# Three-Dimensional Printing of Complex Structures: Man Made or toward Nature?

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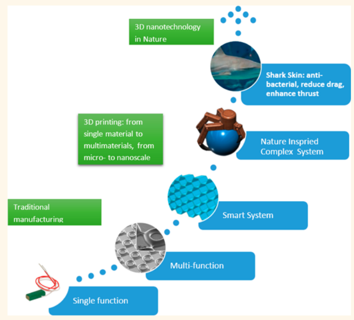
**ABSTRACT** **Current three-dimensional (3D) printing techniques enable the fabrication of complex multifunctional structures that are unimaginable in conventional manufacturing. In this Perspective, we outline recent progress in materials and manufacturing and propose challenges and opportunities for the future development of 3D printing of functional materials. The success of future 3D printing relies not only on multifunctional materials and printing techniques but also on smart design of complex systems. Engineers need to understand advanced materials, additive manufacturing, and, more importantly, creative design. Fortunately, we can learn from many structures that exist in nature and adapt them to engineered structures.**




The traditional approach to fabricating a structure is to address its individual functional requirements separately. For example, in the past, most structural materials have only had load-carrying functions. Recently, however, many load-carrying structures have had non-load-carrying functions, driven by discoveries in multifunctional materials, such as a biomimetic artificial muscle using fiber-mimicking myofibrils[1] and a structural battery[2] created by integrating energy storage into the load-bearing structures. The nature of a complex system drives the need for engineers to consider many factors during the design and manufacturing of multifunctional components. In structural energy storage devices, for example, the energy density of the storage medium is reduced due to less conductive structural materials. Meanwhile, the decrease in the parasitic structure results in weight savings, which, in turn, improves overall energy efficiency for the system.

Recent advances in materials and manufacturing have the potential to enable fabrication of smart structures and complex systems. In the past, it has been difficult for conventional materials to achieve simultaneous improvement in multiple functions. However, with increasing use of composite materials, the potential to make more complex functional systems is being extended. These systems can carry many functions, such as electrical and thermal conductors, plasmonics, energy harvesting and storage, self-healing, sensors, actuators, biocompatibility and biodegradability, *etc*. Previously, three-dimensional (3D) printing has primarily been used to generate replicas of natural and man-made structures, such as bioimplants, toys, art statues, structural metallic components, *etc*. With advanced 3D printing techniques, it is possible to manufacture nano/microscale complex structures that are not feasible by other manufacturing techniques. However, current multifunctional 3D structures lack the design principles necessary to make them simply and efficiently, whereas in nature, many structures carry smart but simply beautiful designs. We are now at a stage to think about how to define the design and manufacturing principles that make 3D printing a technology capable of producing complex structures. Let us take a look at an important smart material, a piezoelectric material, to see how it can be used to manufacture various functional structures. Understanding design and manufacturing of this material will give us some strategies as to how an engineered structure can be made with smart design, learning from the ways that these structures are created in nature.

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**With advanced 3D printing techniques, it is possible to manufacture nano/microscale complex structures that are not feasible by other manufacturing techniques**

Piezoelectric materials, converting compressive/tensile stresses to electric charge or *vice versa*, are of great importance in practical applications, such as medical imaging, telecommunication, ultrasonic devices, and electrical actuators. Currently, most piezoelectric materials utilized in systems are based on brittle ceramics like lead zirconate titanate (PZT), solid solutions such as $Pb(Mg_{1/3}Nb_{2/3})O_3-PbTiO_3$ (PMN−PT) and $Pb(Zn_{1/3}Nb_{2/3})O_3-PbTiO_3$ (PZN−PT), and other perovskite-based oxides like $BaTiO_3$ (BTO).[3] Although PZT possesses a high piezoelectric coefficient of $d_{33}$ > 300 pC/N, it varies depending on composite and processing conditions.[4] Higher piezoelectric coefficients of ∼1500 and ∼2500 pC/N have been achieved for PMN−PT and PZN−PT solid solutions, respectively, due to the enhanced polarizability arising from coupling between two equivalent energy states in a morphotropic phase boundary (MPB). These lead-based relaxor materials in MPB systems are complex perovskites with the general formula $Pb(B_1B_2)O_3$, which have broad and frequency-dispersive dielectric maxima. Although a lower piezoelectric coefficient of ∼460 pC/N was achieved with BTO, lead-free material still drew attention because it is environmentally benign and has a structurally simple composite.[3]

Three-dimensional printing techniques provide a powerful tool to fabricate complex 3D composite structures for polymer composites, opening infinite possibilities in their design and applications. In this issue of *ACS Nano*, Kim *et al.*[4] report a stereolithographic (SLA)-based method for 3D printing of polymer/piezoelectric composites. Barium titanate nanoparticles, synthesized by hydrothermal processes, were selected as the piezoelectric material. The BTO nanoparticles were embedded in a poly(ethylene glycol) diacrylate (PEGDA) matrix and then exposed to a patterned light layer-by-layer. As shown in Figure 1b, a 3-trimethoxysilylpropyl methacrylate (TMSPM) link polymer was used to graft the BTO surface to a PEGDA matrix covalently in order to enhance the stress transfer efficiency. Kim *et al.*[4] claim that a BTO mass

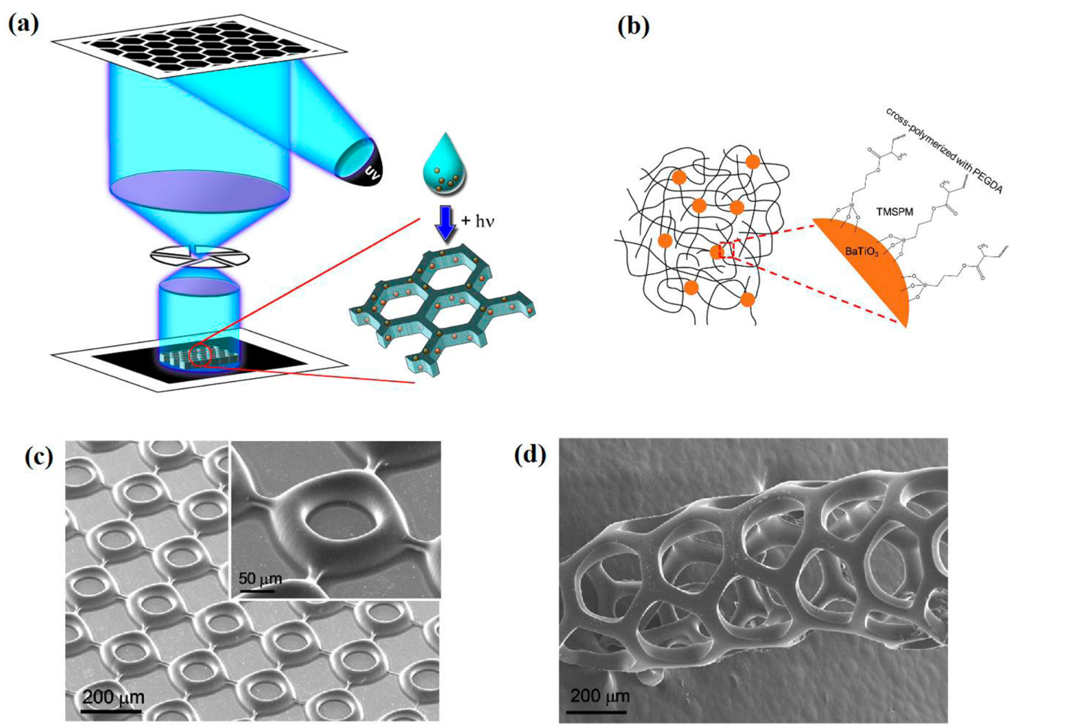


**Figure 1. (a) Schematic of digital projection printing setup that projects dynamic digital masks on the photolabile piezoelectric nanoparticle−polymer composite solution. (b) Schematic showing the piezoelectric polymer composite materials with barium titanate nanoparticles (orange circles) grafted to a polyethylene glycol diacrylate matrix (black lines). The higher resolution inset shows the 3-trimethoxysilylpropyl methacrylate linker covalently linked to the nanoparticle surface and cross-linked with the PEGDA matrix. (c) Collage of piezoelectric microstructures printed using DPP including square arrays with different sized void spaces. (d) Microtubule structure formed by releasing a honeycomb array from the substrate. The film rolls up after release due to slight stress gradients in the film. Reprinted from ref 4. Copyright 2014 American Chemical Society.**

loadings of 1−10 wt % and a 1% photoinitiator create excellent load transfer, thus providing strong piezoelectric outputs and good mechanical properties approaching those of pure polymer. Microscale digital projection printing (DPP) with high-throughput and resolution has been used to achieve resolutions on the scale of 1 $\mu$m for pure polymer and 5 $\mu$m for composites. The 3D printing setup is schematically shown in Figure 1a. Kim *et al.*[4] used this process to print complex 3D structures and microstructures, including square arrays with different sized void spaces (shown in Figure 1c). The structure in Figure 1d is rolled up by the film in Figure 1c. The resolution of printed patterns is strongly dependent on the light−matter interaction of BTO nanoparticles. The transparency of polymer for 365 nm light drops down to 5% when adding 10 wt % of BTO nanoparticles. The decrease of transparency limits the mechanical−electric transfer values.

After 3D printing, the BTO nanoparticles were activated by applying a precise electric field. The activated piezoelectric composites can remain or can be transferred to another substrate for further application. The piezoelectric properties were compared among three composites: (1) composites with 10 wt % BTO nanoparticles only, (2) composite materials without the linker but with carbon nanotubes (CNTs) (1 wt %), and (3) cross-linked films containing TMSPM linker (no CNTs). Under similar loading (1.44 N), the piezoelectric output of cross-linked films is more than two times that of BTO composites with CNTs and more than 10 times that of BTO composites. The quantified piezoelectric coefficient ($d_{33}$) values of 10 wt % BTO-loaded CNT composites and TMSPM-grafted composites are 13 ± 2 and 39 ± 3 pC/N. The latter value exceeds that of pure piezoelectric polymer, such as PVDF. However, this value is still much lower than that of BTO monolithic ceramics (∼200 pC/N). The authors emphasize that the increased mechanical interface between the BTO surface and the PEGDA matrix would greatly increase the piezoelectric coefficient. They mention that their future studies will focus on how grafting density, linker length, and polymer type affect the piezoelectric output of composite materials.

> **In this issue of *ACS Nano*, Kim *et al.* report a stereolithographic-based method for 3D printing of polymer/piezoelectric composites**

The 3D optical printing of piezoelectric nanoparticle−polymer composite materials[4] provides a useful tool to study the directly printed 3D structure platform and its effect on macroscale performance of piezoelectric devices. Prior reports have tried to characterize the role of 3D microstructural features like foam shape and porosity shape in determining the piezoelectric property of piezoelectric foam structures. Venkatesh *et al.*[5] found that the piezoelectric charge coefficient ($d_h$) can be enhanced significantly by modifying the shape of the porosity; for instance, $d_h$ of the equiaxed foam structure of PZT-7A with 30% porosity increases by 175%, by changing the shape of the porosity from a cuboidal shape to a flat-cuboidal shape. They further reported that not only the porosity but also the interconnected geometry and the architecture should be considered in the piezoelectric foam structures. This can be reflected by a 360% higher $d_h$ in close-packed structures compared to sparsely packed structures at the same 3% volume fraction of 3−3 type (PZT-7A) piezoelectric foam structures.[6] Some reports have also focused on the foam structure component piezoelectric coefficient modification; Lekkala *et al.* found that charged closed-cell microporous polypropylene foams show a piezoelectric coefficient of 140 pC/N, which exceeds that of the ferroelectric polymer PVDF by a factor of 5.[7] In addition to nanoparticle−polymer composite materials, solely piezoelectric nanoparticle printing has been studied recently. For example, Priya *et al.* successfully utilized the combination of solution-based aerosol process and selective laser sintering (SLS) to develop BTO-based ceramic 3D structures.[8]

However, limited research has focused on changes in design to improve the performance of piezoelectric structures. One example of learning from nature is a recent report by Iyer *et al.*,[9] who achieved enhanced effective piezoelectric responses by mimicking honeycomb-shaped periodic foams of PZT (Figure 2), proving that structural designs of a single-phase piezoelectric material can enhance the effective piezoelectric parameter. Considering that mechanical metamaterials obtain exotic mechanical transformations from periodic structural strategy, it might be intriguing to expand such strategies based on electrical−mechanical coupling to aim for maximizing energy conversion or harvesting efficiency.

## OUTLOOK AND FUTURE CHALLENGES

Regarding the future outlook and challenges, efforts may be undertaken on both the manufacturing and the design aspects of 3D printing multifunctional structures.

**Approaching the Resolution Limit.** Rapid prototype techniques provide a unique way to design and to fabricate complex 3D structures. However, 3D printing is a relatively time-consuming fabrication process. Current 3D printing processes provide layer resolution around 100 $\mu$m, lateral resolution of 30 $\mu$m, and an estimated write speed of 7 $\mu$m/s.[10] By applying advanced technologies of two-photon direct laser writing lithography (TPL), it pushes the length scale resolution down to

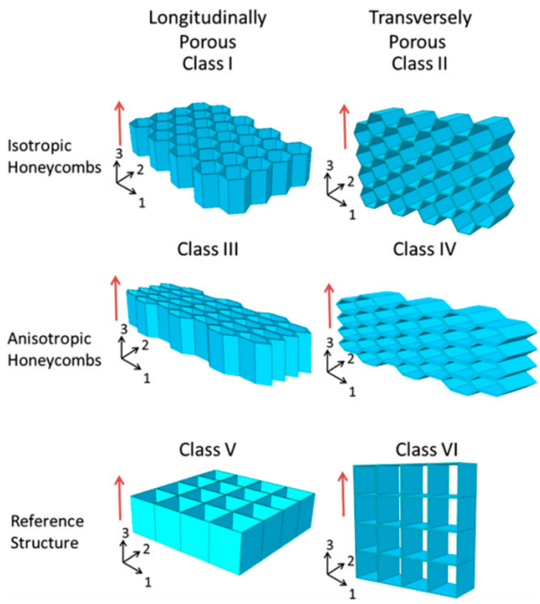


**Figure 2. Honeycomb-shaped porous piezoelectric structures with enhanced properties. Reprinted with permission from ref 9. Copyright 2014 Wiley.**

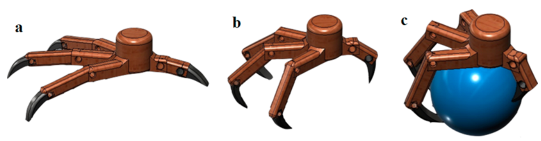


**Figure 3. Schematic of a bioinspired claw design of 3D piezoelectric structures. The snapshot of the structure at different positions: (a) open the claw, (b) close the claw, and (c) grab the ball.**

150 nm.[10] Adopting TPL techniques to print high-resolution 3D piezoelectric components would be a manufacturing challenge for the potential application of microelectromechanical systems (MEMS).

**Weight Ratio of Materials.** The applied method for 3D printing in Kim *et al.*[4] limits the weight ratio of piezoelectric materials in a polymer matrix, thus limiting the piezoelectric output. Other 3D printing methods, such as fused deposition modeling,[11] laminated object manufacturing (LOM),[12] and SLS,[13] have been applied for printing polymer composites. Continuous glass fiber with a high volume ratio of 55% in an epoxy matrix has been used to print 3D structure by LOM.[12] Short carbon fibers with a maximum weight ratio of 50% have been added into polyamide 12 (PA2) by SLS.[13] By applying other 3D printing methods, it is possible to increase the weight ratio of piezoelectric materials to a high value, thus enhancing the piezoelectric output.

**3D Printing of Multimaterials.** Multinozzle 3D printing systems enable material substitutions during the printing process.[14] With new 3D printing technologies, one can define not only the dimension of the printed material but also the composite at any desired spot. In this case, for any existing structure and its stress field under a certain loading, controlling the printed piezoelectric component ratio at different locations can potentially maximize the favored piezoelectric response from a chosen stress orientation.

**3D Printing of Ceramic Structures.** Another challenge is 3D printing of ceramic structures with high strength at various scales. Three-dimensional structures made of BTO were printed by SLS at a millimeter scale.[8] Lightweight and mechanically robust microscale biomimetic structures can be fabricated by a three-step 3D printing process.[15] Polymer skeletons were printed by TPL, and TiN was deposited using atomic layer deposition and then etched out of the polymer to generate ceramic hollow structures. A similar process was also applied to create cancellous bone and other cellular solid $Al_2O_3$ structures. Three-dimensional printed ceramic structures with high strength provide another solution for high-output piezoelectric structures.

**3D Metamaterials.** Three-dimensional printing techniques have also been applied for the fabrication and characterization of mechanical metamaterials, which had previously only been demonstrated in numerical simulations. With piezoelectric composites introduced as new 3D printing raw materials, existing mechanical metastructure designs may transit their unique properties into electrical orders. Specifically, tuning (i) the stress field by structural designs or (ii) the piezoelectric material distribution in polymer structures would promisingly tune the effective piezoelectric property of a particular volume. Other than piezoelectric materials, ferroelectric and ferromagnetic materials also stand as multifunction candidates for metamaterials. Similarly, 3D printing structures or composites with varied electric or magnetic permittivity composites can grant tenability of the effective ferroelectric or ferromagnetic properties. Once the composite possesses multiferroic properties (*i.e.*, magneto-electrical coupling), tailoring it with micro/nanostructural designs would shed new light on solid-state memory.[19]

**Nature-Inspired 3D Design.** By applying the 3D printing technique, it is possible to fabricate evolved structures, such as shark skin,[16] lotus effect,[17] bioinspired sensors,[18] and so on. These advanced structures can also be used for piezoelectric applications. As shown in Figure 3, 3D printing enables the feasibility of claw structures for electro-mechanical transfer. In this complex structure, many functional structures could be printed to make the structure as smart as a crab claw. For example, a position sensor could locate the ball and help the claw move to the target. A piezoelectric material could be used in the bones to apply the force to grab the ball. A controller could be embedded to decide how much force to use to grab the ball and how the claw will open and close. Additionally, the end of the claw could be made from a different material and with a curved/sharp shape to easily grab the ball.

Another amazing 3D structure from nature is shark skin, which helps the shark swim quickly to catch prey. A white shark may achieve burst speeds of 35 miles (56 km) per hour or more, which is seven times faster than the fastest Olympic swimmer. Recently, a biomimetic shark skin was designed for 3D printing. Figure 4A–C shows the image of a bonnethead shark's (*Sphyrna tiburo*) skin surface at different body locations—head, leading edge dorsal fin, and anal fin. "Typical" denticles along the trunk usually have an odd number of top-surface ridges (see Figure 4D–F). When the shark is swimming, the natural flow direction across the denticle surface is from lower left to upper right, from denticle base to tip. Figure 4E shows the shark denticles enlarged from the micro-CT model and then arrayed linearly on a membrane substrate.

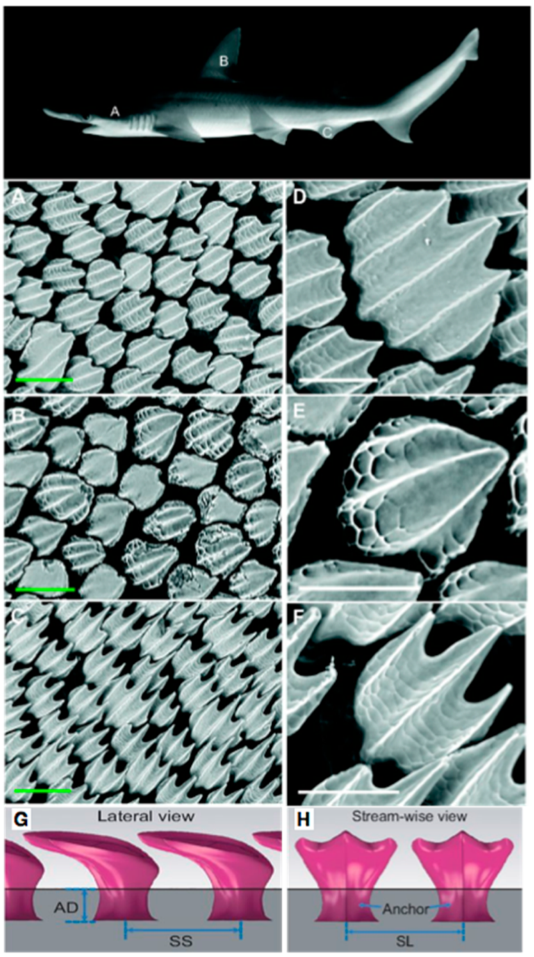


**Figure 4. Environmental scanning electron microscope (ESEM) images of the bonnethead shark skin surface at different body locations.[20] Wide-view ESEM images were taken from skin pieces extracted at the positions of the head (A), the leading edge dorsal fin (B), and the anal fin (C), as indicated in the top panel. (D–F) Closer top-view ESEM images of the skin surface from regions A–C showing details of the three-dimensional structure at each position. (G,H) Lateral (side) and stream-wise views of modeled denticles mounted on the membrane substrate for 3D printing. (Note: Green scale bars, 200 $\mu$m; white scale bars, 100 $\mu$m). Reprinted with permission from ref 20. Copyright 2014 The Company of Biologists, Ltd.**

In biomimetic 3D printing, denticles were printed in hard material, while the membrane substrate was printed in a flexible material. In fact, not only is the shape of the denticles varied at different location, but the tilt angle of the denticles also varies with the swimming speed, resulting in lower flow resistance. So far, there have been no means to design and to manufacture a denticle to realize this smart function. Computational fluid dynamics will help calculate the position of the denticles at various speeds and flow conditions. With the advance of materials, it would be possible to synthesize a material that could mimic the shape and tilt angle of the denticles to minimize the flow resistance during fast swimming.

With the availability of advanced materials and 3D printing techniques, additive manufacturing of multifunctional complex systems is at the forefront of manufacturing. The success of future 3D printing relies not only on the development of multifunctional materials and printing techniques but also on smart designs of complex systems. An engineer needs to understand advanced materials and additive manufacturing and, more importantly, to have a sense of creative design. Fortunately, many smart structures exist in nature that we can model and adapt into engineered structures.

*Conflict of Interest:* The authors declare no competing financial interest.

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