessary for curing⁸⁷. These secondary functional groups were active for Mannich, aldol and cycloaddition reactions.

Stimulus sensing and response

There are many examples of objects printed from stimulus-responsive materials, activated through chemical, mechanical and electrical changes, to name a few^{18,48,56,75,101–103}. The ability to generate programmable chemical composites coupled to the unique geometry-creating capacity of 3D printing can lead to a variety of responsive objects. Highlighting the marriage of geometry and material is the printing of photonic devices and optical waveguides^{49,75,104}.

Of all stimulus-responsive objects, electronically active objects have perhaps garnered the most interest^{56,82,105}. This is evident from the variety of commercially available, conductive FDM filaments. Several forms of conductive materials have been explored by researchers. A silver nanoparticle–silicone composite was printed with robocasting and used as the sound-detection and signal transduction medium of a printed bionic ear¹⁰¹. Conductive nanoparticles have been used in FDM, DIW, inkjet, sintering and melting-based printers. The research groups lead by Travitsky and Huttmacher have used robocasting to print polymeric materials (including starch), which are then carbonized. Graphene and graphene oxide-based materials have garnered much interest as well^{69,70}. Graphene oxide has been incorporated into ABS for FDM printing using solvent exchange¹⁰⁶. Graphene oxide has been used as the primary rheological modifier for generating inks to be used in DIW³⁷. Graphene-based aerogels have been generated by DIW of graphene inks within a non-solvent matrix³⁸.

4D printing is a name that has been given to the design and printing of objects that can change shape in response to an external stimulus^{107,108} (FIG. 5b). Shape control in these objects occurs in two ways: mechanically deformed objects revert to their original shape

upon changes in temperature, and hydrogels swell in response to chemical stimuli. Dunn, Qi and co-workers have printed objects composed of both hydrogels and temperature-controlled, shape-memory polymers¹⁰⁹. Zhao and collaborators have printed magnetic domains within soft materials using DIW, aligning the magnetic particles within the printed material with an applied field¹⁰⁷. The result is a mechanically active material that responds to changes in the local magnetic field.

Molecular storage and separation

Substantial advances have been made on materials that can store gases at higher densities than possible in traditional compressed gas cylinders. MOF and zeolitic materials are in the midst of a renaissance; options for combinations of metal ions and organic linkers, theoretical modelling of active sites and crystalline defects and the allure of applications in storage, sensing and catalysis have caught the imagination of materials scientists¹¹⁰. One of the issues for full deployment of MOFs is that they are synthesized as powders. For applications based solely on storage, the powder-based nature of MOFs is not an issue. However, incorporation of MOFs (and their functionality) into other devices will require that they be processible. Blending MOFs in polymers can have the added benefit of preventing MOF degradation owing to humidity³⁹.

There has been an effort to combine MOF particles with 3D printing technologies. Liu and collaborators have grown HKUST-1 crystals on 3D printed ABS scaffolds³². Several researchers have generated FDM filaments by solvent casting to produce polymer–MOF composites^{39–41}. Erikson has been able to display printing with a 50% blend of MOF and polymer⁴⁰. As some MOFs are environmentally sensitive, we have found that long exposure times during solvent casting can degrade MOF particles during composite preparation⁴¹. For industrial preparation of coloured filaments, polymers need to undergo a melt-blend process with dye powders in twin-screw extruders. We have found this process to be effective in generating polymer–MOF filaments while protecting the MOF from ambient humidity by operating under a constant flow of nitrogen³⁹. Furthermore, the MOF composites, which retain their gas storage capacity, can be incubated in water without any loss of crystalline structure. Rezaei and colleagues have generated DIW inks with 80% MOF loading and printed MOF monoliths that show absorption capacity similar to the unprocessed powder⁶⁵ (FIG. 5c). Additionally, Chin and co-workers have used SLA to magnetically align different MOF crystals within a printed structure⁹².

Electrochemical and information storage

Objects have been printed in order to explore new ways to generate materials and architectures for electrochemical storage^{111–113} (FIG. 5d). A recent review has highlighted many of these efforts¹¹³. Worsley, Li and co-workers have used DIW of graphene–MnO₂ composite materials to print pseudocapacitive electrodes¹¹². Sans and colleagues have used SLA to print objects that contain ionic liquids and polyoxometallates¹¹¹ and tested their photochromic properties to reversibly store information.

Objects for use in tissue engineering

In many ways, researchers printing objects for tissue engineering (TE) have been at the forefront of the effort to print chemically reactive materials^{2,90,114}. For TE, materials must have appropriate structure (on the macroscale, microscale and nanoscale), provide the possibility of nutrient transport and, importantly, facilitate appropriate cell–matrix interactions¹¹⁵. The ability to remodel tissue matrix is a critical factor that determines the ultimate success of cell growth and tissue development¹¹⁶. Efficient remodelling requires both cell attachment to and cleavage of the matrix material. That is, the chemical functionalities that must be present in any 3D printed TE scaffold are binding moieties that attach to cell surface proteins and structural integrity that can be enzymatically degraded and reprogrammed. For this reason, the primary components of many printed TE scaffolds are proteins (collagen, elastin, fibrin, gelatin, silk fibroin and decellularized extracellular matrix)¹¹⁴. These scaffolds are generally produced using robocasting, although inkjet printing and other droplet-based printing methods are also used.

One of the great benefits of these printing styles is that the ink formulation is user defined and is often easy to manufacture. As such, multiple inks can be printed during a single print job, resulting in programmed molecular or cellular gradients along a printed matrix (FIG. 5e). Composite inks that incorporate a number of useful functional materials can be generated at the researcher's discretion. Importantly, these methods are also gentle enough to allow printing of materials that contain living cells.

Microcarriers are micrometre-scale particles that support cell adhesion and can facilitate the expression of specific cellular phenotypes. Levato and colleagues printed gradients of microcarrier ink to support the growth and location-specific differentiation of mesenchymal stem cells in a manner that mimics the gradient of cartilage composition in subchondral bone¹¹⁷.

For some tissue supports or medical implants, a sturdier support structure is needed than offered by the hydrogels generated with robocasting or droplet-based printing techniques. 3D powder-based printing allows for binding inks that contain biologically active materials. Metal or polymer particle sintering or melting and FDM methods can also generate the types of scaffold needed, but these objects must be supplemented with some sort of coating that can facilitate cell adhesion and differentiation⁹¹.

Specific growth factors and nutrients are also important constituents for an effective TE scaffold. Bone growth, supported by 3D printed objects, progresses much better in the presence of hydroxyapatite^{118,119}. To that end, Zhang and colleagues have generated objects using SLA and a resin that contains dimethacrylated PEG and nanoscale hydroxyapatite particles^{118,119}. The SLA process has a higher resolution than robocasting, which is ideal for the generation of narrow channels for nutrient flow.

Outlook

Research on chemically active 3D printed objects is in its early stages. The degrees of freedom in these objects include reactive moieties, matrix materials and object geometry. There are countless possibilities for generating

Melt-blend

The homogeneous mixture of a thermoplastic and other material (another thermoplastic, inorganic nanoparticle, polymer particle, and so on) made at elevated temperatures capable of melting the matrix thermoplastic.

reactive structures from 3D printing. Many advances will come through optimization of these three variables for producing objects that satisfy the particular needs of an application.

One of the aims of 3D printing technology development is to create controlled geometries over multiple length scales (nanoscale, microscale and macroscale). Resolutions vary by the type of printing process. Two-photon polymerization enables the smallest print feature sizes, on the order of hundreds of nanometres, but cannot produce large objects in reasonable print times. Other printing techniques enable the generation of features of more typical sizes, on the order of hundreds of micrometres. In TE applications, programmed control over chemical placement and structural geometry over these length scales are crucial for the success of printed scaffolds.

3D printed objects tend to have homogeneous composition. The generation of chemical composition or mechanical strength gradients along the length of an object is another area of current interest. Gradients of catalysts along a flow channel can facilitate entire reaction sequences instead of individual molecular transformations. Gradients of nutrient availability, molecular recognition sites and matrix mechanical strength are important factors for cellular differentiation and tissue development.

To date, most 3D printing is performed to generate well-defined objects with clean and smooth surfaces.

To facilitate maximal chemical functionality, however, materials must display controlled porosity. There have been several studies that focused on generating programmed porosity in reactive objects^{63,120}. It seems safe to say, however, that much work remains to be done in modelling and designing geometries that best serve a needed application.

Finally, we see great potential in combining multiple application modalities within an individual 3D printed object. Catalytic devices can be designed that facilitate reaction cascades and isolation of reaction products. A heterogeneous photocatalyst, composed of multiple metal oxide materials, can be generated to support reaction chambers in which the wavelength of light dictates which catalyst is activated. Waveguides can be printed with spatially resolved sensing modalities that can communicate both the presence and the location of analytes. Tissue scaffolds that support differentiation while also reporting development parameters can provide real-time analysis of implanted devices.

The future applications of chemically active, 3D printed objects abound. The democratization of manufacturing capabilities is bound to not only excite scientific curiosity across disciplines but also unleash users' imaginations, opening new venues in the chemical sciences with applications far beyond.

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M.R.H. wrote the article. Both authors contributed equally to all the other aspects of the article.

Competing interest

The authors declare no competing interests.

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